The Conceptual LEACH/SE-EW Process

Introduction

The purpose of this document is to provide an overview of the chemical aspects of the process proposed for the Carmacks Copper Project as requested pursuant to the YEA review of Western Copper Corporation's Project Description. The overall LEACH/SX-EW process is shown in Figure-1. As the name suggests, the process consists of three major discrete phases: leaching, solvent extraction, and electro-winning. The solvent extraction phase, in turn, consists of two sub-phases: extraction and stripping. For this document the complete process is described as four individual steps: *leaching, extraction, stripping,* and *electro-winning*, where extraction and stripping collectively make up the SX phase.

Figure-1 also shows that each of the above four steps is successively linked together by three continuously flowing, closed-loop fluid paths: the *leach solution* loop, the *organic solution* loop, and the *electrolyte solution* loop. The organic loop is an oil-based solution (non water-soluble), while the two remaining solution loops are aqueous (water based).

In principle, the organic solution contains organic compounds that have a very high affinity for copper ions. When a copper containing leach solution is mixed with this organic solution, it exchanges its hydrogen ions for copper ions. Since the volume of organic solution used is much smaller then the volume of leach solution, the copper is essentially concentrated in the organic solution.

By next bringing the "copper loaded" organic solution in contact with a strong sulphuric acid solution, the organic exchanges its copper ions for the acid's hydrogen ions. This produces a strong acid solution of much higher copper content then the original leach solution. In the subsequent electro winning step, the copper is removed from the strong acid solution as cathode copper and its acid content is replenished.

Thus, the fundamental principal to the function of the organic solution is that at moderate pH values it exchanges hydrogen ions for copper, but at very low pH values it exchanges copper ions for hydrogen ions.

In practice, in both the extraction and stripping stages, the water-based copper containing leach solution is first vigorously mixed with the organic solution and then allowed to separate. Mixing is represented in Figure-1 by a circle containing a "+" sign. Separation is represented by a square box with diverging arrows. These same symbols are also used in subsequent figures as necessary. Mixing and separation are always used together.

Throughout the LEACH/SX-EW process, copper is present in one of three forms: 1) as chemical copper {*i.e.* chemically bonded to other molecular species}, 2) as ionic copper {ions in solution}, or 3) as elemental copper {nearly pure solid copper}. In each of the four basic steps, copper makes a transition from one of these forms to another as follows:

In the leaching step, copper is dissolved from its ore using a weak sulfuric acid solution (transfer from chemical copper to ionic copper). To accomplish this, the ore when mined is first crushed then stacked on a *leach pad* or, as run-of-mine (ROM) ore, is mined and directly stacked in very large and high *dumps*. The ore is treated with large quantities of the acid solution resulting in a copper-containing solution which is collected for further processing as it exits the ore. In some cases it is fractured in place (*in-situ*) using explosives and leached directly in the ground.

In the extraction step, a special organic chemical with a high attraction for ionic copper extracts the ions from the leach solution by chemically bonding to the ions (transfer from ionic copper back to chemical copper). Nearly all other compounds, including incoming impurities, remain behind in the leaching liquid, rather than being picked up by the organic solution. This chemical form of filtering is important to the economic attractiveness of the process as it isolates and concentrates the copper in solution.

In the stripping step, an aqueous solution with a high concentration of sulfuric acid is used to strip the copper from the organic back into solution (transfer from chemical copper back to ionic copper). Both the extraction and stripping step occur at the SX Plant.

In the final step, electro winning, low DC voltage, and high current are used to plate out the ionic copper from the highly acidic aqueous solution onto cathodes immersed within the solution (transfer from ionic copper to elemental copper). The electro winning process occurs in a separate building from the SX Plant commonly referred to as a *tankhouse*.
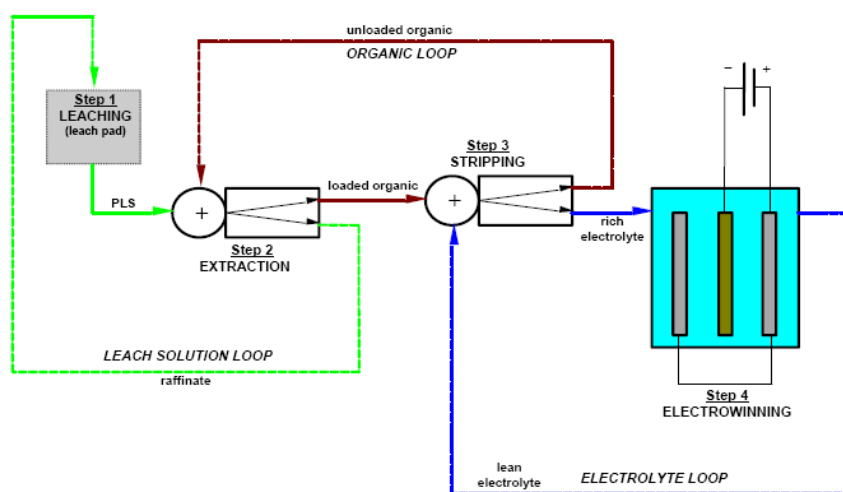

Figure-1 SXEW Basic Process Flow Diagram

NO SCALE

SX Process

General

The details of solvent extraction involve using special oil-based chemicals to extract copper ions from one aqueous solution and then yield the same copper ions over to a second aqueous solution, leaving behind impurities in the process, while at the same time increasing the concentration of copper ions.

The SX process is primarily conducted in a series of mixing vats and open or enclosed horizontal rectangular tanks. The process also includes piping, valves, pumps, chemical additive systems, instrumentation systems, and other support facilities including a control room and process laboratory. The location of each SX facility in relationship to adjacent processes will vary from site to site.

1. Mixing and Separation

In the extraction step at the SX plant, the copper laden leach solution, or PLS, is vigorously mixed with an organic liquid having a strong attraction for ionic copper. The copper in the PLS is in the form of Cu^{2+} ions in solution. The mixing occurs in one or more large cylindrical vats, where a vertical-shaft electric motor above the vat rotates disc-mounted impeller vanes near the bottom of the vat.

During mixing, the organic molecules chemically bond to the copper ions, extracting them from the pregnant leach solution. The clean organic, initially light brown in color, turns almost black in the process. This reaction takes place primarily during mixing. The organic liquid is now rich with copper and is said to be *loaded*.

From the mixer, the water/oil mixture discharges into a large, rectangular settling tank. Here, slow, horizontal travel produces laminar flow which accompanied by long retention time permits the organic (oil) and water components (raffinate) to separate because of non-solubility, with the organic floating to the top because of its lower specific gravity (~0.9).

Figure-2 shows a conceptual cross section of a typical settling tank used for separation, where the flow encounters the under/overflow baffle system. The height of these baffles is often manually adjustable to compensate for varying flow conditions. The organic solution overflows into a launder, which directs it out of the tank.
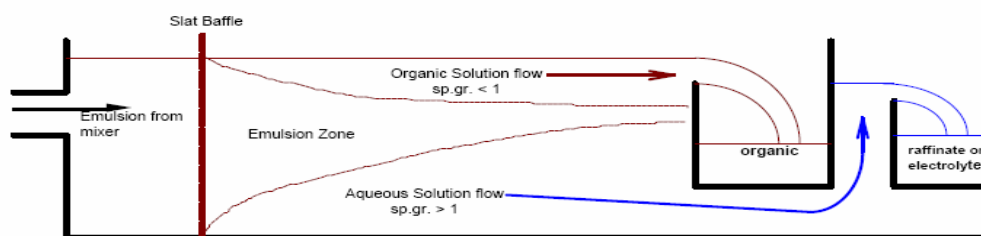
Figure-2 Side View of Solvent Extraction Settler Tank

Typical for both extraction and stripping
NO SCALE

The aqueous raffinate, now depleted of much of its copper ions, underflows the baffle and then flows up and over into a second launder. From here it is redirecting back to the leaching process. In the stripping step of the SX plant, a similar process occurs. However, in this step the incoming fluids to the mixer are the loaded organic containing chemically bonded copper, and a highly acidic aqueous electrolyte solution returning from the tank house. This returning electrolytic has a high concentration of both sulfuric acid and some residual copper sulfate (ionic copper). The high acid concentration is necessary if stripping is to occur effectively.

2. Chemical Reactions

Below, in simple terms, is a review of the chemical reactions taking place in the solvent extraction process.

a) Extraction Stage
The extractant chemical is the key to this process. This family of chemicals is an example of "designer" molecules and fall into the general class known as hydroxyphenyl oximes (commonly derived from aldehydes and can be recognized by an OH group bonded to a nitrogen atom, which in turn, is double bonded to a carbon atom, as shown in Figure-3), with two subclasses: salicylaldoximes and ketoximes. In essences, these molecules are based upon benzene ring-type structures attached to a saturated hydrocarbon chain. This ring complex has a strategically located hydrogen atom easily removed as an H^+ ion, shown in bold in Figure-3.
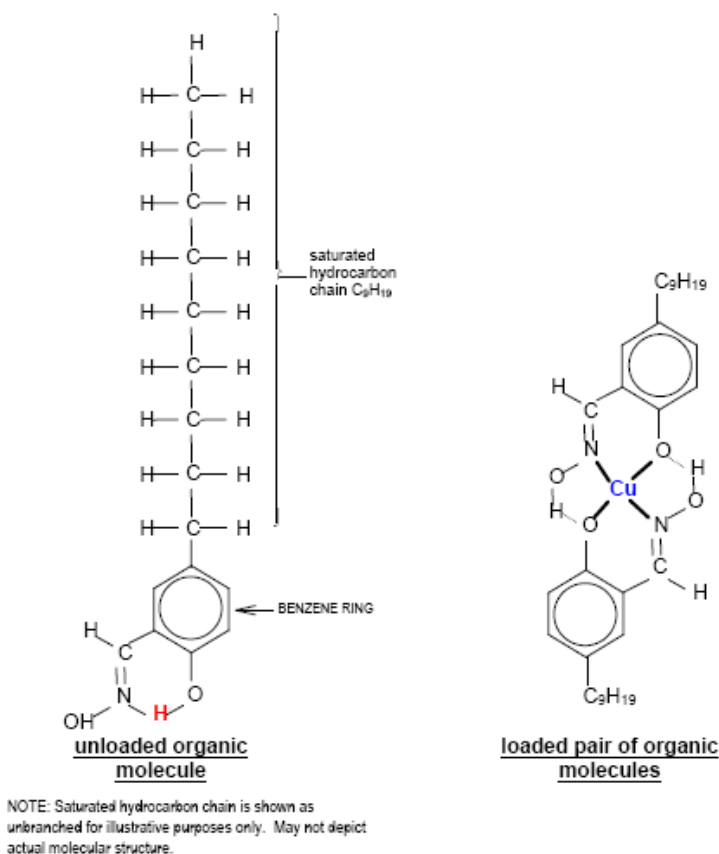
NOTE: Saturated hydrocarbon chain is shown as unbranched for illustrative purposes only. May not depict actual molecular structure.

Figure-3 Typical Extractant Molecule

Upon losing their respective H^+ ions, it is likely that two extraction molecules act together as ligands to capture one Cu^{2+} ion using four coordination bonds as shown in Figure-3. Using R to represent all atoms in the extraction molecule except the strategic hydrogen (represented by H), we can write a basic chemical equation for the process as follows:

$$2HR + Cu^{2+} \leftrightarrow 2H^+ + CuR_2 \quad \{B\text{-}1\}$$

Where: HR = the clean (unloaded) organic extractant molecule including the easily removable hydrogen.
Cu^{2+} = copper ion in solution.
H^+ = hydrogen ion in solution. The concentration of these is measured by the solution's *pH* value.
CuR_2 = loaded organic molecule pair with captured copper atom.

Note that this simplified version of the overall reaction does not include, among other things, spectator ions. Spectator ions would include the sulfate radical, SO_4^{2-}. Also note the very important characteristic that this reaction is reversible. *LeChatelier's principle* states that a reversible reaction will go in the direction that establishes equilibrium, *i.e.*, with all other things equal, the reaction will proceed in the direction that reduces any excess concentration of reactants or products.

Entering the extraction step, the concentration of reactants (left side of equation B-1) is higher than the products (right side). Coming into the mixing chamber, the PLS is relatively high in ionic copper and low in sulfuric acid, represented by few surplus H_+ ions. Thus, the chemical reaction tends to proceed to the right, where the extractant becomes loaded with chemically bonded copper, and the raffinate gains H_+ ions, thus becoming more acidic.

b) Stripping Stage
Chemical reaction B-1 also applies to stripping. However, in this process the loaded organic, CuR_2, is mixed with highly acidic electrolyte returning from electrowinning. High acidity means an excess of H^+ ions. Hence, the products on the right side of equation B-1 are now greater than the reactants on the left side.

The reaction proceeds in the reverse direction (to the left) in an effort to reestablish equilibrium (again, LeChatelier's principle). The organic releases Cu_{2+} ions into the electrolyte in favor of recapturing H_+ ions. The net result: the organic is stripped of its chemical copper (unloaded) while the acidity of the electrolyte decreases. The electrolyte leaving the SX plant for the tank house is labeled as *rich*.

c) Extractant Chemicals
Table-1 lists some manufacturers of extractant chemicals and also lists examples of the products by trade name. The specific choice of extractant for any specific application is based upon a variety of factors, which are too detailed to describe here but include such issues as the strength of the PLS, the rate of PLS flow available, the desired minimum acceptable extraction efficiency, and cost.

Table-1

EXTRACTANT CHEMICALS

Manufacturer	Address	Trade Name Products
Henkle Corporation	S. Kensington Rd. P.O. Box 191 Kankakee, IL 60901-0191	LIX®-84, -860, -860-IC, -984, -984N, and -985
INSPEC USA	Alternate 69 Hwy Galena, KS 66739	MOC®-80TD and -100TD
Zeneca, Inc.	Wilmington, DE 19897	ACORGA® M5774, M5397, and P-50M

DILUENT CHEMICALS

Manufacturer	Address	Trade Name Products
Conoco/Penreco	c/o Penreco P.O. Box 4274 Houston, TX 77210	170 ES (Exempt Solvent)
Phillips 66 Mining Chemicals Division	c/o Phillips Petroleum Co. Bartlesville, OK 74004	Orfom® SX-7 and SX-12

d) Diluents

The organic solution, as used, is not pure extractant chemical. The extractant is diluted with a nonpolar liquid essentially consisting of refined kerosene. This dilution increases the surface exposure of the extractant to the aqueous solutions by balancing the flow rates of the two solutions entering the mixer.

Mixing ratios of extractant to diluent vary depending upon a number of factors including the strength of the extractant, the type of diluent, the strength of the PLS, flow rate balance, and the number of stages of extraction or stripping. The diluent chemicals and their manufacturers are also listed in Table-1.

3. Multi-Stage Extraction

In practice, a single stage of mixing and separation proves to be inefficient. To resolve this problem, virtually all operating SX plants are set up to conduct multi-stage extraction. A typical flow diagram for a two-stage extraction process can be seen in Figure-4. Note that the flow of PLS and organic are in opposite directions through the system. The strongest extractant (most unloaded) mixes with the weakest PLS and vice versa. This scheme maximizes the chemical driving force needed to sustain reaction B-1.
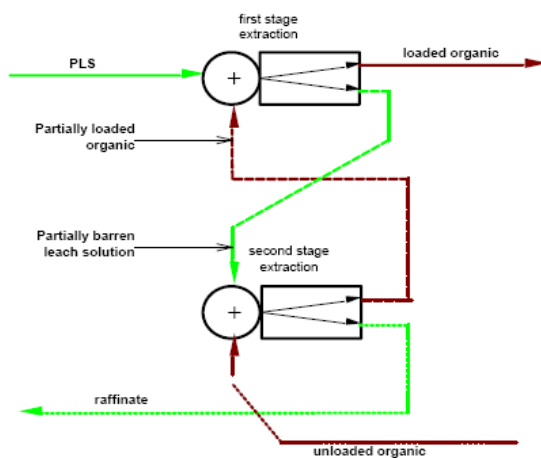
Figure-4 <u>SXEW Two-Stage Extraction</u>

NO SCALE

Figure-5 represents a three-stage extraction process, which follows the same basic opposing-flow scheme as the two-stage process and is used as frequently as the two-stage extraction.
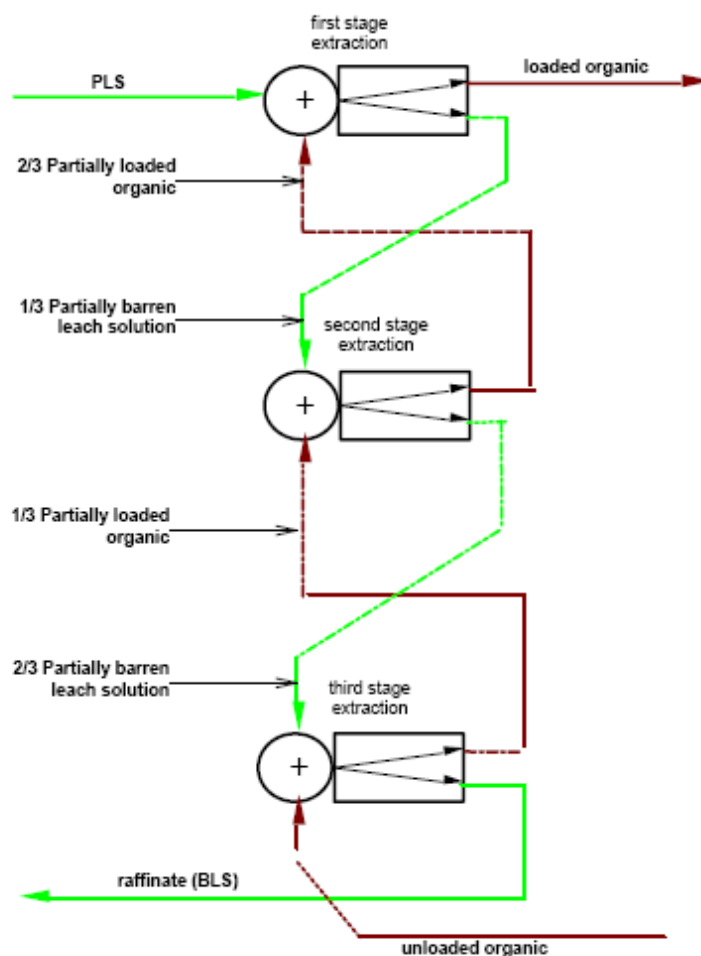
Figure-5 <u>SXEW Three-Stage Extraction</u>

4. Multi-Stage Stripping

As with extraction, the stripping process can be conducted in multiple stages, as shown by the two-stage version in Figure-6. Again, the flow of the two fluids are in oppose directions so that the strongest organic (in this case the most loaded) mixes with the weakest electrolyte in terms of ionic copper, but the strongest in acidity. The use of multi-stage stripping is less common than multi-stage extraction.
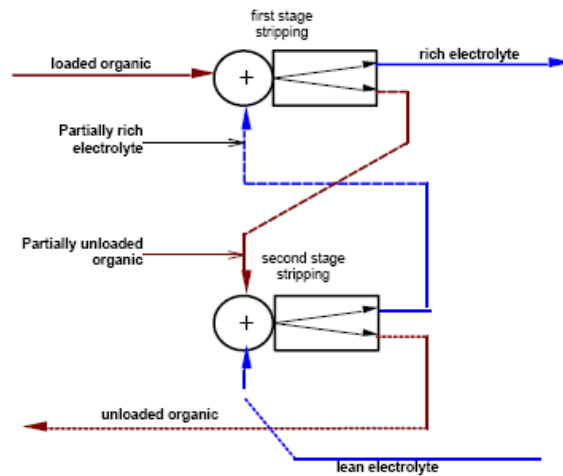
Figure-6 <u>SXEW Two-Stage Stripping</u>

5. Wash Stage

In some applications, a wash stage is applied to the loaded organic prior to stripping. In this stage, clean water is used to wash sediment and other trace contaminants from the loaded organic. This process is depicted in Figure-7.
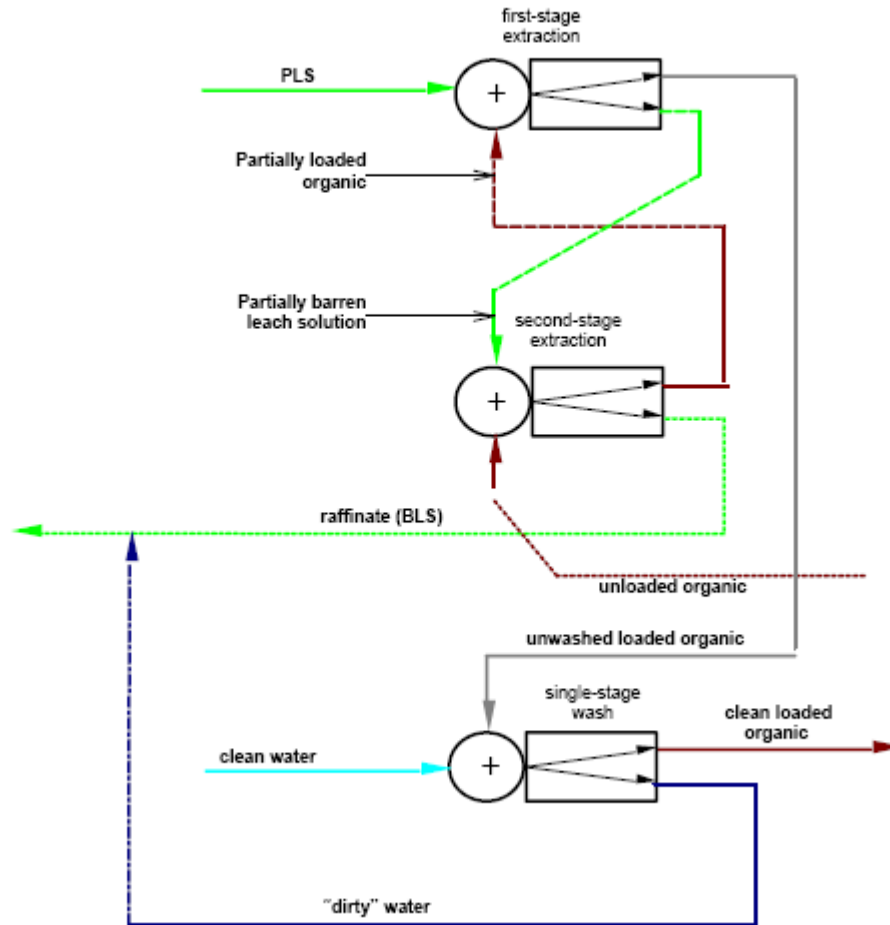
Figure-7 <u>SXEW Two-Stage Extraction with Wash</u>

EW Process

1. General

Electrowinning utilizes a DC voltage and current to drive ionic copper onto cathode plates connected to the negative side of the voltage source. The process is conducted in banks of long, horizontal, rectangular tanks open at the top and placed side-by-side. Each tank is referred to as a *cell*. Cells vary in length from about 8 feet to over 25 feet. Cell widths are typically about 4 feet. The number of cells in a bank can vary from less than 20 to more than 120. Two side-by-side banks of cells usually make up one operating train.

Each cell is equipped with two copper bus bars running the length of the cell, one on top of each of the barriers between cells. One copper bus is at a negative potential with respect to the opposite bus.

Each cell is filled with anode and cathode plates. This is accomplished by attaching each plate to a copper crossbar, or *hangerbar,* as an assembly and then laying the assembly across the cell bus bars. The plate assemblies alternate between anode and cathode until the cell is full from front to back.

There is always one more anode than cathode so that each cathode has an anode on both sides. Anode/cathode pairs can vary from less than 20 to more than 60 per cell.

Each anode-plate hangerbar is in contact with the positive cell bus and insulated from the negative bus. Alternately, each cathode-plate hangerbar is in contact with the negative cell bus and insulated from the positive bus. Since the cells are electrically connected in series, the negative cell bus for one cell acts as the positive cell bus for the next cell, and so on.

The rich electrolytic solution, laden with ionic copper, moves through the cells lengthwise in a slow, continuous manner. The solution is pumped into each cell through a valved supply pipe usually entering the cell from the outboard end. Each cell supply pipe receives flow from a supply header. At the inboard end of the cell, the solution enters an overflow drain that leads into a drain header and eventually back to the SX plant. The overflows may or may not be covered; however, where covers are provided, they are lightweight and easily removed for visual inspection to verify cell flow.

2. Cathodes

One of two types of cathode plate is used. If the cathode plate is to be part of the final product, then the plate itself is made of copper and usually referred to as a *starter* plate. In some cases, stainless steel or titanium cathodes are used. These are usually referred to as *blanks*. The copper ions plate onto these blanks as elemental copper, but are not chemically bonded to the steel or titanium. After the blanks are removed from the cell, the plated copper is peeled off of the blank as a sheet (one sheet from each side of the blank). The peeling operation is done either by hand using a hammer and chisel, or by a machine with a chisel on a hydraulic piston. The peeled copper sheets are either sold as a final product, or used as starter sheets and attached to hangerbars for final electrowinning.

They are also sometimes sold to other SXEW operators as starter plates. Although EW times vary, in general, it takes 7 to 9 days of continuous plating to yield sufficient copper on the cathode to consider it marketable. The finished cathodes are typically removed from a cell in groups using an overhead traveling crane equipped with a special spreader bar. The hooks on the spreader bar interlock with openings on the top of each cathode.

Not all plates within a cell can be removed at one time, as this would disrupt current flow throughout the entire cell bank. Typically, 1/4 to 1/3 of the cell's cathodes are removed in each lift. The finished plates are rinsed and then prepared for further processing. New cathodes are inserted into the cell in place of the removed plates before removing the next group of cathodes within the cell. As a general rule, only the cathodes are removed from the cells during production.

3. Anodes

Anodes are made from an alloy of lead, tin, and calcium, with lead being the principle component. The tin and calcium improve the strength of the plate and discourage scavenging of lead into the electrolyte, which would contaminate the plated copper. Anodes are often provided with insulating straps or spacers to reduce the likelihood of anode-to-cathode shorting. Straps may be removable, or permanent.

4. Tankhouse

As previously stated, the electro-winning cells are enclosed within a building commonly referred to as a tankhouse. Support equipment typically includes offices, control room, laboratory, electrical switchgear and rectifier room, and electrical substation. Floors are usually of concrete and provided with corrosion resistant coatings or membranes. Each cell is usually made of a concrete shell with a corrosion-resistant membrane or a polymeric insert. The tankhouses are most often found at lower elevations than their associated SX plants, unless those plants are adjacent to the tankhouse.

5. Cell Operation

A simplified cross-section of an electro winning cell is shown in Figure-8 and Figure-9. The polarity of the power source is set by the process. Average cell voltages typically varied between 2.0 and 2.2 volts per cell. Rich electrolyte continuously enters the cell and migrates through it. For any given volume of electrolyte passing through the cell, only a small fraction of the ionic copper is recovered as plated, elemental copper, on the cathode plates. Recovery rates can vary from as little as a few grams of copper per liter of solution, to over ten grams per liter. The electrolyte leaving the cell for return to the SX plant is referred to as *lean* because of its lowered ionic copper concentration.
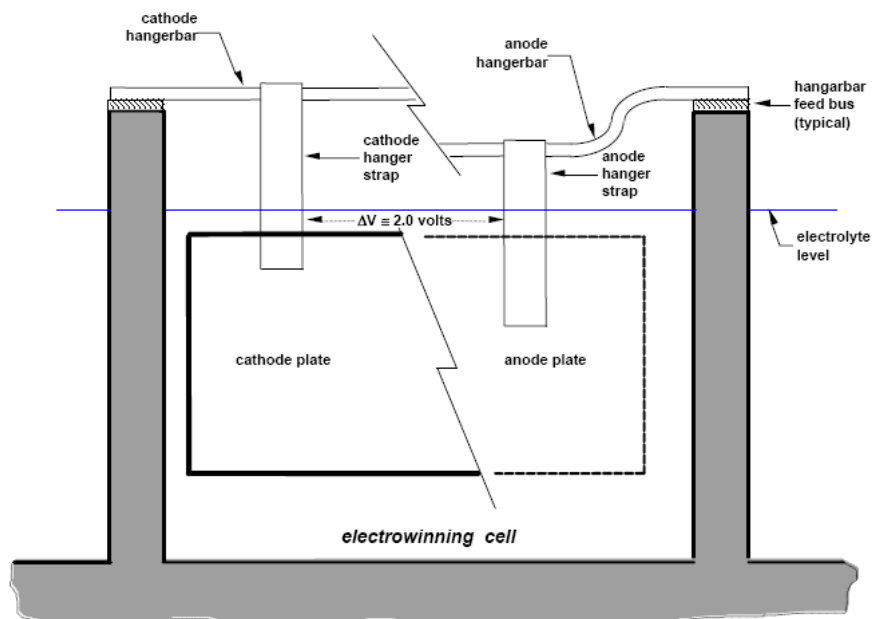
NOTE: Hangarbars are shown at electrical feed ends.   Unviewed ends are insulated from feed bus.

Figure-8 <u>Transverse Cross Section of Electrowinning Cell</u>

NOTE: Hangarbars straps are made of copper to provide electrical continuity from each hargarbar to its plate.
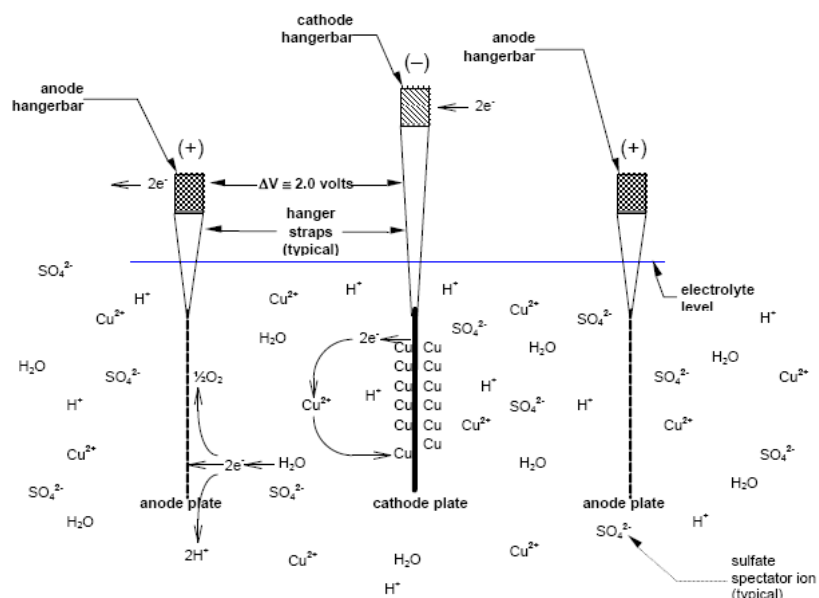
Figure-9 <u>Longitudinal Cross Section of Electrowinning Cell</u>

NO SCALE

5. Normal Electrochemical Process

Under normal conditions, two separate electrochemical reactions are simultaneously occurring, one each at the anode and the cathode. A reduction half-reaction occurs at the cathode. An oxidation half-reaction occurs at the anode.

At the cathode, power supply electrons create a negative charge, attracting Cu^{2+} ions. As these ions contact the plate, they gain the two electrons needed to make them neutral atoms, thus reducing them to elemental copper. In this form, the copper atoms metallically bond to adjacent copper atoms, thereby building up essentially pure copper on the plate. The reduction half-reaction is:

$$Cu^{2+} + 2e\text{-} \rightarrow Cu(s) \ \{C\text{-}1\}$$
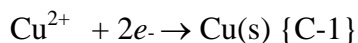
This reaction requires the application of 0.34 volts across the cell (at standard conditions of 25°C, one atmosphere, and a 1-Molar ion concentration).[3]

While reduction is taking place at the cathode (supplying electrons), oxidation is taking place at the anode (removing electrons). Only three species in the electrolyte are candidates for undergoing oxidation: hydroxyl ions (OH^-), sulfate ions (SO_4^{2+}), and water (H_2O).

Because the solution is highly acidic (excess $H+$), hydroxyl ions are essentially nonexistent and not directly available as electron contributors. Furthermore, to oxidize sulfate ions, hydroxyl ions are also necessary. Hence, water turns out to be the only practical candidate available for oxidation. The oxidation half reaction for water is listed below [3]:

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e\text{-} \ \{C\text{-}2\}$$
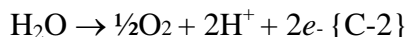
In this reaction, oxygen is given off as a diatomic gas. The oxygen generated at the anode surface rises to the top of the cell liquid as a continuously flowing sheet of gas bubbles. As the gas is generated, hydrogen ions go into solution. This increases the acidity of the lean electrolyte before returning to SX.

The benefit of increased acidity of the electrolyte entering the SX stripping stage was previously identified. Note that the generation of $H+$ in electro-winning compensates for the loss of H^+ when the loaded organic is stripped of its copper.

The energy potential needed for this oxidation is 1.23 volts (at standard conditions similar to the reduction reaction). Hence, the total threshold cell voltage needed to initiate the total reaction is 1.23 – 0.34 = 0.89 volts. In practice, 2.0 to 2.2 volts is normally provided for each cell to account for resistance voltage drop losses, deposition overvoltages needed to drive the reaction at a meaningful rate, and conditions varying from standard temperature and concentration.

6. Abnormal Electrochemical Process

Under certain conditions an electro winning cell can transition from normal to abnormal operation. When this happens the electrochemical dynamics of the cell changes. This change takes place at the cathode where a different reduction half-reaction takes over. Of particular importance is the adverse condition of ionic copper depletion. If certain conditions occur, such as extended interruption of electrolyte flow to a cell, excessive copper depletion will take place. That is, the level of ionic copper will decrease substantially as copper ions plate out and are not replaced with fresh electrolyte. As the concentration of copper ions decreases, the relative availability of hydrogen ions increases. The cathode half-reaction transitions from C-1 above to reaction C-3 below.

$$2H^+ + 2e\text{-} \rightarrow H_2 \quad \{\text{C-3}\}$$
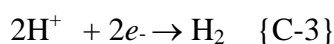
The voltage threshold for this reaction is 0.0 volts (by definition) [3]. The net applied voltage across a cell needed for the overall reaction to occur (equations C-1 and C-3) becomes: 1.23 – 0 = 1.23 volts.

The single most important ramification from the C-3 cathode half-reaction is the generation of hydrogen gas. However, any copper that does continue to plate out will be of a very poor quality. The copper in depleted cells tends to fall off the cathodes as a brownish granular powder when removed from the electrolyte and dried. In a depleted cell, the generation of hydrogen occurs along the cathode surface similar to the generation of oxygen along the anode. In fact, even under abnormal conditions, anode oxygen generation continues.

7. Acid Misting from Electrowinning

Oxygen bubbles created at the anode rise to the surface of the electrolyte. At the surface, these bubbles expand above the liquid and then break, releasing the entrapped oxygen into the atmosphere. The liquid in the bubble wall just before it breaks is made up of the acidic electrolyte solution. As the liquid wall ruptures, it disintegrates into extremely small droplets that readily become airborne.

The macroscopic effect of this process is to create an acrid, acid mist above the cells. This mist is typically handed with by one or a combination of strategies: forced ventilation with the exhaust gases being scrubbed, partial covering of cells, the use of surfactants, and the use of floating media (balls or beads) on the electrolyte surface. These strategies mitigate potential health and safety risks from the electrowinning process.