When printed circuit board (PCB) fabrication firms are starting new operations or modifying existing facilities is the ideal time to establish a coordinated effort between the engineers in manufacturing and in facilities so that pollution prevention and waste minimization techniques can be implemented successfully, right before start-up. The goal of a design team for a new facility in Puerto Rico was to minimize hazardous waste production. The practical steps taken and ideas presented here may be applicable to your operations.

A new facility was designed recently, to house multilayer PCB manufacturing, using the solder mask over bare copper (SMBBC) process. The site included a dedicated 116,000 ft² building, of which 66,000 ft² contained the wet process equipment. It was projected that this shop would eventually (five years after start-up) produce up to 1,600 double-sided and completed multilayer panels (18 x 24-in.) per 20-hr work day. One-oz inner layer and 0.5-oz outer layer were to be used.

### Design Requirements & Goals

The design team recommended that the requirement for an "acceptable discharge" from this facility be at 20 percent of the limits described in gray box on page 46—except for aluminum, silver, BOD and COD. (That is, the system supplier must issue a performance guarantee to produce an effluent in which copper would be equal to, or less than, 0.2 mg/L). The designers defined what was considered an "acceptable" effluent.

### Prioritizing Efforts To Recover Copper

The team began by calculating the quantity of hazardous waste to be produced from every source at maximum production. Existing facilities can determine this through chemical analysis and a knowledge of the waste volumes produced. Let's first address how to determine the quantity of copper to be recovered from a yet-to-be-constructed PCB facility.

#### The largest source of wasted copper—
Of the copper etched from this facility, 93 percent would originate from the inner and outer layer panel-etching operation. The designers persuaded the operations group to use alkaline ammoniacal chloride etchants (for both inner-layer and outer-layer etching, in two different etching machines). As a result of the expense and liability of purchasing new chemistry and in shipping the spent etchant back to the continental United States, an alkaline etchant recycling system, including the capability for copper recovery, was purchased.

#### Microetching applications—
The mass emission rates for the microetch baths were calculated, based on the maximum number of panels to be processed/hr, etching depths of 2.5 micrometers (µm or 100 µL) in the oxide (with only 50 percent of the area available to etch) and electroless copper lines, and a 0.75 µm microetch in the pattern-plating line. These applications produced the second-largest source of potentially wasted copper.

In the following example, the expected quantity of copper to be etched (and, thereby, recovered) is calculated:

**Basis:** a 50 µ-in.-deep etch is desired in 333 (18 in. X 24 in.) inner layer panels per hr, in an oxide line, with only 50 percent of the copper exposed.

The rate of production is calculated:

18 in. X 24 in. X 2 sides X 0.5 = 3 ft² of exposed copper per panel

3 ft² X 333 panels per hour = 1,000 ft²/hr

The depth of copper etched is converted to feet as follows:

50 µ-in. X (8.3 X 10⁻⁶ ft/µ in.) = 4.15 X 10⁻⁵ ft

The volume of copper etched per hour is then calculated:

4.15 X 10⁻⁵ ft X 1,000 ft²/hr = 4.15 X 10⁻³ ft³/hr

Converting this to mass of copper etched (and to be recovered):

4.15 X 10⁻³ ft³/hr X (559.1 lbs Of Cu/ft³) = 2.3 lbs of copper/hr etched by this bath

### Normal drag-out applications—
The amount of copper that would be contained in a rinse was calculated using a solution drag-out rate of from 64.6 to 86.1 milliliters of solution per surface square meter of exposed copper (equivalent to 6 to 8 mL/surface ft²). An 18 X 24-in. panel has 0.56 square meters [m²] or 6 ft² of surface area (including both sides). Therefore, for a 100 m²-per-hour operation, a drag-out rate of from 6.46 to 8.61 liters/hr would be produced from a single bath.

The designers knew that a typical spent 10-percent acid bath contains from 100...
to 300 mg/L of copper, while the acid copper electroplating bath may contain 22 grams (22,000 mg/L) of copper per liter. Maximum copper discharge rates calculated from various sources, other than inner- or outer-layer etching, are listed in Table 1 (used to create Fig. 1).

In high-volume multilayer facilities, more inner-layer panels are processed than the number of outer-layer panels. The inner-layer operations that produce an aqueous discharge include the image developing operation, the inner-layer etching operation, the resist-stripping operation, and the oxide operation. The oxide operation includes a microetching step to remove exposed copper from the surface. More panels are processed through that microetch bath than the other microetch baths. Figure 2 provides the relative amounts of copper produced from the common locations where microetch baths can be located.

The designers specified the quantity of copper to be recovered from each operation, then addressed how to reduce the quantity of other hazardous wastes.

A factor of safety (in units of grams of copper/hr) was added to the above in the request for proposals. As the rinse flow rate-per-rinse tank had been specified, the design team prepared its request for proposals, which was distributed to potential suppliers. The designers thereby created the factor of safety.

**Rinsewater Reduction Techniques**

The equipment cost to remove copper from a rinse, using ion exchange, is a function of the rinse flow rate. The lower the rinse flow rate, the lower the equipment cost. To minimize the cost to recover copper, the team evaluated methods of minimizing the rinse flow rate containing copper. Some of the methods used are listed below.

Air-agitated counterflow immersion and pulsating spray rinse tanks were incorporated into the process equipment design, so that the wastewater volume would be minimized. Photoelectric cells were used on conveyortized lines with solenoid valves, flexible orifice-type flow restrictors, timers, and push buttons.

In fact, the projected volume of rinsewater amounted to less than 152 liters/day, per assembled multilayer panel (40 gal/day/panel). This was significantly lower than other facilities processing an equal number of similar-sized panels with a similar number of inner layers.

**Copper Recovery**

**Copper removal via selected cation exchange**

Copper removal from non-complexed rinses, and low-copper-containing acidic dumps, by selective cation exchange was incorporated into the system. Two (2) shallow-bed, 15.2 cm deep (6 in.), selective ion exchange modules, used in series, were purchased.

The shallow-bed ion exchange system and the copper recovery systems performed in an almost flawless manner. Designers are encouraged to reduce the cost and liability for hauling copper containing sludge by selecting ion exchange with electroplating, wherever possible.

The shallow-bed exchange columns produce a higher concentration of copper (containing up to 30 grams of copper per liter in the regenerate), in a lower volume of regenerate, than conventional deep bed ion exchange columns.

**Copper Removal From EDTA-Based Electroless Cu**

Copper removal from electroless copper bail-out and bath dumps

Because of its low equipment cost (less than $800 in U.S. funds), copper from this source was to be continuously deposited onto, and filtered by, a proprietary coated plastic medium (often referred to as "sponges") housed in a plastic container. Two units were placed in series, one located adjacent to the electroless tanks.

The autocatalytic technique is usually recommended because of its low capital investment. The container, housing the sponges, should be placed close to the electroless copper tank. The bail-out should be slowly (at about 0.5 gal/min) and continuously metered through the sponges at the bath operating temperature to remove the copper. Continuous
flow through the container is required to activate the system.

Depending upon the effluent requirements, this waste may be discharged, following pH adjustment, to the sanitary sewer. However, this waste still contains EDTA and is a significant source of both COD and BOD. Approximately 45 to 60 lbs of copper metal can be removed/filtered in a set of sponges before replacement sponges are needed. Our client decided that the copper and the plastic medium were to be hauled off-site as a hazardous waste.

Other Pollution Prevention & Waste Minimization Techniques

*Tin as the etch-resist*

Tin, from a tin sulfate bath, was effectively used as the etch-resist in place of solder. This reduced the number of discharge points containing lead, thiourea, and fluoride.

*Eliminate nitric acid*

Nitric acid was not required (the tin-strip bath contained hydrogen peroxide, \( \text{H}_2\text{O}_2 \), and ammonium bifluoride), while a sulfuric acid-hydrogen peroxide etching bath was successfully used to strip copper off the plating racks.

*Remove particulate copper and pumice*

The deburr operation and all pumice scrubbers had their own particulate filtration systems.

*Remove photoresist skins at the source*

The resist-stripping machines contained “filters” to remove the insoluble photo-resist skins.
Produce non-hazardous sludge & provide limited reduction
The installed system incorporated a separate "treatment and dewatering" step for spent resist stripper and (both dry film and solder mask) developer baths. These systems have produced solid wastes which have been categorized as "non-hazardous."

Eliminate permanganate dumps
The permanganate (desmear) tank contained an electrolytic oxidizing system to maintain the permanganate ion (MnO₄⁻). This eliminated the need to dump this process bath.

Eliminate the oxide dump
Bath filtration was supplied for the brown oxide bath. This eliminated the need to dump this process bath.

Drag-out tanks
Drag-out tanks were positioned to follow the organic conditioner bath, the permanganate bath (used for bath makeup), and the etch prior to the catalyst bath. A portion of the drag-out was returned to the permanganate bath. Drag-out tanks are used to reduce the waste load entering the adjacent rinse.

Eliminate the need to use iron chemistry
The HASL preclean line chemistry used a microetch bath without iron, which could foul ion exchange columns and electroplating systems.

Unanticipated Problems & Lessons Learned
Higher rinewater flows
The actual rinewater flow rates matched predictions exactly. Numerous "other" sources of wastewaters were found, however. Typical examples include the fresh water being used to wash the screens on the resist-stripping machines and the fresh water used to increase the conductivity in the bussed saddles on the electroplating tanks. When all plating baths were in operation, the water flow from this latter source, alone, doubled the actual flow from the pattern-plating machine, compared to the originally calculated flow.

Conductivity controllers bypassed the flow restrictors
Flow indicators were to be installed on every rinewater inlet pipe to each rinse tank. Some conveyorized production equipment was supplied with conductivity controllers and separate water feed lines into selected rinse tanks to allow rinewater to bypass the flow indicator. Flow rates as high as 15 times (15X) or more than those originally specified were observed, causing collection tanks to overflow in the treatment area during start-up. Afterward, the controllers were deactivated.

Excessive flow from the tab plating line
The tip (nickel and gold electroplating of the "fingers") plating machine was found to produce five times (5X) the flow rate initially assumed. Flow restrictors were then installed.

Periodic rinse tank maintenance not anticipated
The periodic, sometimes daily, rinse-tank dumps were not anticipated. This became a problem when the volume of rinewater surging into a waste collection tank exceeded the "filled to the brim" volume of that collection tank. The volume listed in a drawing for a collection tank should not include the tank's freeboard (which should be at least 31 cm [12 in.] of height). A larger waste collection tank was an obvious solution.

The limits of a gravity-settling system
Neither a conventional nor a sulfide precipitation system can consistently produce an acceptable effluent while receiving an inconsistent and variable incoming waste.

Always install a filter following a clarifier
The chemical analysis of the treated clarifier discharge verified our visual observation that suspended solids containing metals (primarily iron) periodically occurred.

Filter sink discharge pipes
One source of particulate lead originated in the sink, adjacent to the hot air leveling machine, used to wash the cleaning rags. By installing a filter, this source of lead was eliminated.

Anticipate the volume of collection tanks
Do not forget that process tanks are washed with water, before being refilled. This washwater will enter a dump collection tank.

Some process and waste treatment equipment requires water to flush bearings, provide better conductivity, or to backwash ion exchange columns. These sources must be identified and suitable collection volume must be provided.

Advantage of a cross-flow filtration system over a clarifier
One advantage of a cross-flow filtration system is the ability of that system to effectively treat variable incoming wastes easier than precipitation/filtration systems. In retrospect, a cross-flow filtration system may have performed with less operator assistance than the sulfide system installed.

The Ideal Can Become Reality
Designing a system with pollution prevention and waste minimization objectives requires a detailed evaluation of all production equipment and its chemistry. The ideal "design team" is composed of manufacturing and facilities engineers, and works as follows: The engineers in manufacturing closely coordinate their efforts to specify equipment in concert with the engineers in facilities. The facilities engineers define what is "hazardous." The manufacturing engineers specify wet process equipment designed to minimize waste. They also evaluate process chemistry that will prevent or minimize pollution.

About the Author
Peter Moleux is president of Peter Moleux, P.E. and Associates, Newton Centre, MA.

Moleux is a professional chemical engineer and a registered environmental professional, specializing in safety and environmental (emission controls, water and wastewater) engineering for the metal finishing industry. His company focuses on OSHA, environmental site assessments, and pollution and waste minimization. Moleux is chairman of the AESF OSHA Committee, and a member of the Environmental Committee and Publications Board and the Boston Branch of the Society.

This is an edited version of a case study that was presented at the 15th AESF/EPA Pollution Prevention and Control Conference, January 24-27, 1994, Orlando, FL.

Attend the OSHA Session
At SUR/FIN® '94—Indianapolis
Wednesday afternoon, June 22
(See final program for time, room.)