

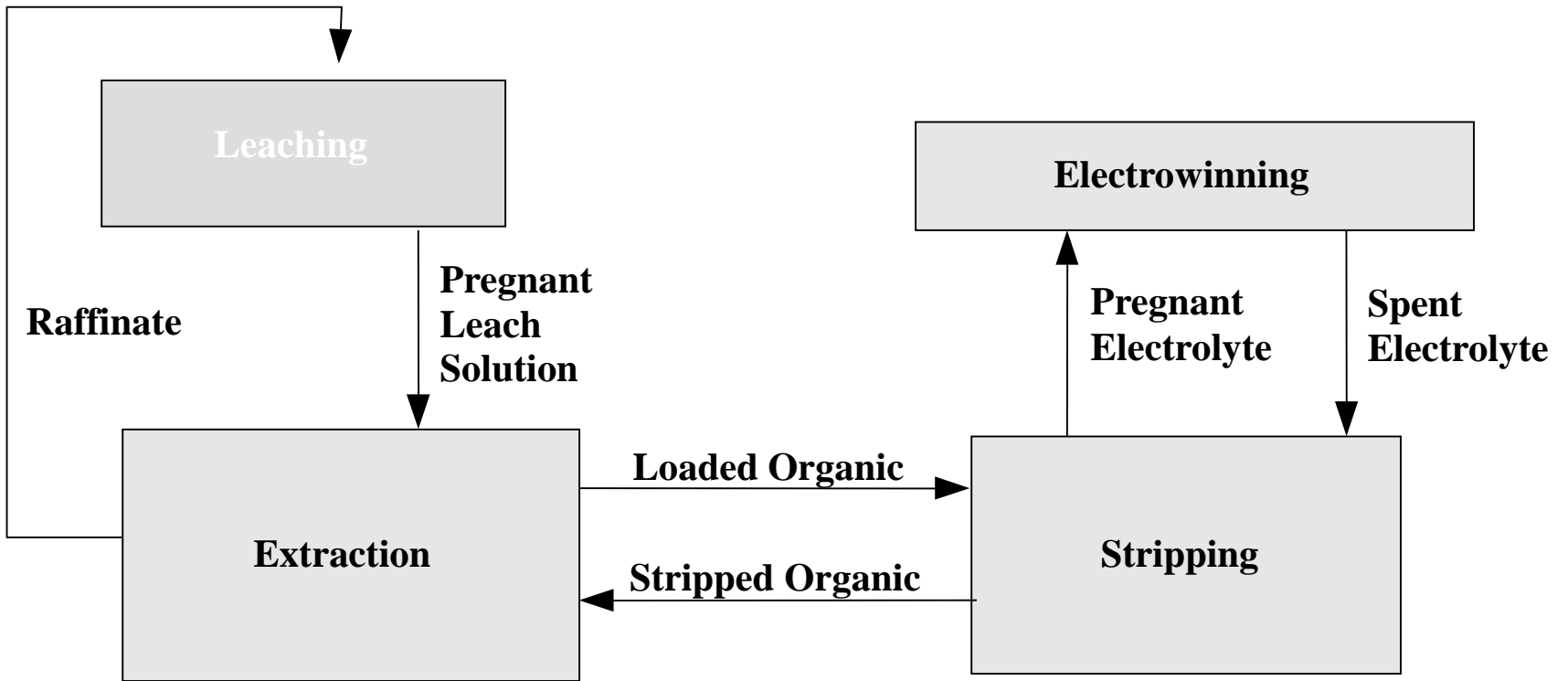
Copper Solvent Extraction Training

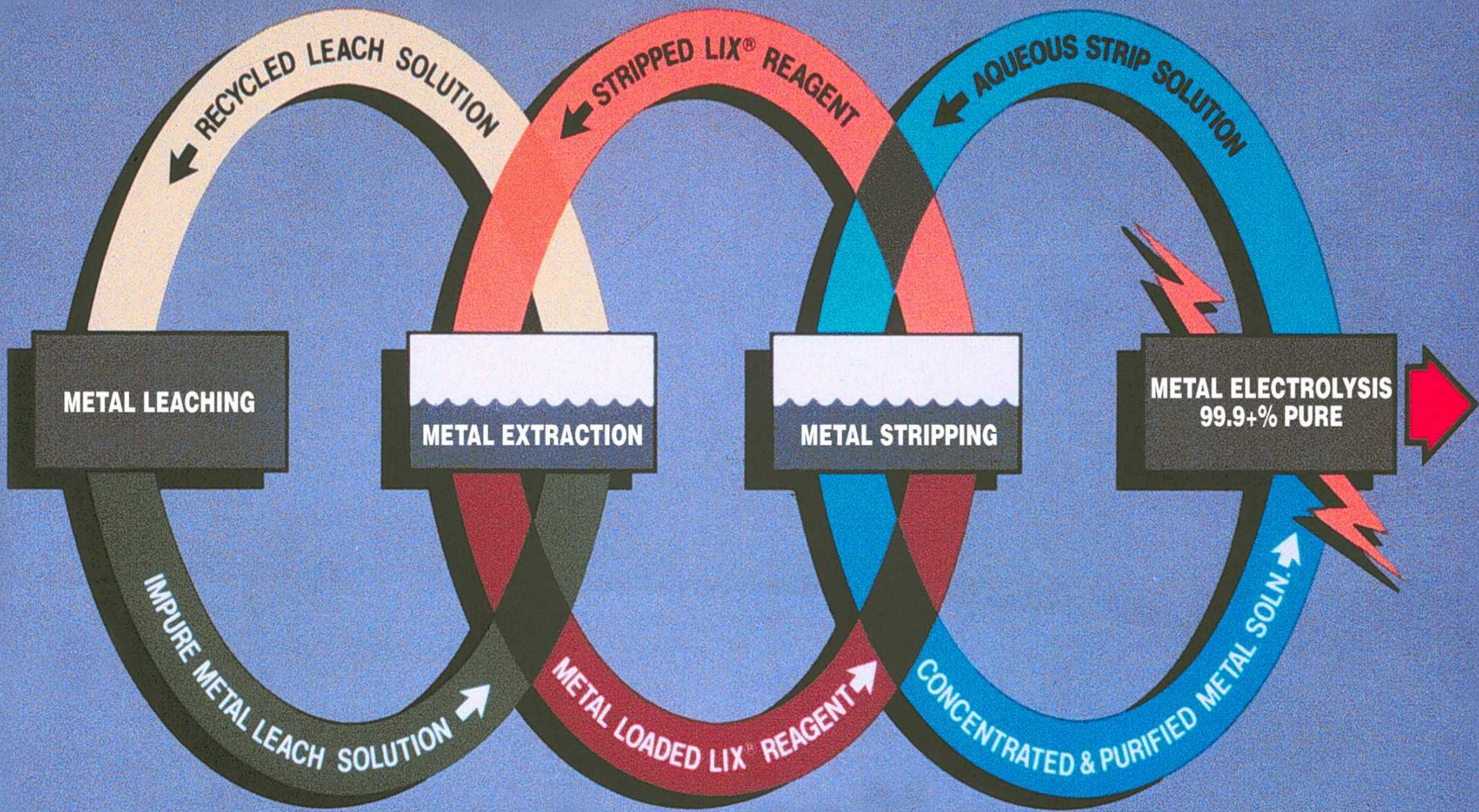
Key Facts About Copper Solvent Extraction

- **First plant in 1968, now practiced on 6 continents**
- **Most plants produce LME quality copper**
- **Small (~ 1000 T /yr) to large**
- **Very simple (1 train at 2E,1S leaching one type ore)**
- **Complex (4 trains at 2E,2E,1W,1S leaching antacamite and chalcocite)**
- **Very complex (4 SX plants, 3 tankhouses, dump leach, heap leach, concentrate leach, oxide and sulfide ores)**
- **Six types of leaching**
 - **Heap, dump, in situ, vat, agitation, autoclave**

Copper Recovery Process Composed of 3 Individual Processes

- **Leaching**
 - Puts copper in an acid water solution
- **Solvent Extraction**
 - Transfer copper from leach to electrowinning
 - Transfer acid from electrowinning to leach
- **Electrowinning**
 - Transfers copper from solution to metal





Typical Sulfuric Acid Leach Solutions

Type	g/l Cu	pH
Dump, Heap, In Situ	0.5 - 8	1.3 - 2.2
Ferric Cure, Thin Layer	3 - 8	1.5 - 2.2
Vat	6 - 40	1.5 - 2.0
Agitation Oxide Ores	1 - 15	1.5 - 2.0
Agitation Sulfide Ores	12 - 25	< 1 - 1.6
Pressure Leach Cu Cons	25 - 80	< 1 - 2.0
Bioleach Cu Cons	25 - 55	< 1 - 2.2

Common Features: Fe²⁺, Fe³⁺, sulfate salts of many metals including Mn, Mo and U at times

Typical Tankhouse Electrolytes

Electrolyte	Copper (g/l)	Sulfuric Acid (g/l)
Spent	33-38	150-180
Pregnant	45-55	116-146

Leaching



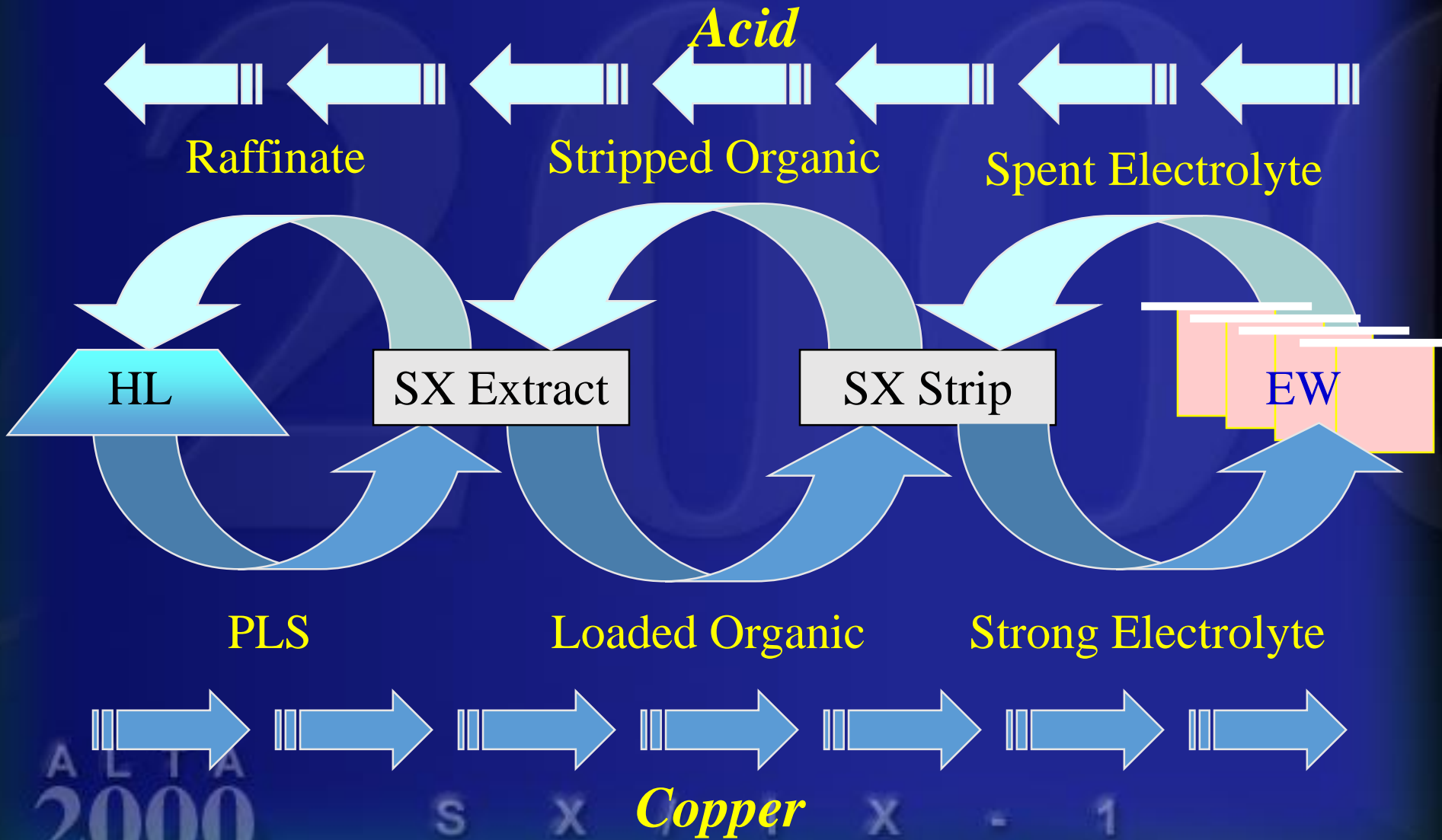
Solvent Extraction



Electrowinning



Process Description



Objectives of Solvent Extraction

- **Purification of copper**
 - Extract copper, leave other metals behind
- **Concentration of copper**
 - In most cases from under 10 g/L up to 55 g/L
- **Conversion from one anion to another**
 - Chloride to sulfate
 - Ammonia to acid sulfate

Agitation Leach Plants are Normally the Most Difficult L/SX/EW Plants to Run

- **Solids in the leach solution**
- **Chemicals used in solids / liquid separation**
- **Variable copper concentration in leach solution**



Solids in the Leach Solution

- **SX plants handle solids better if mixers are organic continuous**
 - Crud goes to the interface
- **Solids flip mixers to aqueous continuous**
 - Crud floats and moves to next mixer
 - Unstable plant or maybe a crud run
- **Solids cause crud generation**
 - Reduce flow capacity of plant, maybe a plant shutdown
 - Crud removal is a labor intensive unpleasant job
 - Organic losses are high in crud
- **Solids in electrolyte**
 - Rough cathodes
 - Impurities in cathodes
 - Carries organic to the tankhouse
 - Cathodes stick to blanks
 - Organic on cathode

Chemicals used in solids / liquid separation – Flocculants and Coagulants

- **Use too little gives solids in leach solution**
- **Use too much and these chemicals are in the leach solution along with solids**
 - **Gives lots of sticky crud that may float and move or it may form a gelatinous mess that is very difficult to remove and treat**

Running the CCD circuit properly to flocculate the solids without using too much flocculant is a very important job!



Variable Copper Concentration in Pregnant Leach Solution

- **Impact Production**
- **Impact Selectivity**
- **Operating parameters must be adjusted to optimize plant performance.**
 - **Reagent Concentration**
 - **Advance O/A ratios (flow rates)**

Variable Copper Concentration in Pregnant Leach Solution

- **Why does this make running a copper solvent extraction plant more difficult?**
 - Reagent concentration is designed for a certain copper concentration at the plant design flow
 - Reagent concentration can be easily increased but not easily decreased
 - Copper not extracted is partially lost to tailings
 - Too much reagent raises costs and increases impurity transfer
 - Not transferring enough copper reduces production
 - Transferring too much copper may end up precipitating copper sulfate in pipelines, settlers, filters, etc.

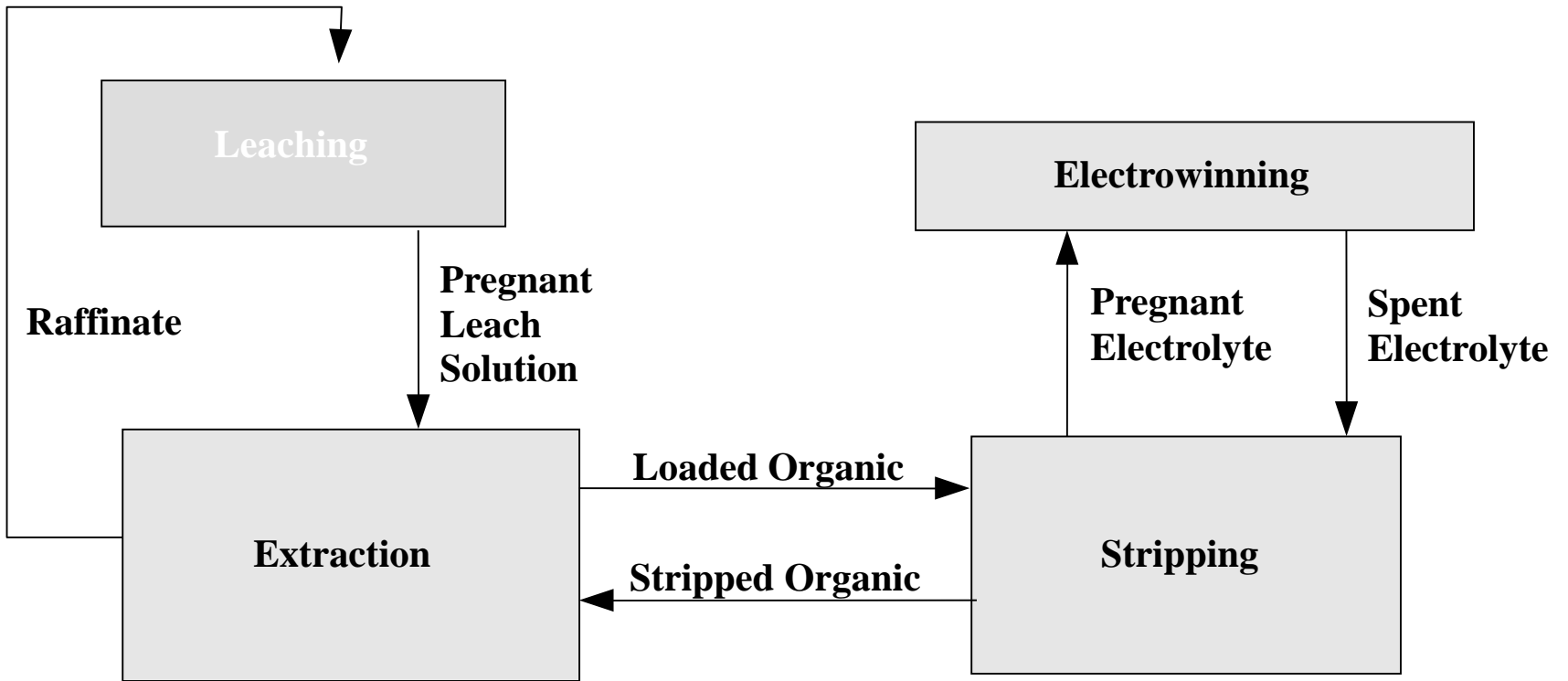
What Should be Done

- If possible blend ore from mine to achieve a more constant grade
- Use a reagent that gives good performance over a range of conditions, LIX 984N
- Use a reagent concentration designed to give the desired copper transfer at design organic flow
- If increase in copper in the PLS is for the short term increase organic flow
 - Must have enough organic in the surge tank to handle increased organic flow
 - Most mixer settlers can treat a flow well above design, especially for a short time
- If increase in copper in the PLS is for the long term increase reagent concentration
- If copper in PLS decreases in the short term increase PLS flow and / or decrease organic flow.
- If copper in the PLS decreases for the long term decrease reagent concentration

Calculating Correct Flows

- **Mass Balance Calculations**

- **Copper cannot be created or destroyed in a leach / solvent extraction / electrowinning operation. It can only be transformed and / or transferred.**
 - **When copper is leached is the copper transformed or transferred or both transformed and transferred?**
 - **In a solvent extraction step is the copper transformed or transferred or both transformed and transferred?**
 - **When copper is plated in an electrowinning operation is the copper transformed or transferred or both transformed and transferred?**
- **Therefore copper leached must over time equal copper produced plus copper lost to tails.**



Leaching



Solvent Extraction



Electrowinning



Mass Balance - Leaching

The mass of copper leached from the ore in a given period of time is equal to the increase in the mass of copper gained by the leach solution in that same period of time.

Example: 10,000 MT ore at 1.2 % copper agitation leached / day at 96 % leaching efficiency and 98% washing efficiency. Flow of leach solution is 750 m³ / hour off the first stage of CCD. Copper in raffinate entering CCD circuit is 0.44 g/l Cu. What is the copper concentration in the leach solution?

Cu leached = 10,000 MT ore/day x .012 MT Cu/MT ore x 0.96 = 115.2 MT/day

115.2 MT Cu x 0.98 = 112.9 MT Cu in leach solution / day

112.9 MT / day / 24 hour / day = 4.704 MT / hour

Copper gained by leach solution

[(4.704 MT / hour) (1000 kg / MT) / (750 m³ / hour)] = 6.27 kg/m³ (g/l)

**Copper concentration in leach solution = copper in raffinate + copper gained
= 0.44 g/l + 6.27 g/l = 6.71 g/l**

Mass Balance - Extraction

In the extraction section of solvent extraction the mass of copper lost from the leach solution in a period of time is equal to mass of copper gained by the organic phase in that same period of time.

Example: 750 m³ / hour of PLS having 6.71 g/l Cu is treated in a copper SX plant with 2 extraction stages and 2 strip stages with an organic solution containing 20 volume % LIX 984N flowing at 800 m³ / hour. The stripped organic contains 2.6 g/l Cu and the copper recovery is 93.44 %. What is the copper concentration on the loaded organic?

Copper lost by aqueous = copper gained by organic

750 m³/hour x (6.71 kg / m³) (0.9344) = 4702.5 kg/hour lost by aqueous

Copper gained by organic = 4702.5 kg/hour / 800 m³/hour = 5.878 kg/m³

**Copper on loaded organic = copper on S.O. plus copper gained =
2.6 g/l Cu + 5.878 g/l Cu = 8.478 g/l Cu**

Mass Balance - Stripping

In the strip section the mass of copper lost from the organic phase in a period of time is equal to the copper gained by the electrolyte phase in that same period of time.

Example: The barren electrolyte has 35 g/l Cu and 189.3 g/l acid while the pregnant electrolyte has 50 g/l Cu. What is the flow rate of the electrolyte?

Copper lost by organic in stripping = copper gained by electrolyte in the same period of time.

$800 \text{ m}^3 / \text{hour} (\text{loaded organic} - \text{stripped organic}) = \text{copper lost by organic}$
 $800 \text{ m}^3 / \text{hour} (8.478 \text{ kg Cu} / \text{m}^3 - 2.60 \text{ kg Cu} / \text{m}^3) = 4702.5 \text{ kg Cu} / \text{hour}$

$4702.5 \text{ kg Cu} / \text{hour} / \text{by gain in copper by electrolyte} = \text{flow electrolyte}$
 $4702.5 \text{ kg Cu} / \text{hour} / (50 \text{ kg Cu} / \text{m}^3 - 35 \text{ kg Cu} / \text{m}^3) = 313.5 \text{ m}^3 / \text{hour}$

What is the copper in the pregnant electrolyte if the electrolyte flow drops to $300 \text{ m}^3 / \text{hour}$?

Mass Balance - Electrowinning

In EW the mass of copper plated in a given period of time is equal to the mass of copper lost from the total electrolyte volume in that same period of time.

Example: If the barren electrolyte has a copper concentration of 35 kg Cu / m³ and the pregnant electrolyte has a copper concentration of 50 kg Cu / m³ at a flow of 313.5 m³ / hour for 24 hours how much copper is plated?

Copper plated in a period of time = copper lost from electrolyte in the same period of time.

$$\begin{aligned}\text{Copper lost from electrolyte} &= (313.5 \text{ m}^3 / \text{hour})(24 \text{ hr /day}) (15 \text{ kg Cu / m}^3) \\ &= 112,900 \text{ kg Cu / day} = 112.9 \text{ MT Cu / day}\end{aligned}$$

Mass Balances

A mass balance can be done for the entire circuit or for a single stage

Example: Circuit modeling using Cognis Isocalc® program on 2E, 2S with the feed, electrolytes, organic and recovery of preceding pages gives following data.

PLS = 6.71 g/l Cu

Extraction stage 1: Organic = 8.482 g/l Cu Aqueous = 2.518 g/l Cu

Extraction stage 2: Organic = 4.551 g/l Cu Aqueous = 0.436 g/l Cu

Strip stage 2: Organic = 2.60 g/l Cu Aqueous = 37.6 g/l Cu

Strip stage 1: Organic = 3.61 g/l Cu Aqueous = 50.0 g/l Cu

O/A extraction = $800 / 750 = 1.06667$

O/A stripping = 2.556

Mass Balances for Acid in a Copper SX Circuit

Cu Extraction/Stripping Equilibrium



When one Cu^{2+} is extracted one molecule of H_2SO_4 is created

When one molecule of H_2SO_4 strips organic one Cu^{2+} is liberated

The mass of H_2SO_4 is 98 amu and the mass of Cu is 63.54 amu.

Thus 1.54 mass units of sulfuric acid equals 1 mass unit of Cu.

Said in another way 1.54 grams of acid = 1 gram of Cu across SX

Electrowinning Reactions

Cathode



Anode



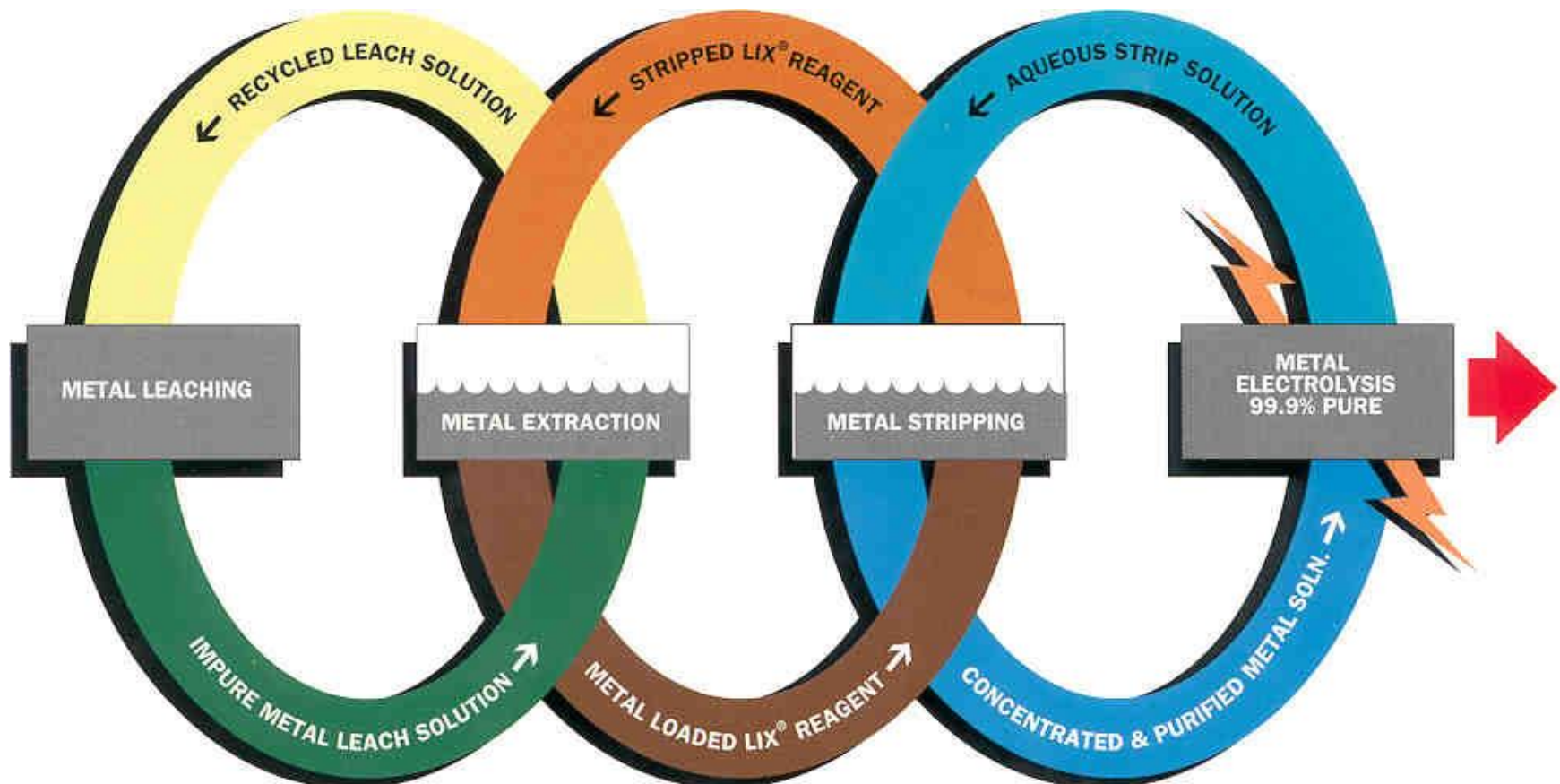
Overall



In electrowinning one Cu is plated and one sulfuric acid is generated. Thus 1.54 grams of acid is generated when one gram of copper is plated.

Copper and Acid Mass Balances in a Copper Leach / SX / EW Plant

- For every gram of copper extracted from the leach solution 1.54 grams of acid is added to the raffinate
- For every gram of copper stripped from the loaded organic 1.54 grams of acid is lost from the electrolyte
- For every gram of copper plated in the tankhouse 1.54 grams of acid are produced
- Example: What is the acid in our pregnant electrolyte?
 - BE: 35 g/l Cu, 189.3 g/l acid
 - PE: 50 g/l Cu, 166.2 g/l acid
 - Calculation: $[189.3 \text{ g/l acid} - (15 \text{ g/l Cu} \times 1.54 \text{ g/l acid/g/l Cu})]$



Why Are Mass Balances Important

- Give information on flowmeters
- Give information on mixer efficiencies
- Give information on excessive entrainment
- Used to detect theft
- Used to optimize leaching economics
- Used to detect leaks
- Others??

Determination of the Advance O/A Ratios

1. From flowmeters. Organic flowmeters often not accurate
2. Sample the mixers. Depends on where the mixer is sampled
3. From copper analysis. Usually the most accurate

Example Extraction:

$$[\text{g/l Cu(PLS)} - \text{g/l Cu(raf)}] \times \text{PLS flow} =$$

$$[\text{g/l Cu L.O.} - \text{g/l Cu B.O.}] \times \text{Organic flow}$$

$$\text{Advance O/A extraction} = \text{Organic flow} / \text{PLS flow} =$$

$$[\text{g/l Cu(PLS)} - \text{g/l Cu(raf)}] / [\text{g/l Cu(L.O.)} - \text{g/l Cu(B.O.)}]$$

$$[6.71 - 0.44] / [8.48 - 2.60] = 6.27 / 5.88 = 1.066$$

Example Stripping:

$$\text{Advance O/A stripping} = \text{Organic flow} / \text{Electrolyte flow} =$$

$$[\text{g/l Cu(P.E.)} - \text{g/l Cu(B.E.)}] / [\text{g/l Cu(L/O.)} - \text{g/l Cu(B.O.)}]$$

$$[50 - 35] / [8.48 - 2.60] = 15 / 5.88 = 2.56$$

Mixer Efficiency

Mixer Efficiency is defined as the copper transfer in a mixer / the copper transfer at equilibrium. For extraction stage 1

- 1. Analyze organic and aqueous phase entering a mixer**
- 2. Sample organic and aqueous phases exiting mixer then analyze for Cu.**
- 3. Mix organic and aqueous phases entering the mixer at the advance O/A ratio then shake vigorously for 10 minutes. Analyze each phase for Cu. (equilibrium values)**

Calculations for extraction stage 1.

From organic analysis

$$\frac{\text{E1 mixer org g/l Cu} - \text{E2 org g/l Cu}}{\text{Equil E1 org g/l Cu} - \text{E2 org g/l Cu}} \times 100 = \text{Mixer Efficiency (Org)}$$

From aqueous analysis

$$\frac{\text{PLS g/l Cu} - \text{E1 mixer aq g/l Cu}}{\text{PLS g/l Cu} - \text{Equil E1 aq g/l Cu}} \times 100 = \text{Mixer Efficiency (Aq)}$$

Mixer Efficiency Continued

EXAMPLE for E1:

$$\frac{\text{E1 org g/l Cu} - \text{E2 org g/l Cu}}{\text{Equil E1 org g/l Cu} - \text{E2 org g/l Cu}} \times 100 = \% \text{ Efficiency}$$

$$\frac{5.45 - 4.32}{5.55 - 4.32} \times 100 = 91.9\%$$

$$\frac{\text{PLS g/l Cu} - \text{E1 aq g/l Cu}}{\text{PLS g/l Cu} - \text{Equil E1 aq g/l Cu}} \times 100 = \% \text{ Efficiency}$$

$$\frac{2.44 - 1.54}{2.44 - 1.48} \times 100 = 93.7\%$$

Values taken from an operating plant in Arizona

Stage Efficiency

Stage Efficiency is defined as the copper transfer in a stage / the copper transfer at equilibrium. For extraction stage 1

- 1. Analyze organic and aqueous phase entering E1 mixer**
- 2. Sample organic and aqueous phases exiting E1 settler then analyze for Cu.**
- 3. Mix organic and aqueous phases entering the E1 mixer at the advance O/A ratio then shake vigorously for 10 minutes. Analyze each phase for Cu. (equilibrium values)**

Calculations for extraction stage 1.

From organic analysis

$\frac{E1 \text{ org weir g/l Cu} - E2 \text{ org weir g/l Cu}}{\text{Org}} \times 100 = \text{Stage Efficiency}$

(Org)

Equil E1 org g/l Cu - E2 org weir g/l Cu

From aqueous analysis

$\frac{PLS \text{ g/l Cu} - E1 \text{ aq weir g/l Cu}}{PLS \text{ g/l Cu} - \text{Equil E1 aq g/l Cu}} \times 100 = \text{Stage Efficiency (Aq)}$

PLS g/l Cu - Equil E1 aq g/l Cu

Mixer Efficiency and Stage Efficiency

Mixer efficiency from organic analysis should be very close to mixer efficiency from aqueous analysis.

Stage efficiency from organic analysis should be very close to stage efficiency from aqueous analysis.

Mixer efficiency should be equal to or only slightly less than stage efficiency.

Most people do not distinguish between mixer efficiency and stage efficiency.

Why is Mixer / Stage Efficiency Important?

- **Poor mixer efficiency gives poor metal recovery, i.e., metal transfer must take place in the mixer or it will not take place at all.**
- **Poor mixer efficiency may point out a problem with mixing equipment.**
- **Poor mixer efficiency may point out a problem with contamination of plant organic.**
- **Typical mixer efficiency values**
 - 92% \pm 2% extraction stage 1**
 - 94% \pm 2% extraction stage 2**
 - 97% \pm 2% extraction stage 3 or parallel stage of extraction**
 - \geq 98% stripping stages**

Net Copper Transfer on the Organic

EQUATIONS:

$$\text{L.O g/l Cu} - \text{S.O. g/l Cu} = \text{Total Net Cu Transfer}$$

$$\frac{\text{L.O g/l Cu} - \text{B.O. g/l Cu}}{\text{V/V \% LIX 984N}} = \frac{\text{Net Cu Transfer}}{\text{V/V\% LIX 984N}}$$

EXAMPLE: $8.48 - 2.60 = 5.88 \text{ g/l Cu Total Net Cu Transfer}$

$$5.88 / 20 \text{ V/V\%} = 0.294 \text{ g/l Cu per V/V\% LIX 984N}$$

Net transfer numbers can be used to adjust the reagent concentration or the advance O/A ratios to compensate for fluctuations in the PLS Cu grade.

Net Transfer Continued

Net Transfer per V/V% LIX 984N used to adjust Reagent Concentration:

PLS Grade Increase: The PLS Grade increases from 6.71 g/l Cu to 7.05 g/l Cu? This represents an increase of 0.34 g/l Cu.

EQUATION:

$$\frac{\text{g/l Cu increase in PLS grade}}{\text{Net transfer V/V\% (0.294 g/l Cu)}} = \text{Increase in Vol\% reagent needed}$$

EXAMPLE:

$$\frac{0.34 \text{ g/l Cu}}{0.294 \text{ g/l Cu}} = 1.16 \text{ v/v\% more LIX 984N needed}$$

Net Transfer Continued

Net Cu transfer value used to adjust Advance O/A ratios

PLS Grade Increase: The PLS Grade increases from 6.71 g/l Cu to 7.05 g/l Cu. This represents an increase of 0.34 g/l Cu.

Note: Total Net Transfer = L.O. - B.O or $8.48 - 2.60 = 5.88$ g/l Cu

Equation To Adjust the Organic flow

Org Flow (Total Net Transfer + g /l Cu increase in PLS) = New Org Flow Rate
Total Net Transfer

EXAMPLE:

$$\frac{800 \text{ m}^3 / \text{hour} (5.88 + 0.34)}{5.88} = 846 \text{ m}^3 / \text{hour} (\text{New Org Flow Rate})$$

Best Way to Handle Increase in Copper Concentration of PLS?

- **When do you increase reagent concentration?**
 - If change in PLS copper concentration is long term
 - If organic flow cannot be increased
 - If O/A ratio far away from 1/1 and mixer efficiencies affected
- **When do you increase organic flow rate?**
 - If change in PLS copper concentration is short term
 - If organic flow rate is not at maximum and O/A ratio is near 1
 - If you have no reagent to increase reagent concentration

LIX®984N Concentration Determination

Under the conditions outlined in the Cognis Quality Control Procedures the maximum copper loading capacity for each v/v% of LIX 984N is 0.53 g/l Cu, so 10.0 V/V% loads 5.30 g/l Cu.

$$\text{Reagent Concentration} = \frac{\text{Organic Max Load g/l Cu}}{0.53 \text{ g/l Cu}}$$

Example: $8.48 \text{ g/l Cu} / 0.53 \text{ g/L Cu} / \text{Vol\%} = 20.0 \text{ V/V\% LIX 984N}$

What Will Cause a Poor Mass Balance

- **Inaccurate Flow Measurements**
- **Inaccurate Analyses**
- **Inaccurate Sampling**
- **Inaccurate Calculations**
- **High Entrainments (Aq in Org)**

Electrowinning

Typical Tankhouse Electrolytes

Electrolyte	Copper g/l	Sulfuric Acid g/l
Spent	33 - 40	150 - 200
Pregnant	45 - 55	116 - 182

Electrowinning

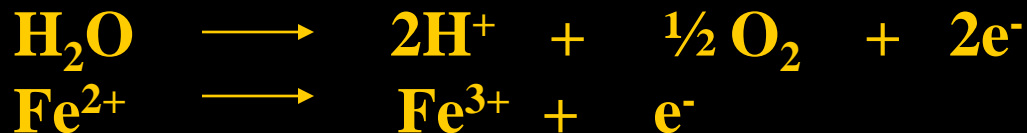
- **Electrowinning Reactions**
- **Cathode Quality**
- **Electrolyte Quality**
- **Solvent Extraction**

Electrowinning Reactions

Cathode



Anode



Overall



Cell Voltage ~ 2.1

Cathode Quality

- **Impurities occluded in the cathode**
 - PbSO_4 , PbO_2 , Silica, solids carried to tankhouse, electrolyte, organic
- **Organic burn caused by circuit organic in tankhouse**
 - Copper SX reagent enhances porous copper burn
- **Rope around edge of cathode**
 - Can be porous
 - smaller anode than cathode

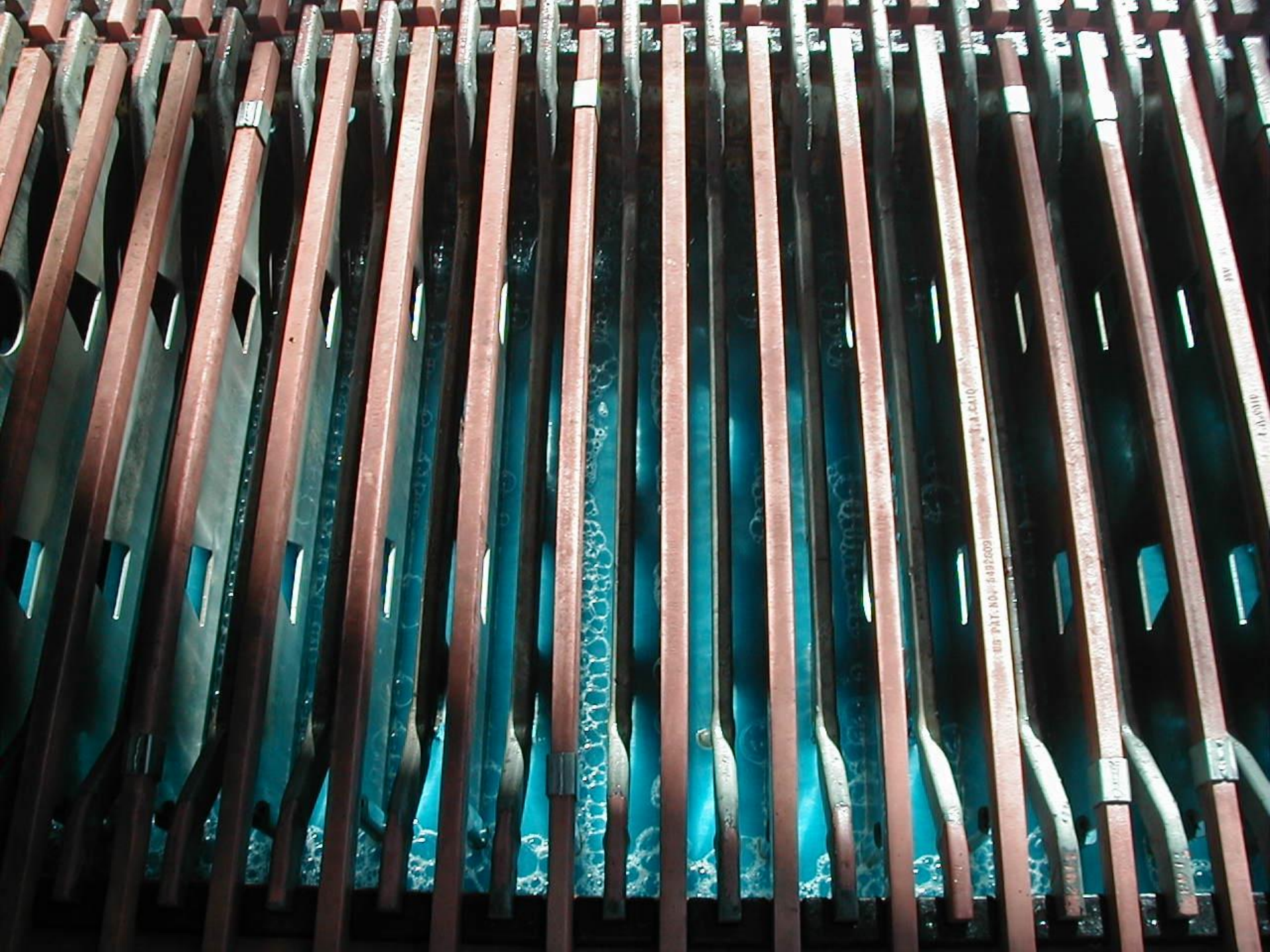


High Purity Cathode

- **Promote smooth, dense deposit**
- **Stable lead anode**
- **Clean electrolyte**
- **Prevent direct contact of anode and cathode**
- **Wash cathodes effectively**

Promote Smooth Dense Deposit

- **Consistent anode-cathode spacing & alignment**
- **Lowest practical current density**
 - Design 260 to 280, run 260 to 340 amps / m²
- **Highest practical copper concentration**
 - Electrolyte entering cell (35 to 41 g/l Cu)
 - Good electrolyte circulation in cell (3 g/l Cu drop)
- **Temperature - 45 to 50 °C**
- **Smoothing agent - EW guar, polyacrylamide**
- **Excellent house keeping**



US PAT. NO. 4,492,000

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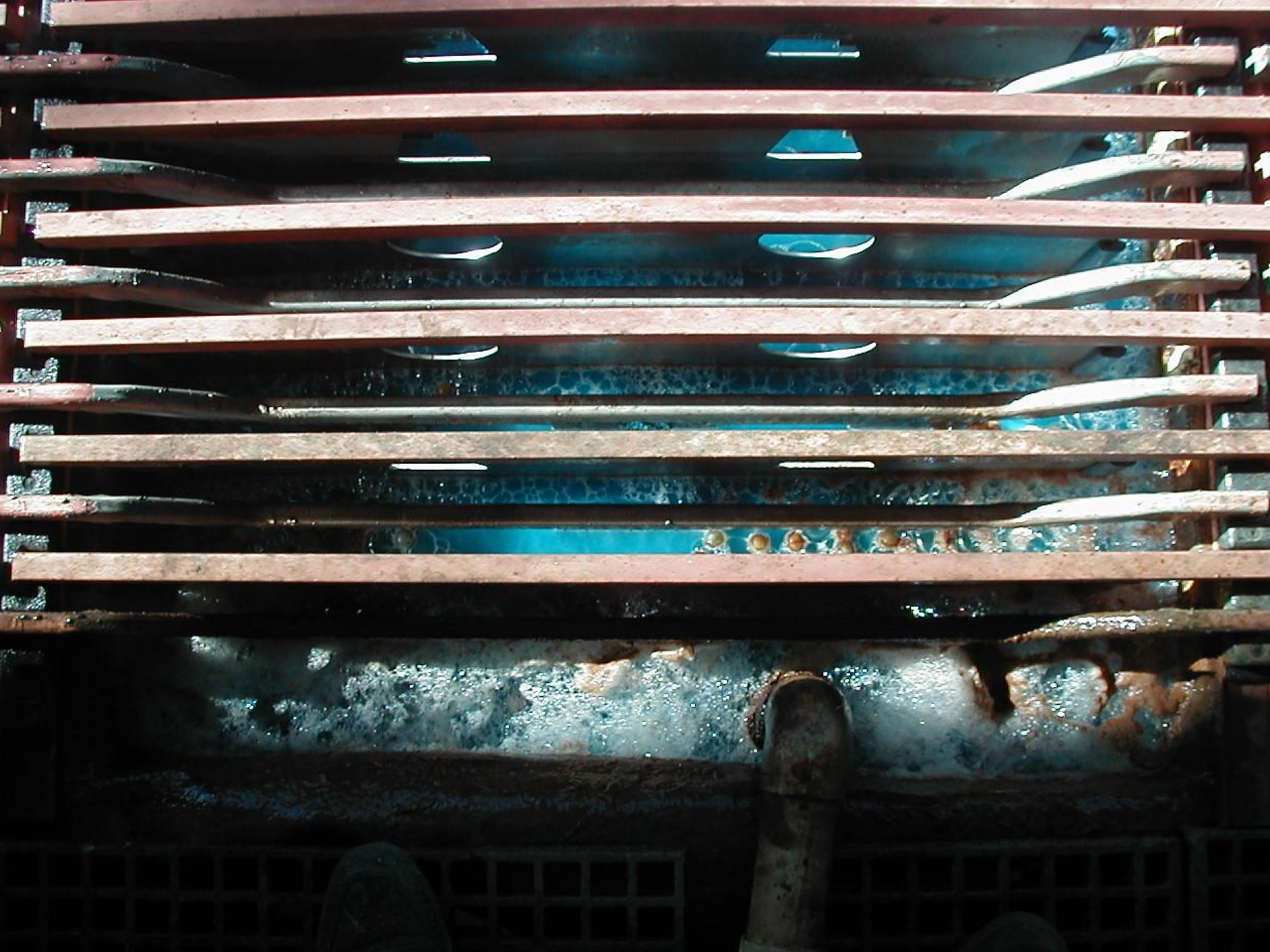






Electrolyte Quality

- **SX provides high copper concentration**
- **SX can provide good chemical purity**
 - **Reagents very selective for copper**
 - **Entrainment of aqueous in loaded organic**
- **Remove organic entrainment from electrolyte**
 - **settling, flotation, filtration**
- **Remove solids from electrolyte**
 - **settling in cell, filtration**

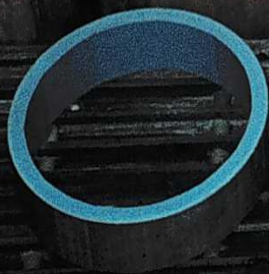


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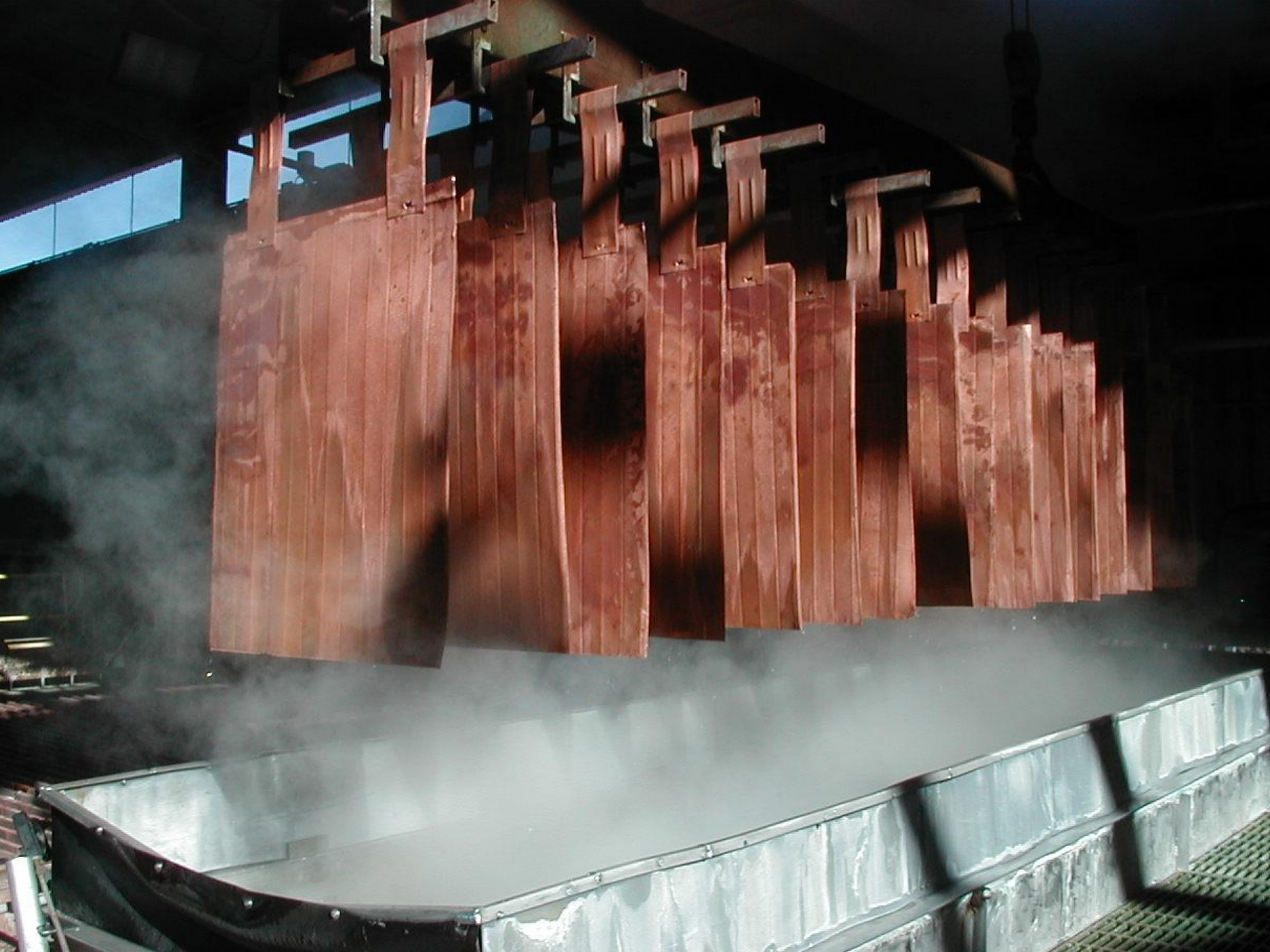
Stability of Lead Anode

- **Formation of lead oxide on anode surface**
 - **Choice of lead alloys**
 - **cobalt in electrolyte**
 - **manganese in electrolyte**
 - **Maintain power to the tankhouse**
- **Physical stability**
 - **Cast or rolled anodes**
 - **Current densities**

Prevent Direct Anode/Cathode Contact

- Straight, rigid starter sheets or SS cathode blanks
- Insert starter sheets / blanks carefully
- Pull cathodes carefully
- If using starter sheets press 2 day cathode
- Remove warped anodes
- Anode / cathode insulators
 - Buttons, hairpins, plastic runners, anode feet













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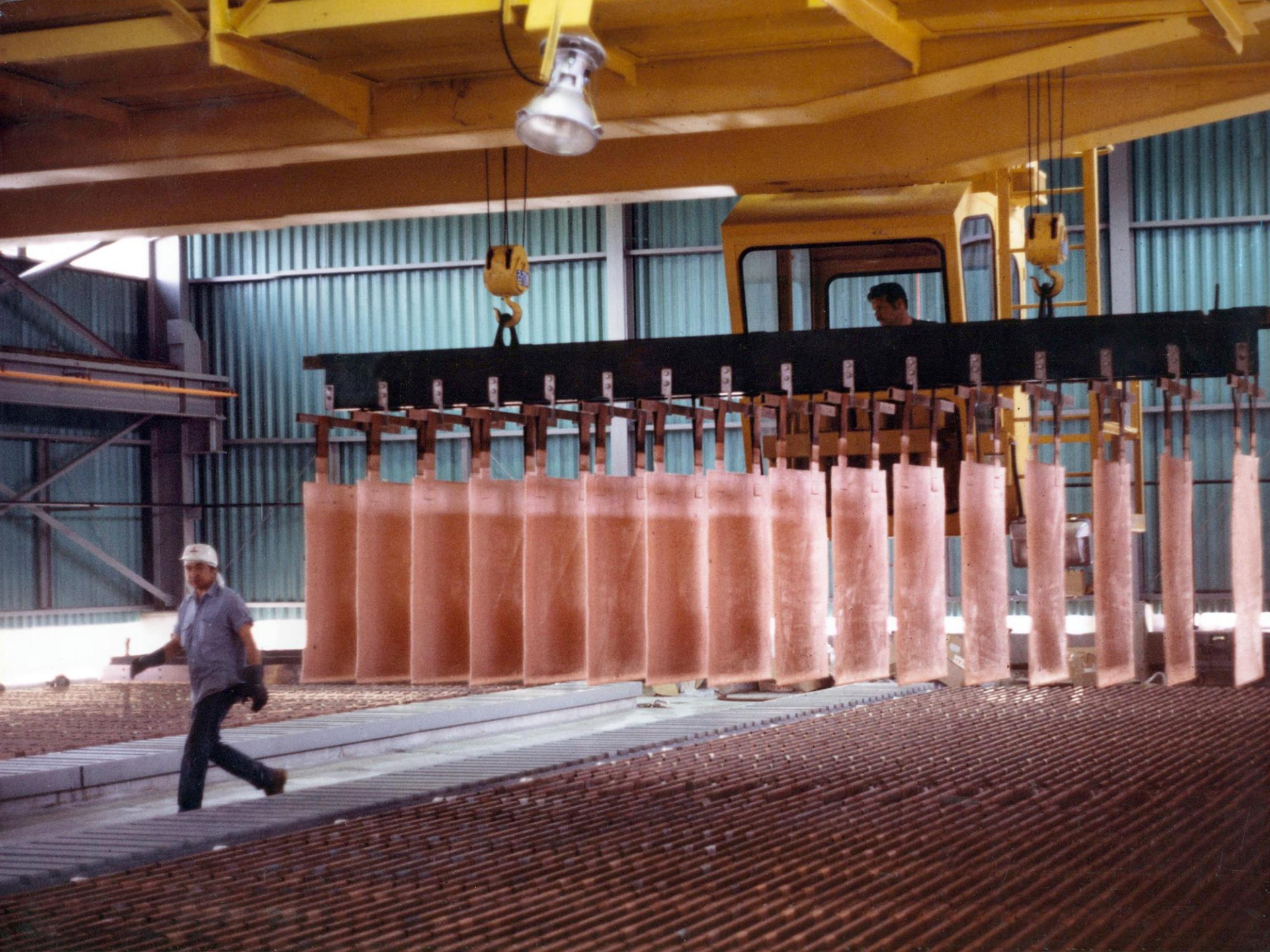
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Wash Cathodes Effectively

- **Immediate rinse when cathodes pulled**
- **Hot water soak (pull cycle)**
- **Cool down (pull cycle)**
- **Final hot water wash**



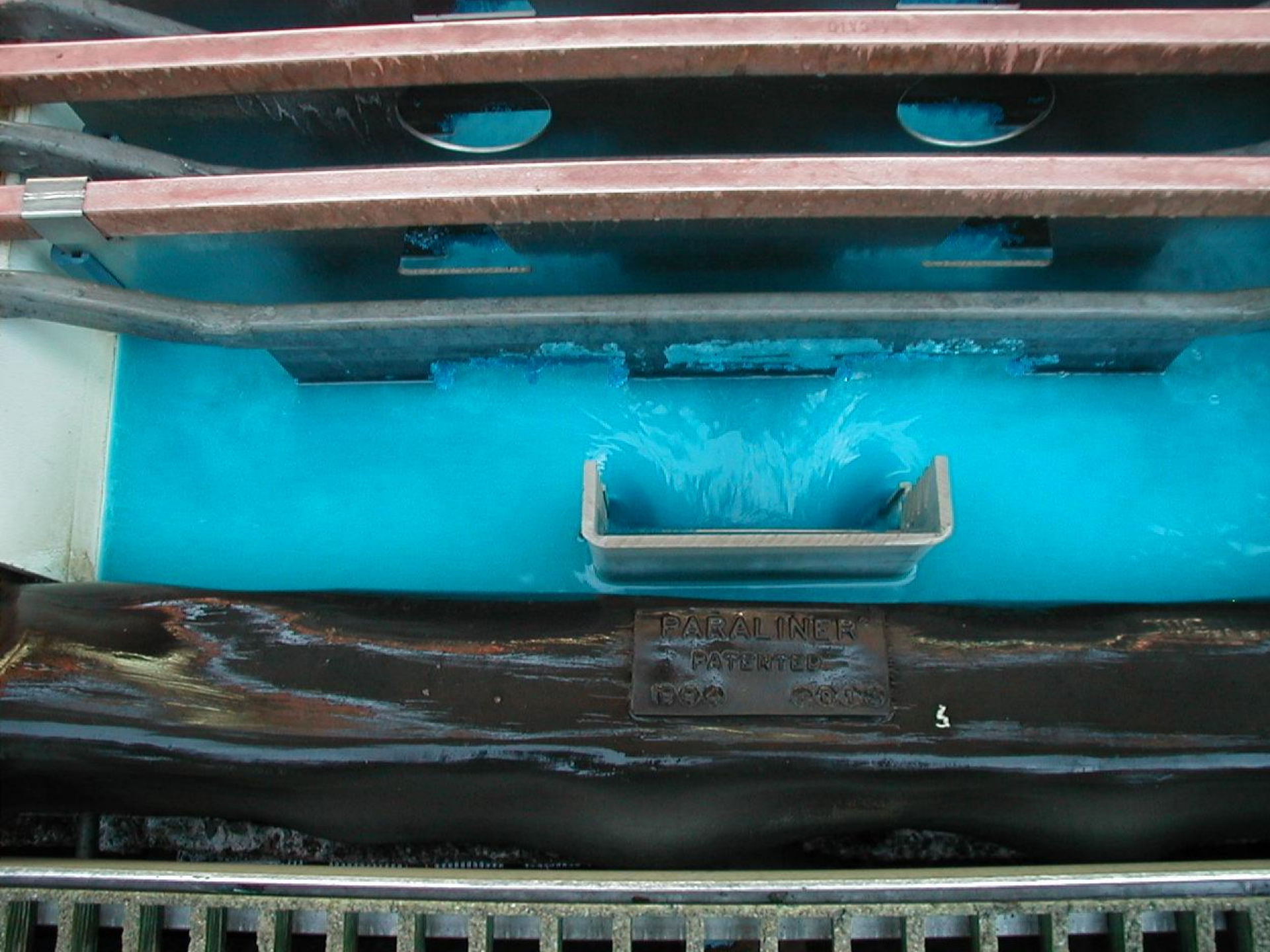






Other Considerations

- **Run lower strip acid**
 - less corrosive acid mist
 - longer anode life
 - higher copper quality
- **Run higher copper pregnant electrolyte**
 - higher copper quality
 - less entrainment of organic in electrolyte
- **Mist control - mechanical or chemical?**



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