IMPROVED INNER LAYER ETCHING BY SIMULTANEOUS CUPRIC REGENERATION & COPPER RECOVERY SYSTEM

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ACID ETCHING USING CUPRIC CHLORIDE

- Acid cupric chloride is used widely in the PCB industry as an effective etching solution for removing unwanted copper from copper printed circuit boards.

- The etching reaction can be expressed ionically as: -

$$Cu^{O} + Cu^{2+} \Rightarrow Cu^{+} + Cu^{+}$$

- Etching one atom of copper (Cu^{O}) with one cupric ion (Cu^{2+}) produces two cuprous ions (Cu^{+}). These cuprous ions are inactive in etching terms and, as their concentration in the solution increases, the etch rate falls.

- To maintain the desired etch rate it is therefore necessary to either regenerate the etchant or replace spent etchant with fresh chemistry. Regeneration is the action of oxidising the cuprous ions to convert them back to cupric.

- Two methods of regeneration of the etchant are currently employed, namely chemical and electrolytic.

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CHEMICAL REGENERATION

- The technique involves the use of chemical oxidation using chlorine gas or hydrogen peroxide for example to convert the cuprous ions to active cupric ions. Surplus cupric chloride is produced, which increases the level of dissolved copper in the etching until it reaches a level where etching is inhibited. Therefore excess solution must be removed to compensate for the additions in order to maintain the correct copper concentration. This process is generally carried out by means of a feed and bleed pumping system, with excess solution stored ready for disposal.

- The oxidation reaction can be expressed as:-
- Two Cuprous ions produced during etching + Hydrogen peroxide => two Cupric Ions

$Cu^{+} + Cu^{+} + H_2O_2 \Rightarrow Cu^{2+} + Cu^{2+}$

- One Cupric Ion in the solution is required to maintain copper concentration for etching, the other is removed by adding hydrogen peroxide for example and HCl and water to maintain the correct chemical balance and copper concentration.

- The result is a large volume of excess etchant which has to be disposed of.

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ELECTROLYTIC REGENERATION

- Electrolysis is the action of producing chemical changes by passing an electric current through an electrolyte. The cupric chloride in this case is the electrolyte.
- The process is achieved by the use of a divided cell containing an anode in one compartment and a cathode in the other, separated by a cationic membrane. An electrical current is passed through the membrane.
- Reactions taking place at the anode, or +ve electrode, are oxidations, (removal of electrons) and those occurring at the cathode, or –ve electrode, are reductions, (addition of electrons).
- Electrolytic regeneration of cupric chloride is achieved by taking advantage of these two simultaneous reactions.
- The oxidation reaction at the Anode can be expressed as:-

Cu^{+} + Cu^{+} - two electrons => Cu^{2+} + Cu^{2+} Similar to that of chemical oxidation. Two Cupric Ions are now present.

- At the cathode, cupric ions are converted to metallic copper by reduction allowing the etchant to be continuously regenerated while removing excess dissolved copper, in metallic form. This can be expressed as:-

Cu^{2+} + two electrons => Cu^{O}

- Copper metal is plated onto the Cathode within the cell
- Copper represents the only significant waste product from the process and uses no chemical additives to achieve the conversion apart from replacement of losses in the system due to drag out or evaporation.

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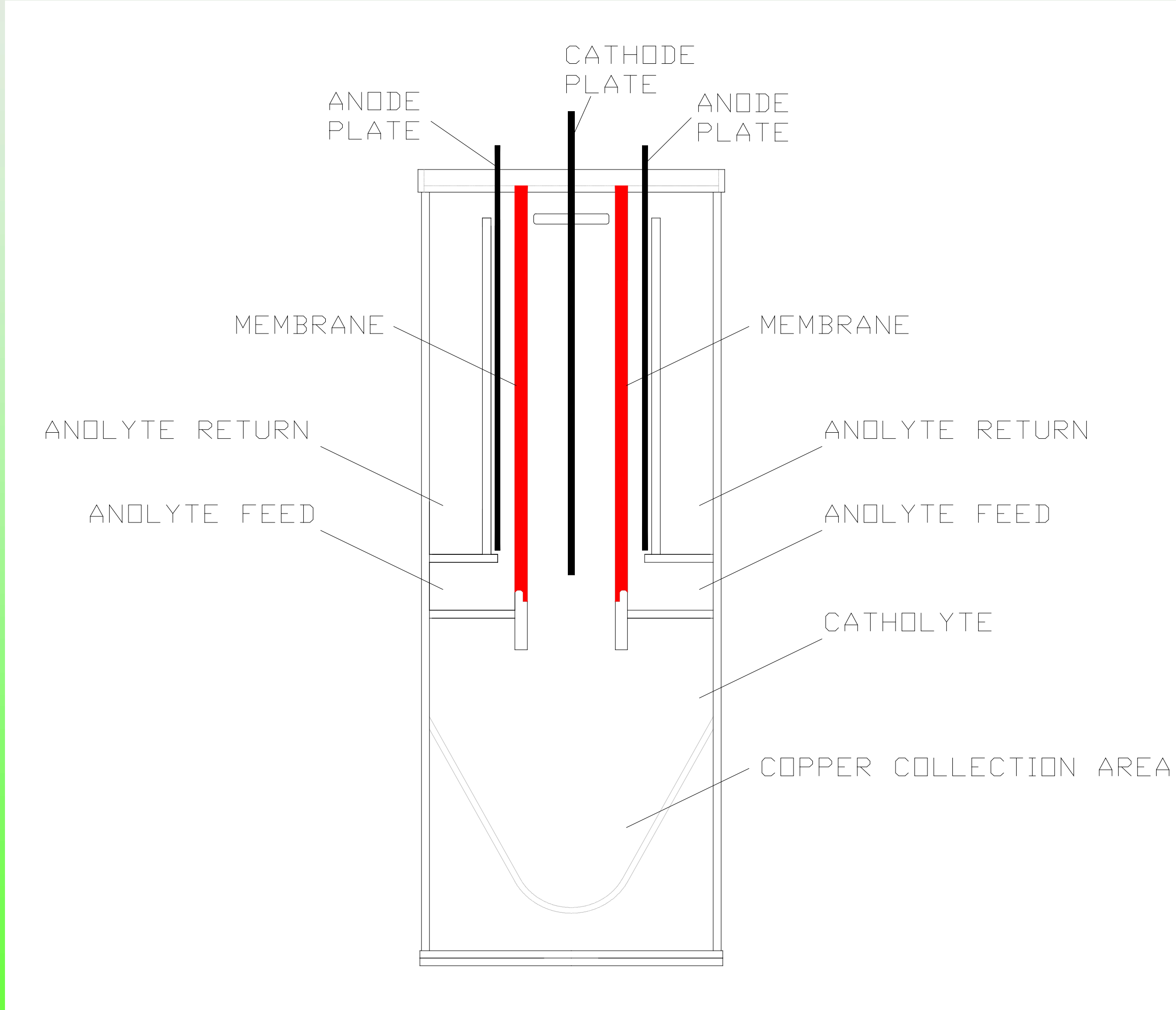

TYPICAL 2Kg CELL OVERVIEW

- The cell is divided into three chambers, two Anolyte and one Catholyte.
- The center chamber contains the Catholyte with the Anolyte located either side.
- The Anolyte and Catholyte are separated by semi-permeable membranes.
- The Copper metal, which is plated on the Cathode plate automatically transferred into the Copper collection chamber.

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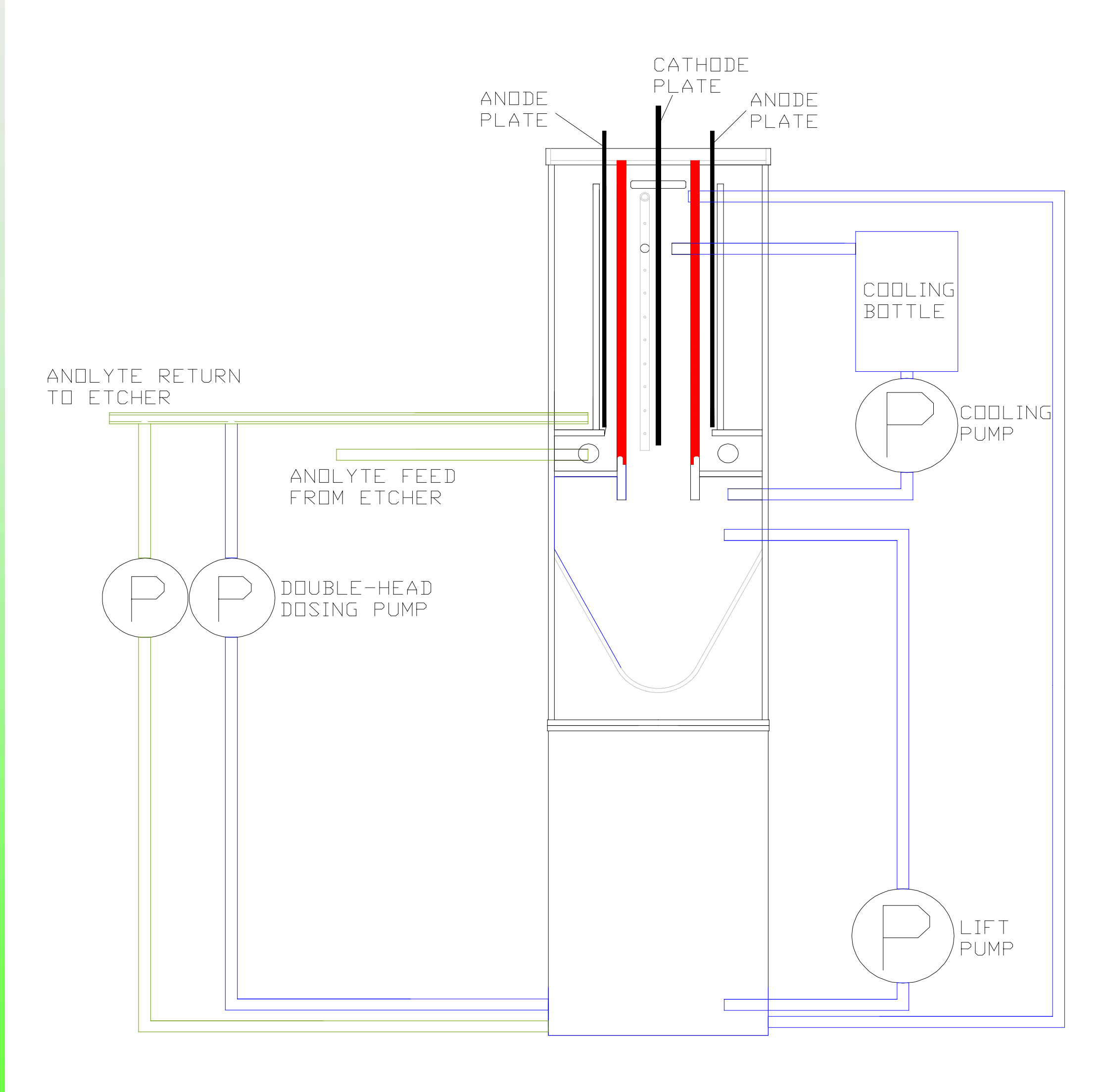

TYPICAL 2Kg PROCESS OVERVIEW

The process has four stages

Anolyte is fed to the Anode plate and returned to the etcher

Catholyte is fed to the Cathode plate and returned to the sump

Catholyte is circulated within the cell to be cooled

Solution transfer between the Anolyte and Catholyte and return.

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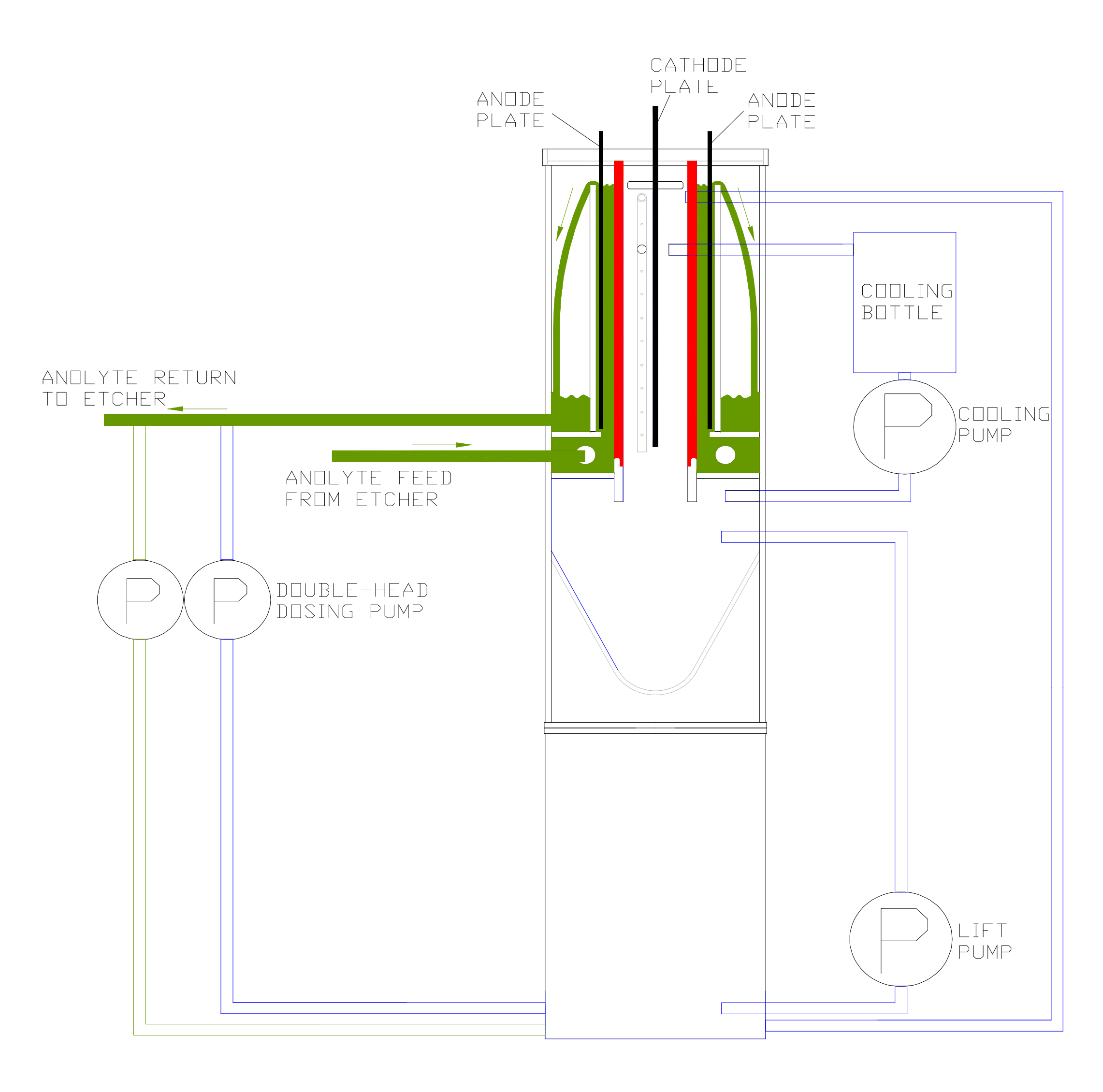

PROCESS STAGE 1

Anolyte

- The Etching solution from the etch system “Anolyte” is pumped to the cells, and feeds both sides of the cell.
- The Anolyte enters the cell and rises up inside, passing between the Anode plate and the membrane.
- The Anolyte weirs over at the top of the Anode plate, and returns to the bottom of the cell.
- The Anolyte is returned to the Etch system

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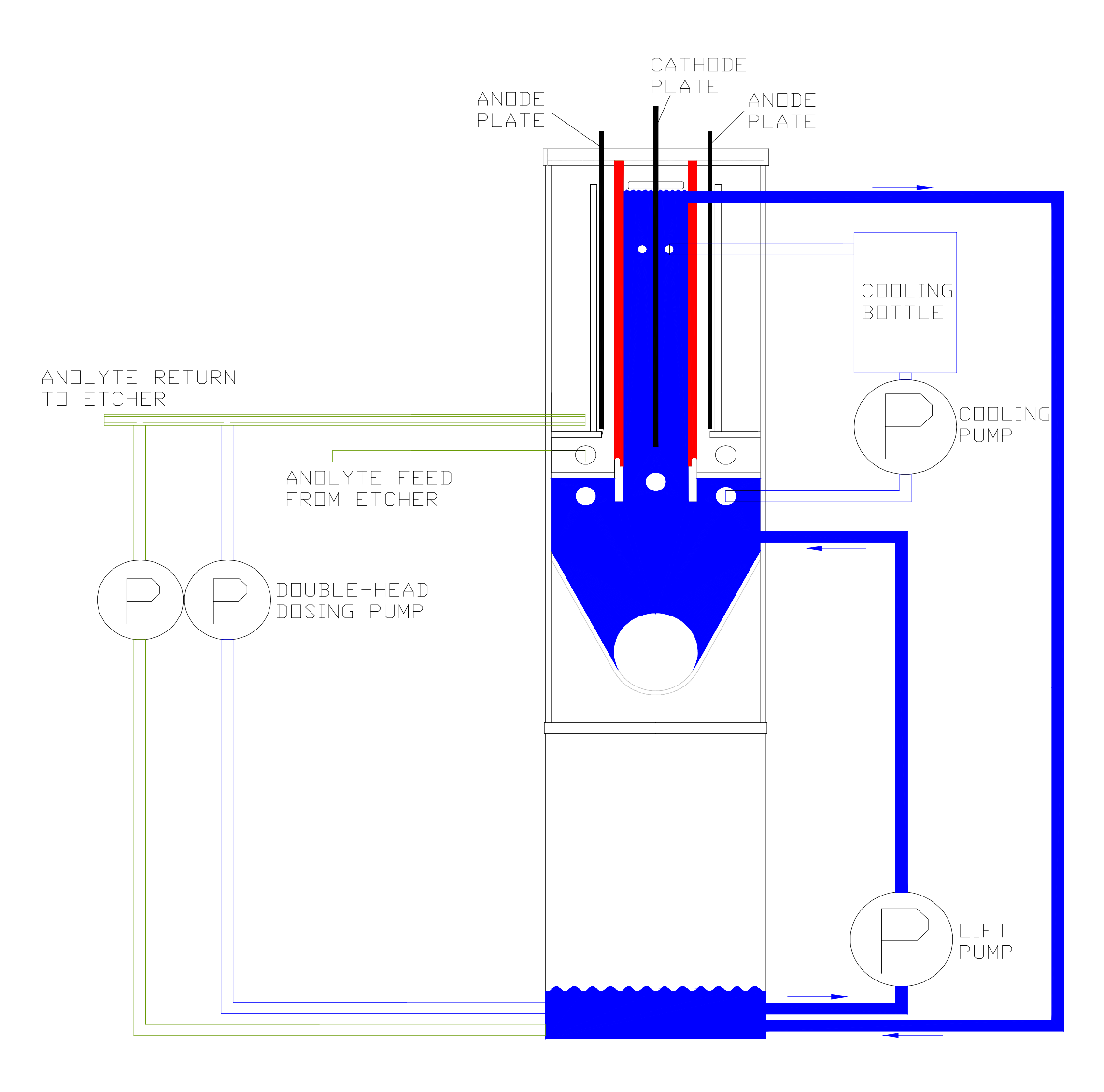

PROCESS STAGE 2

Catholyte Lift

- The Plating solution from the lower sump “Catholyte” is pumped to the cell by the lift pump,
- The Catholyte enters the cell and rises up inside, passing over the Cathode plate, between the two membranes.
- The Catholyte weirs over at the top of the Cathode plate, and returns to the lower sump.

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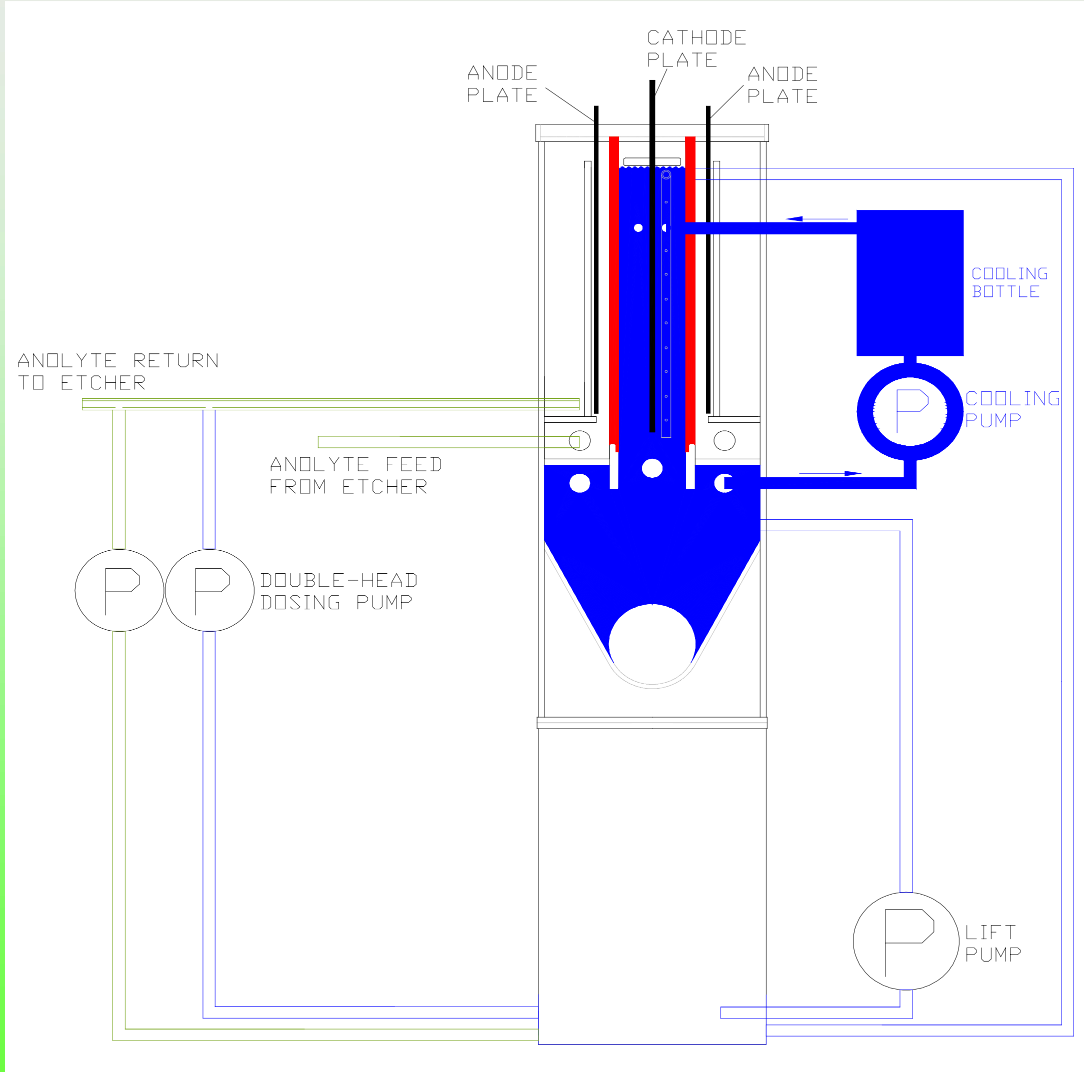

PROCESS STAGE 3

Catholyte Cooling

- The Catholyte is pumped from the cell by the cooling pump,
- The Catholyte enters a Glass cooling bottle and is cooled to approximately the same temperature as the incoming Anolyte.
- The Catholyte is returned to the cell

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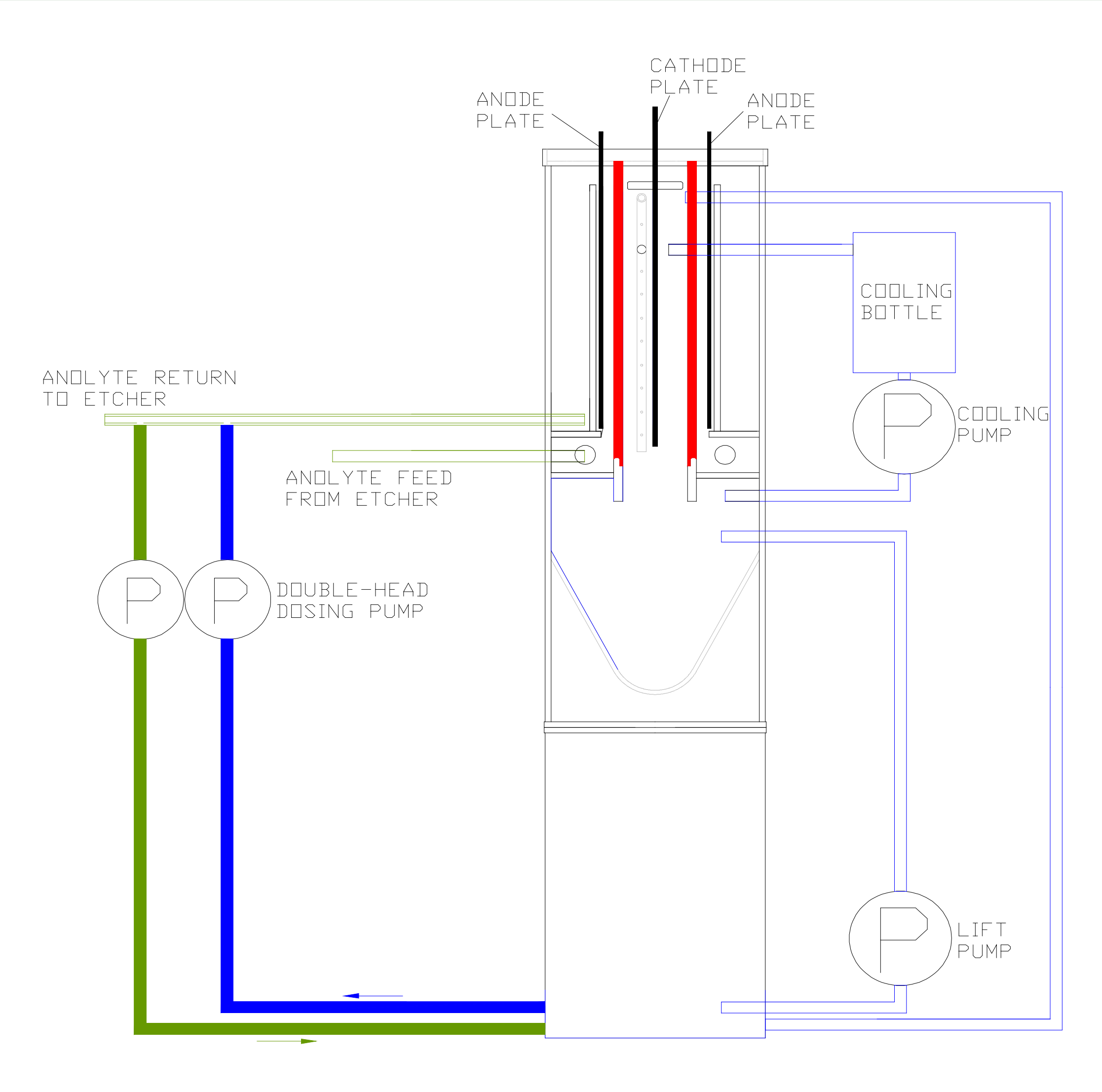

PROCESS STAGE 4

Anolyte/Catholyte Transfer

• Solution transfer is required in order to move surplus Cupric Ions from the Anolyte to the Catholyte so as to maintain the Copper concentration in the Catholyte, and feed the plating process.

• These surplus Cupric Ions were created by the oxidation of Cuprous ions in the Anolyte cycle

• In order to plate out 2Kg of Copper / Hr, 2Kg of Copper ions must be introduced to the Catholyte.

• To maintain the Catholyte volume, an Identical quantity of Catholyte is pumped to the Anolyte. This is accomplished by a pair of matched and calibrated diaphragm pumps.

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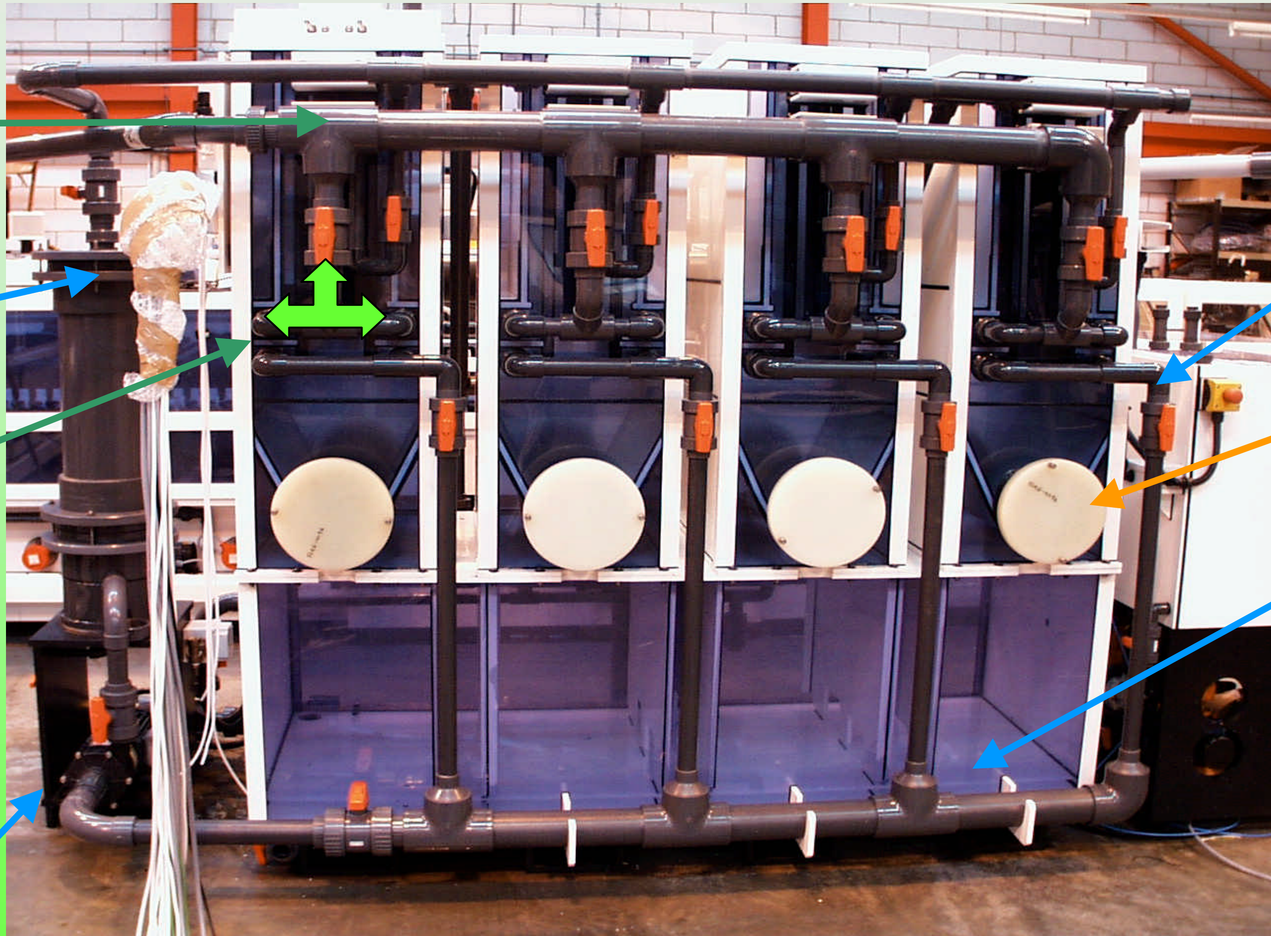
Module Description



Anolyte feed from etcher

Catholyte cooling bottle

Anolyte feed split to each side

Catholyte cooling pump

Catholyte cooling return

Copper metal removal hatch

Catholyte Sump

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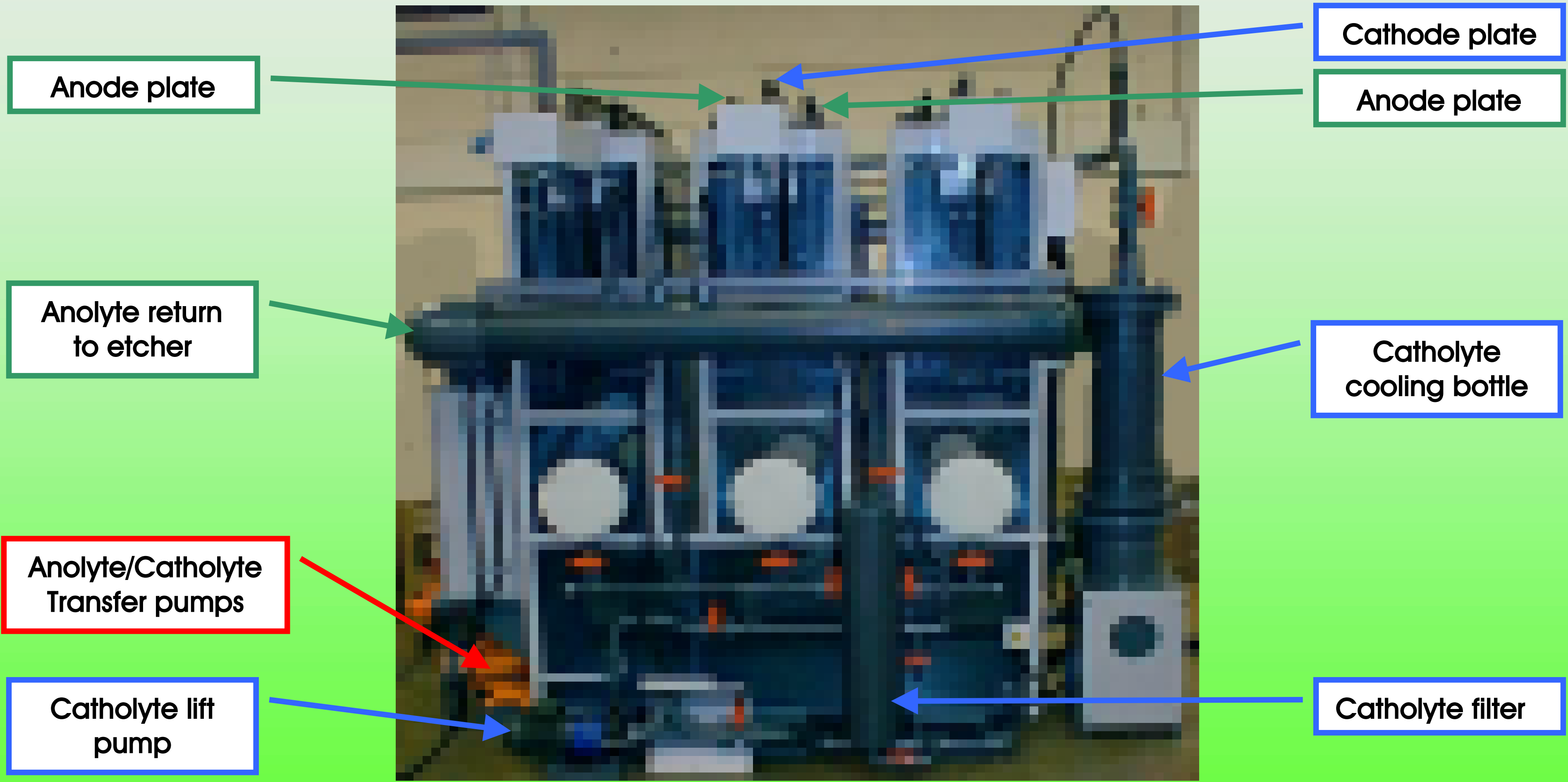
Module Description



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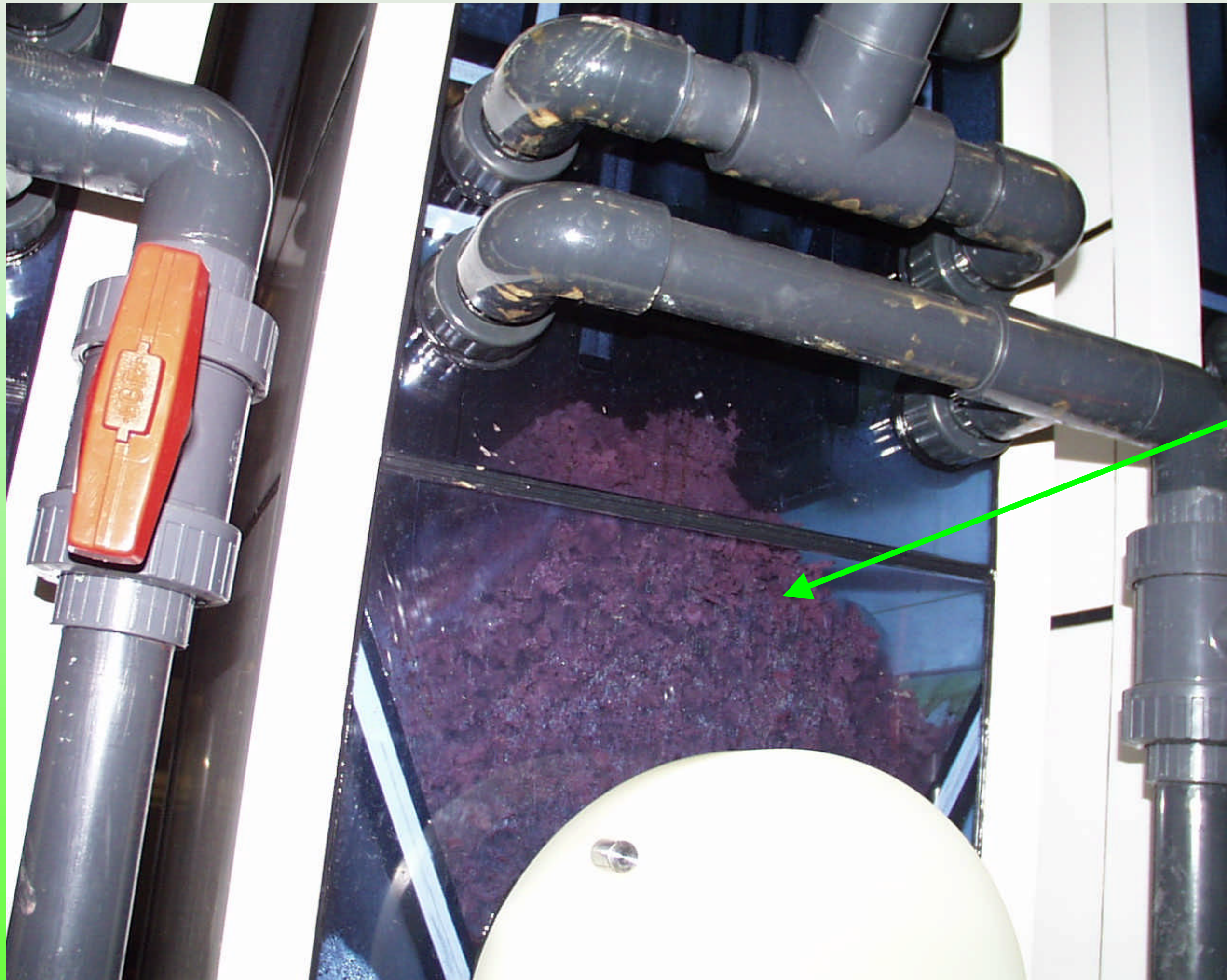
Process Photos



Copper metal in Regen cell

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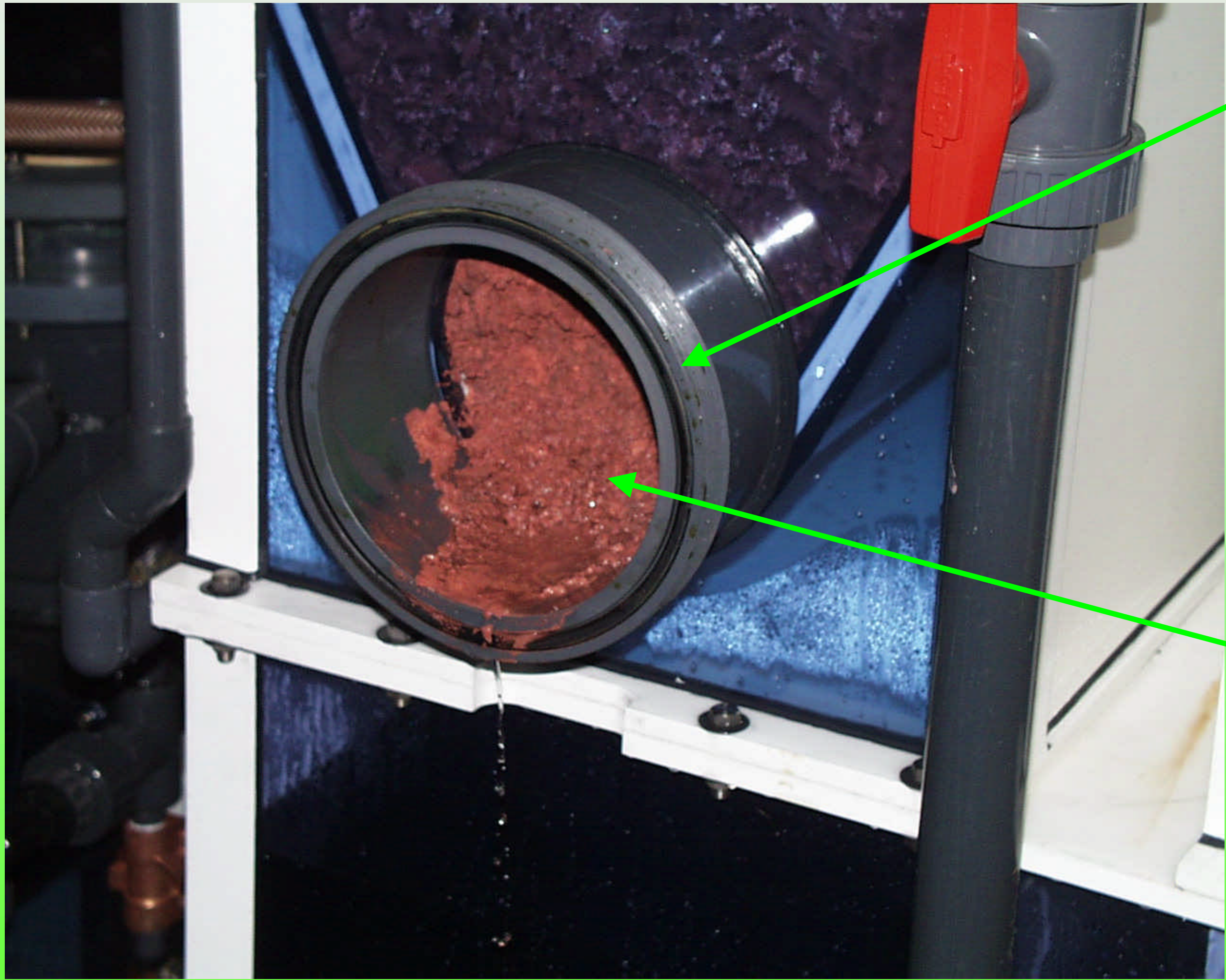
Process Photos



Open copper removal hatch

Dendrytic copper metal

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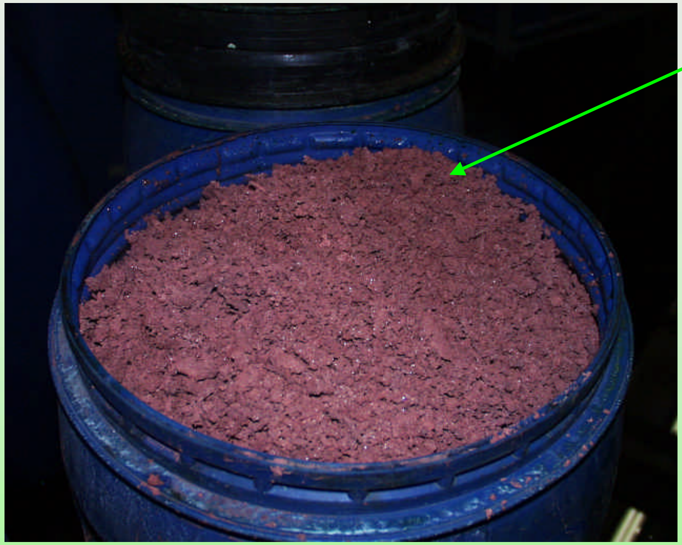

Removed copper metal aprox 60kg per cell every

Pressed copper granules

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Rectifier

Connection from Rectifier to Regeneration unit

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PROCESS SUMMARY

•Etchant comprises CUPRIC ions (Cu^{2+})

•During the etching process one CUPRIC ion (Cu^{2+}) becomes two CUPROUS ions ($Cu^{+} + Cu^{+}$)

•During the electrolytic oxidation process at the Anode the two CUPROUS ions ($Cu^{+} + Cu^{+}$) are converted to two CUPRIC ions ($Cu^{2+} + Cu^{2+}$) . The Copper removed from the PCB is now in the form of a surplus CUPRIC ion (Cu^{2+}) in the Etch solution (Anolyte). This is the same result as is achieved by using the Peroxide oxidation process.

• Rather than removing this surplus Copper as waste solution, the ions are removed by being plated out as copper metal.

•The surplus CUPRIC ion (Cu^{2+}) is transferred to the Catholyte (plating solution) by a dosing pump, sufficient to feed the plating process at approximately 2Kg per cell per hour. The copper concentration in the Catholyte required to achieve the correct plating rate can be set manually or controlled automatically using a density controller.

•During the reduction process at the Cathode, the surplus CUPRIC ion (Cu^{2+}) is converted to copper metal, plated in a dendrytic form onto the carbon graphite Cathode plate.

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PROCESS BENEFITS

- Consistent etch results due to tight process control
- No Chemical oxidising agent required (excludes natural losses)
- Low Copper level in Etchant promotes a sludge free process sump
- High Etchant Flow Rate provides quick response to changes in etchant solution
- No Waste, only by-product is copper.
- No running costs due to profit from sale of the recovered copper.
- Short term payback on investment

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