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CORPORATION

Technical Information

Process Guidelines for Cupric Chloride Etching

Introduction

Cupric chloride as the main etchant for panels using non-metallic resists began to become common in the late 60's to early 70's. Ferric chloride was the most common etchant for non-metallic resist panels up until then because of its fast etch rate and high metal holding capacity. However, cupric chloride is capable of continuous regeneration and, as such, can be operated in a steady state condition, an advantage that soon made it the top choice in spite of an etch rate of half that of fresh ferric chloride. Regeneration made the metal holding capacity of cupric chloride in essence infinite, an advantage that overcomes any other objection. Today cupric chloride is used to etch a majority of the inner layers produced in the world. Almost half the etch systems sold by Chemcut in the last five years have been cupric chloride systems.

This bulletin will cover the advantages and disadvantages of using cupric chloride as an etchant, the chemical reactions and processing parameters of cupric chloride, equipment parameters and system design considerations.

Advantages of Using Cupric Chloride

- Cost per pound of copper etched is typically less than alkaline etch
- Much easier to obtain steady state control for precision etching
- Copper in rinse water is not complexed and removing it from the waste water is not a problem for most waste treatment systems
- More tolerant of oxide films on the surface of panels to be etched

Disadvantages of Using Cupric Chloride

- Attacks most plated metallic resists
- Slower etch rate than alkaline etch – approximately 1.0 to 1.6 mils/min as opposed to 1.9 to 2.5 mils/min for alkaline
- More undercut than alkaline etch – a ratio of 3 to 1 for downward etch to lateral etch in contrast to a 4 to 1 ratio for most alkaline baths

- Could be expensive to dispose of excess etchant if no metal reclaimer is willing to take it

Chemical Reactions

Cupric chloride is an acidic solution with a pH of <1 at the concentrations used for etching. The best etch rate occurs between copper concentrations of 125 gpl Cu and 175 gpl Cu. This corresponds to a specific gravity range of 1.2393 to 1.3303 (28^o Be to 36^o Be).

The etching reaction:

- $Cu^o + Cu^{+2}Cl_2 \rightarrow 2Cu^{+1}Cl$

The addition of chlorine to the bath will reoxidize the Cu^{+1} ion to the Cu^{+2} ion by the following reaction:

- $2Cu^{+1}Cl + 2Cl^{-1} \rightarrow 2Cu^{+2}Cl_2$

There are several methods to introduce chlorine into the etch bath. They are:

1. Chlorine gas pulled directly into the system
2. Reaction between Hydrochloric Acid and Hydrogen Peroxide in the etch bath
   - $H_2O_2 + 2HCl \rightarrow 2Cl^{-1} + 2H_2O$
3. Reaction between Hydrochloric Acid and Sodium Chlorate in the etch bath
   - $NaClO_3 + 6HCl \rightarrow NaCl + 6Cl^{-1} + 3H_2O$

The chemical cost of regeneration per lb. of copper etched varies from location to location and by volume but in most cases introducing chlorine gas directly into the solution is the least expensive alternative. Depending on local regulations and environmental concerns the cost can be half that of hydrogen peroxide or sodium chlorate. In many localities, however, the use of chlorine is banned or severely discouraged. In these cases methods 2 and 3 are a viable alternative for supplying chlorine to the bath for regeneration. The costs of both are about the same and there are no process-related differences. There is a potential disadvantage in the use of sodium chlorate as the oxidizer, however, if the sodium chlorate is purchased as a crystal and mixed on site. As can be seen from the reaction equation above one of the byproducts of the reaction is sodium chloride (NaCl).

Salt is not very soluble in an acid solution at this low a pH and the salt crystals formed are very abrasive. As a result there is more equipment wear in terms of seals and nozzles than with other methods of regeneration. A potentially more important disadvantage is that salt in the spent etchant may interfere with the copper recovery. Many metal reclaimers will not take cupric chloride contaminated with salt. Be sure to check on this before selecting a chlorate system. Chemcut recommends that commercially available 45% to 50% sodium chlorate solutions be used since the NaCl build-up is much less.

The regeneration system for the Chemcut cupric chloride etch system can be set up to handle any one of these three methods.

Chemical Processing Parameters for Cupric Chloride Etch

There are four chemical factors that contribute to the etch rate and undercut of cupric chloride etchant. They are:

- ORP (Oxidation – Reduction Potential)
- Free Acid level
- Specific Gravity
- Temperature

Each of these has an effect on etch rate and undercut which must be balanced to get the best compromise of fastest etch rate and least amount of undercut; although the balancing act is not as delicate as that with alkaline etch. The effects of each of these factors are discussed in the following paragraphs.

ORP or Oxidation / Reduction Potential

For cupric chloride the ORP is a measurement of the ratio of Copper II ions to Copper I ions. This measurement is used to trigger the addition of chlorine to the etchant in order to re-oxidize the Cu^{+1} ions to Cu^{+2} ions and maintain a steady state etch rate. Probes are available commercially that measure ORP and express it as millivolts output. ORP is expressed mathematically by the Nernst equation:

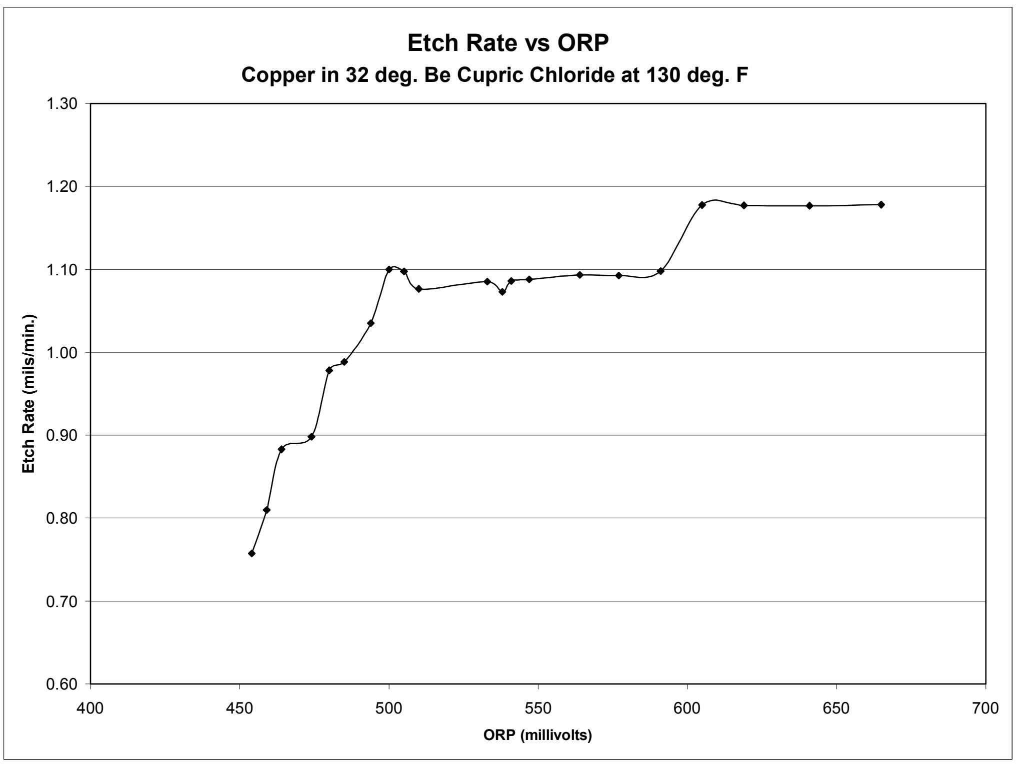
$$E = E^0 + \frac{2.303RT}{n} \text{Log} \frac{Cu^{+2}}{Cu^{+1}}$$

Where: E^0 = Standard potential of the electrode

R = Gas law constant in electrical units (8.314 V-^{o}K)
T = Absolute temperature (^{o}K)
n = Number of electrons transferred per molecule

In normal etching conditions E^0, R, T, and n are all constant so E is directly affected only by the amount of Cu^{+1} ions in solution in relation to the number of Cu^{+2} ions. As copper is etched from the panel surface the concentration of Cu^{+1} in the etch bath rises and the value of the ORP reading falls. The regeneration process in turn reoxidizes the Cu^{+1} to Cu^{+2} causing the ORP reading to rise. Typically a freshly made cupric chloride etch bath at 150 gpl copper and 130^{o} F with very few, if any, Cu^{+1} ions will have an ORP reading of 650 + mv. The addition of as little as 0.1 gpl copper in the form of Cu^{+1} ions (etched copper) will quickly drop the ORP into the 550 mv range. This large response to a small bit of copper etched makes ORP a very sensitive control parameter.

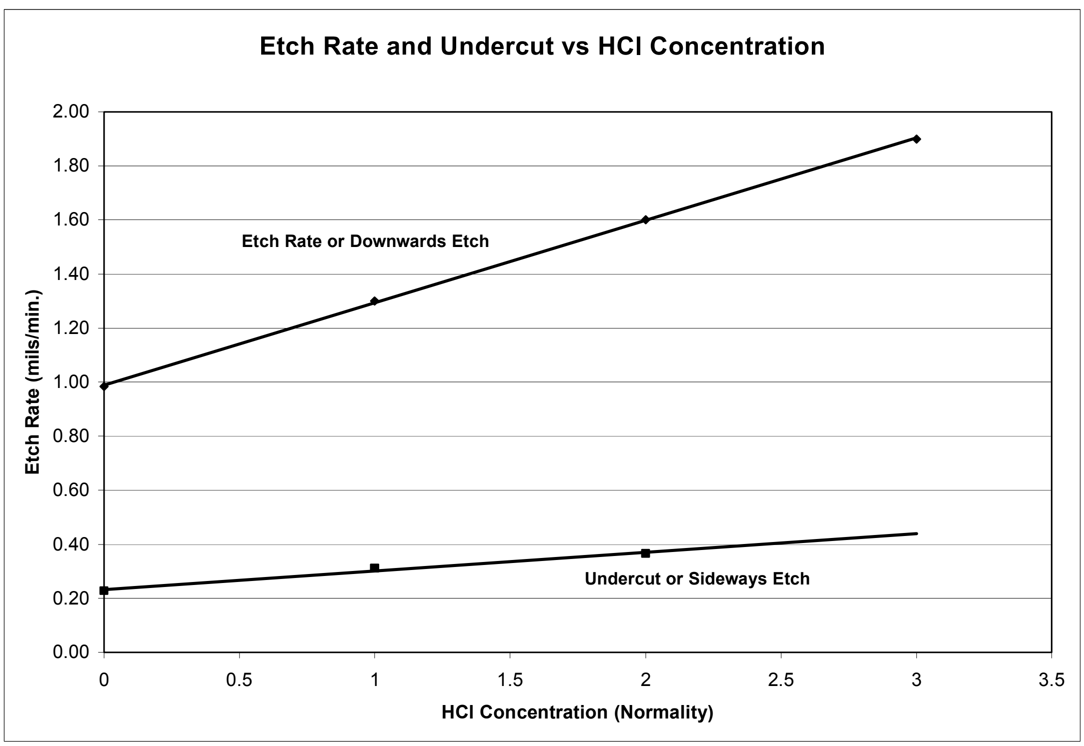
The following graph of etch rate vs. ORP displays another interesting property of cupric chloride etchant.



The etch rate of cupric chloride changes fairly rapidly as the ORP changes except for the region between 500 mv and 600 mv where the etch rate remains fairly steady. Since this plateau occurs at a fairly high etch rate it provides an excellent range to use as a control setting. Setting the ORP controller to the midpoint of this plateau, between 540 mv and 550 mv, allows a relatively wide variation in ORP without much effect on the etch rate. Using a set point over 600 mv is discouraged since there are not enough Cu^{+1} ions in solution in this range to absorb all the chlorine put into the etchant and there is a chance of free chlorine escaping into the atmosphere.

Free Acid Level

Free acid is a measure of the amount of hydrochloric acid in the system. Cupric chloride etchant must have at least some detectable free acid in it for optimum etch efficiency. Hydrochloric acid keeps the relatively insoluble cuprous chloride (CuCl) molecule in solution where it can be regenerated and also removes any traces of copper oxide from the surface of the copper metal being etched. Copper oxide forms almost immediately on the surface of etched copper and cupric chloride alone is not very aggressive towards copper oxide. The hydrochloric acid dissolves the copper oxide and allows the cupric chloride to attack the copper metal directly. Without some HCl in the etchant the etch rate of cupric chloride would be cut at least in half. As the HCl level increases so does the etch rate as seen in the graph below.



Unfortunately, as also shown on the graph, increasing the acid concentration also increases the rate of undercut or lateral etch. The rate of undercut almost doubles between 0.1N HCl and 3N HCl. If the etch bath is run at an HCl concentration of more than 3N for any length of time it will begin to attack the metallic components of the etcher which are generally made of titanium for corrosion resistance. For this reason Chemcut specifies a maximum HCl concentration of 3N. Most cupric chloride etch baths are run at HCl concentrations of between 1N and 2N. Chemcut can provide an acid controller capable of maintaining the acid level at ±0.05N. This feature is relatively inexpensive either as an add-on for existing systems or built in to a new etcher. Since a small change in acid level can have a fairly large effect on etch rate, new systems should be ordered with an acid controller, especially those for etching panels with tight specifications on line width.

Specific Gravity

Specific gravity control is not nearly as important in cupric chloride etching as in alkaline etching. The maximum etch rate for cupric chloride occurs between the specific gravities of 1.2393 (28^o Be or 260 gpl $CuCl_2$) and 1.3303 (36^o Be or 370 gpl $CuCl_2$). The difference in etch rates between the highest and lowest points within this range is only about 0.12 mils/min so that extremely tight control of specific gravity is not necessary. Undercut also does not change significantly within this range so specific gravity control to within ±0.0070 (0.5^o Be or 10 gpl $CuCl_2$) is adequate even where tight line width specifications must be held. Most cupric chloride etch baths operate at specific gravity between 1.2832 (32^o Be) and 1.3303 (36^o Be).

Temperature

The temperature of the etch bath has very little effect on undercut for cupric chloride so most cupric chloride etch systems are run at the maximum temperature possible to get the highest etch rate. This is generally 130^o F for PVC equipment and 160^o F for polypropylene equipment.

Summary of Typical Operating Chemical Parameters for Cupric Chloride Etchant

- ORP - 540 to 560 mv
- Free Acid Level - 1N to 2N HCl
- Specific Gravity - 1.2832 (32^o Be) to 1.3063 (34^o Be)
- Temperature - 130^o F

Equipment Parameters

This section provides information useful for sizing, control considerations and other equipment parameters that may affect the etching process.

Equipment Sizing

Chemcut etchers are modular so they can be put together in any combination or number needed to meet production goals. The exact number of etch chambers required is of course dependant on panel size and throughput requirements, the thickness of the copper to be etched and the etch rate of the cupric chloride in use.

The first calculation is to determine the required conveyor speed to meet production goals. This is calculated by multiplying the throughput in number of panels per minute by the length of the panel plus the space between panels:

Required conveyor speed = Panels/min. x (Length of panel + Space between panels)

In order to calculate the effective etch length needed to achieve this throughput the total etch time is needed. The copper thickness divided by the etch rate will give the time needed to etch through the copper to the substrate, known as the breakthrough time. The overetch factor is the extra etch time needed to remove the foot and straighten the sidewalls as much as possible. In most cases the extra etch time needed for foot removal and sidewall straightening is assumed to be 20% of the breakthrough time and an overetch factor of 1.2 is used for estimating total etch time:

$$\text{Total Etch Time} = \frac{\text{Copper Thickness}}{\text{Etch Rate}} \times \text{Overetch Factor}$$

Note: When etching high density circuits (lines and spaces < 5 mil) the total etch time should be increased by an additional 20% to account for diffusion layer effects. In this case use an overetch factor of 1.4

The total length of effective etch chamber length is determined by multiplying the required conveyor speed needed by the total etch time:

Length of etch chamber needed = Conveyor speed needed x total etch time.

This result is the minimum effective length of etch chamber needed to meet production goals and once it is known, the required number of etch chambers needed for the system is easy to determine.

The following is a list of the effective lengths of various etch chambers.

Effective Conveyor Lengths for various Etch Chamber Combinations

- 547 XLi PEM - 37 inches
- 547XLi DPEM - 74 inches
- Sigma OS06 - 46 inches
- Sigma OS08 - 59 inches

Example Calculation: A customer wants a cupric chloride etching system capable of running 200 panels per hour. His panels will be 1 oz. foil and panel size is 24 in. by 18 in. Normal spacing between panels is 2 inches and the customer is not sure what the free acid level is in his etchant to estimate etch rate.

Solution:

- Minimum conveyor speed needed to reach 200 panels per hour:

$$\frac{200 \text{ panels/hr}}{60 \text{ min/hr}} \times (18 \text{ inch panel length} + 2 \text{ inch space between panels}) = 66.67 \text{ inches/min.}$$

$$= 5.56 \text{ ft / min.}$$

- Total etch time:

In the absence of free acid level data assume an etch rate of 1.1 mils / min. Most cupric chloride etchants will have enough acid to achieve at least this rate.

$$\frac{1.35 \text{ mils Cu(1 oz.)}}{1.1 \text{ mils /min. Etch rate}} \times 1.2 \text{ overetch factor} = 1.47 \text{ min.}$$

- Minimum conveyor length:

66.67 in./min. conveyor speed x 1.47 min. etch time = 98 inches

The customer will need an etch chamber with an effective length of 98 inches to get the production rate he requires under the above conditions. From the list on the previous page it can be seen that a combination of 1 OS06 and 1 OS08 etch chamber or 1 547XL PEM and 1 547XL DPEM will meet his needs.

Question: After going through these calculations the customer mentions that the panel design for his main product includes some high density areas with 4 mil lines and spaces. Will this make any difference in the calculations?

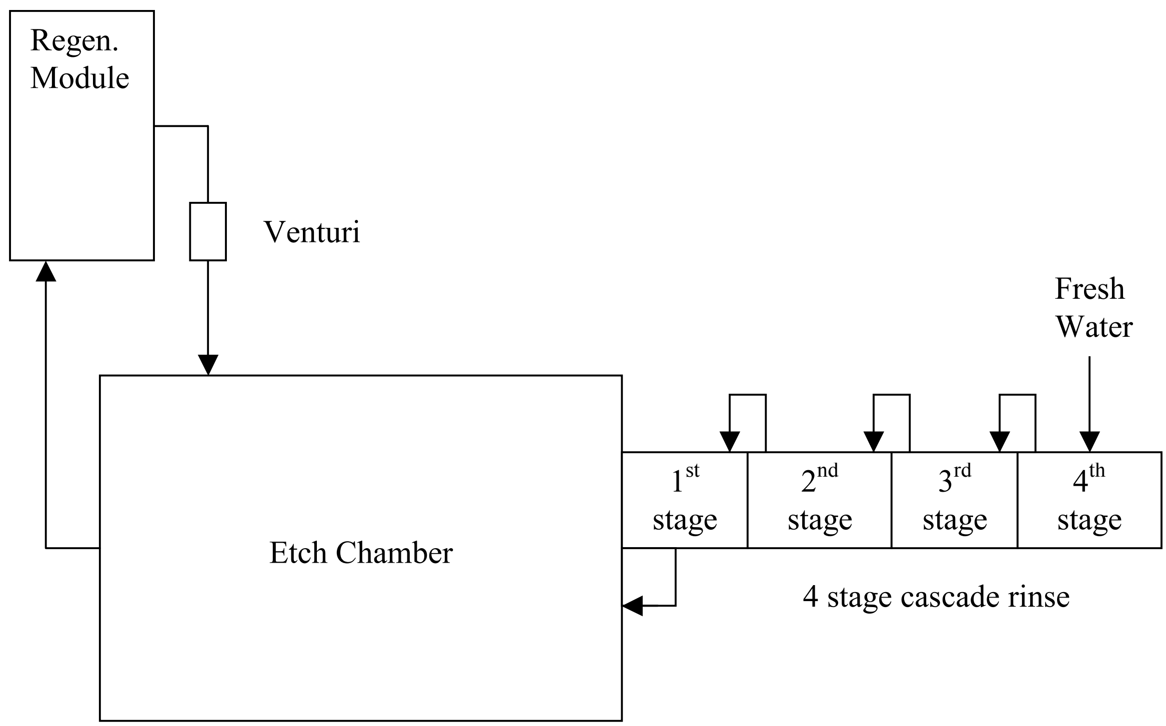
Answer: Yes it will. When etching circuits with less than 5 mil lines and spaces extra etch time must be allowed for. These high density areas take longer to etch because it takes longer for the fresh etchant to diffuse to the copper surface than in areas with more space between the lines. In this case we should have used an overetch factor of 1.4 instead of 1.2 to take into account the extra etch time needed for the 4 mil line and space circuitry. That would change the total etch time to 1.72 minutes which would in turn increase the minimum conveyor length to 114.6 inches. As can be seen from the list of conveyor lengths the etch system would have to have two OS08 etch chambers to guarantee the production rate the customer wants. The combination of 1 547XL PEM and 1 547XL DPEM is marginal but will probably meet production needs unless 100% of the product for this line has high density circuitry.

In the calculations above, the 1.1 mil / min. etch rate, the 1.2 overetch factor used to account for the 20% extra etch time needed to finish etching a line, and the 1.4 overetch factor to account for the extra time needed for dense circuitry, are all on the conservative side. There is enough safety factor in all of them that they can be used with confidence in all situations without having to worry that the etch system as delivered will not be able to meet production goals.

Equipment Related Process Control Issues

The etch system comes with controls for etchant temperature, conveyor speed and spray pressure. The regeneration module is separate and has the controls for ORP and specific gravity. A free acid controller is optional but every cupric chloride system should have one. The operation of temperature, conveyor speed and spray pressure controls are self-explanatory and don't need to be covered in detail here. ORP, specific gravity and free acid controls are also relatively straightforward but there are a few considerations with these that do need some discussion.

Below is a block diagram of a typical cupric chloride etch system for reference:



ORP (Oxidation / Reduction Potential) Control:

ORP probes are mounted on the regeneration module and consist of a platinum tipped ORP probe and a reference probe. The controls for adjusting set points and add times will be on the system control panel. Etchant flows into the regeneration module by gravity from the etch module and is returned under pressure through a venturi. The flow of the etchant through the venturi provides the low pressure used to draw the regeneration chemicals into the system. When the ORP falls below the set point a solenoid valve is opened and the oxidizer is pulled into the system. This design eliminates the need for metering pumps and minimizes the amount of chlorine gas released if there is a break in the supply line. The regulator on the chlorine tank will shut the tank off if it senses no pressure differential between the inside and outside of the supply line. Therefore, in case of a break in the chlorine supply line the only gas released to the atmosphere is what is already in the line and not the whole chlorine supply.

In addition to the ORP set point, add times for the addition of oxidizer and HCl are also operator settable. The controller opens the oxidizer solenoid when the ORP falls below the set point and keeps it open for a set period of time. Once the add time is achieved, the controller will check the ORP again and, if it still below the set point, will open the solenoid again and continue this cycle until the ORP returns to the set point. Being able to adjust these add times allows the operator to balance the chemical additions to the workload. If too much oxidizer is added then it is possible to over chlorinate and release chlorine to the atmosphere. If too little oxidizer is added then the regeneration will not be able to keep up and the ORP will fall, affecting the etch rate. The user of a chlorine gas system can manually control the flow rate of the chlorine gas with a gas rotameter that is mounted to the side of the regeneration cabinet.

The regenerator module comes in two models, the “C” model for chlorine gas and the “H” model for hydrogen peroxide or sodium chlorate chemistries. Physically, these versions are nearly identical except for differences in plumbing for chlorine gas as opposed to liquid H_2O_2 or $NaClO_2$. The primary difference between the two models is the capacity to regenerate etched copper. The H model is able to handle 3000 oz. of copper etched per hour while the C model can regenerate a maximum of 1000 oz. per hour due to the fact that the density of chlorine gas is much less than the densities of the two liquid oxidizers. It is important to keep this difference in mind since a two-chamber etcher can easily approach the 1000 oz./hr of copper etched limit of the chlorine gas regeneration system. Anything over three etch chambers would require more than one chlorine gas unit in order to keep up with the regeneration requirements.

The Chemcut regeneration system has proven itself in several hundred installations worldwide. The system provides very effective steady state control of the cupric etch process. The simple, reliable design requires only minimal periodic maintenance such as cleaning the probes on a monthly basis.

Free Acid Control:

The transducer for free acid control is placed in the feed pipe between the etcher and regeneration modules. The probe is toroidal or donut shaped and needs a relatively smooth flow through it for best results. A transmitter on one side of the hole sends a signal to a receiver on the other side and the strength of the signal is compared to a calibration curve and the HCl concentration is displayed as acid normality. When the HCl level falls below the set point a solenoid is activated in the regeneration module and HCl is added until the set point is again satisfied. System calibration is sensitive to specific gravity and a change in specific gravity will displace the calibration curve. HCl readings will be high if the specific gravity is lower than what it was at calibration and low if the specific gravity is higher. The displacement is about 0.1N for every 0.0115 (1^o Be) change in specific gravity. The system is factory calibrated for a specific gravity of 1.2832 (32^o Be).

The Chemcut acid controller has been in use for several years and is extremely reliable for cupric chloride systems. It is typically used to control the HCl solenoid on the regeneration module but could be used with a metering pump if a separate HCl addition system is desired.

If the HCl controller is not present then control of the HCl solenoid reverts to the regeneration module. This method does not control the HCl but merely adds HCl to the system based on a set time when the oxidizer solenoid is activated. With experience it is possible to set the HCl add timer to keep the HCl level relatively stable but it is still recommended that the HCl level be checked at least twice a shift.

Specific Gravity Control:

The regeneration module also manages specific gravity control. The specific gravity controller consists of a float in a sight glass with a light source. As the specific gravity of the etchant increases the float rises and breaks the light beam. The breaking of the light beam opens the water add solenoid and water is added until the float drops back to the proper level as the specific gravity decreases. When the proper specific gravity is reached the float no longer breaks the light beam and the water add solenoid is closed. The set point for the specific gravity is changed by a simple screw adjustment that changes the fluid level in the chamber housing the float.

For both water conservation and dragout control most cupric chloride systems are set up like the block diagram on page 10, with a four stage cascade rinse after the etcher. The water for specific gravity control is taken from the first stage of the rinse as shown and is replaced by fresh water added to the fourth stage of the rinse. In this way most of the copper dragged out of the etcher on the panel surfaces is returned to the etcher. When water is needed for specific gravity control the water add solenoid is opened and fresh water flows into the fourth stage of the cascade rinse. This cascades forward to the first stage where it overflows into the etcher.

It is important to keep in mind that the different regeneration systems have different water requirements for specific gravity control. Each pound of copper etched requires 0.79 gallons of water to maintain specific gravity. With a chlorine gas regeneration system all the water must come from an outside source. With hydrogen peroxide and sodium chlorate systems, however, much of the water is introduced with the regeneration chemicals. A hydrogen peroxide system, for instance, uses 35% H_2O_2 as the oxidizer. The other 65% of the solution is water. Concentrated hydrochloric acid is usually between 30% - 35% acid with the balance of the solution being water. About 55% of the water necessary for maintenance of specific gravity is brought in with the hydrogen peroxide and HCl so only about 0.36 gal. of water are needed from the outside. Sodium chlorate systems need only about 0.39 gal. of outside water*. With a chlorine gas system the amount of water needed for specific gravity control alone will run the cascade rinse efficiently (19 gallons per hour for a single chamber OS06). Peroxide and chlorate regenerated systems will require extra flow into the fourth stage of the rinse to keep it relatively fresh. This can add to the cost of the chemicals because this extra flow will need to be treated.

*Note: This amount of water is based on a 600 gpl solution (45%)of sodium chlorate.

Regeneration Chemical Use Table

For each pound of copper etched the following chemicals will be used:

Chlorine Gas Systems

- Chlorine gas – 1.1 lbs.
- Water - 0.79 gal. for specific gravity control

Hydrogen Peroxide Systems

- Hydrogen Peroxide – 0.16 gal. of 35% H_2O_2
- Hydrochloric Acid - 0.32 gal. of 30% HCl
- Water - 0.36 gal. for specific gravity control

Sodium Chlorate Systems

- Sodium Chlorate - 0.11 gal. of 600 gpl $NaClO_3$ solution
- Hydrochloric Acid –0.32 gal. of 30% HCl
- Water - 0.39 gal. for specific gravity control