Printed Circuit Board Wastewater Recovery: Overview & Case Study

by Philip M. Kemp,* and Alan Karg

Printed circuit board manufacturing uses purified water for many of its manufacturing processes. This water doesn't come free. Not only is there a cost to purchase and further purify the water, there is a cost to dispose of it. Beyond economic issues, there is increasing pressure to limit the supply and disposal of industrial water. These factors and many others make water recycling very attractive. An effective water program must balance required recycled water quality, wastewater contaminant types and the capabilities of various decontamination processes. A case study of the development of one such recycle program is presented.

Water quality is key to effective rinsing during printed circuit (PC) board manufacturing. Most PC board manufacturing processes use different chemicals dissolved in water. These chemicals may not be compatible with chemicals used in subsequent processes. For example, the drag-in of alkaline cleaner residue has a catastrophic impact upon a copper-etching bath's effectiveness. The purpose of rinsing is to prevent cross-contamination of the various baths used in the manufacturing process. Not only must the rinse water remove contaminants from the board; it must not add new contaminants. Consequently, a large volume of high quality water is required for rinsing. The rinses between the different steps are major contributors to water use and are prime candidates for recycling.

Nuts & Bolts: What This Paper Means to You

Printed circuit board manufacturing uses purified water for many of its manufacturing processes. This water doesn't come free. Not only is there a cost to purchase and further purify the water, there is a cost to dispose of it. In light of all of this, water recycling looks better all the time. This paper presents a case study of one such recycle program.

Wastewater Recycling: Technical Considerations

Printed circuit board manufacturing processes

Understanding the chemical makeup of water to be treated is key to effective wastewater recycling. To accomplish that, we must consider the manufacturing process. A typical manufacturing process uses different types of operations to transform copper clad laminate (CCL) into a printed circuit board. Some of these operations are repeated at different times during the manufacturing process for the addition layer circuits.

Surface preparation

Surface preparation gets exposed surfaces ready for the next manufacturing step. The first step in the entire manufacturing process is the cleaning of the copper clad laminate. Likewise, the final step in the manufacturing process is the cleaning of the finished printed circuit board. In between these two steps, surfaces are chemically treated to provide better adhesion. Two main chemistries are used in surface preparation: alkaline cleaners and acidic, persulfate microetches. Surface preparation rinses may contain either of these types of compounds. Rinse water from alkaline cleaners will be basic; rinse water from persulfate microetches will be acidic and oxidizing.

Imaging and developing

Applying photo-resist, a polymerizable organic acid, to the copper surface and exposing it to ultra-violet (UV) light causes the resist to polymerize, making it insoluble. Immersion in a basic chemical bath causes the resist that was not exposed and did not polymerize to dissolve, leaving both exposed and covered copper for either etching or plating. Soluble carbonate salts are used to dissolve the organic material that was not exposed to the UV light, so that developing rinses will contain a mixture of carbonate and organic acid salts.

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Etching

Etching removes unprotected copper from a copper clad laminate or printed circuit board. Only unprotected (unmasked) copper is removed. Etching baths use cupric salts, or copper (II), to dissolve the exposed copper metal on the board. In the process, both the bath and metal are converted to cuprous, or copper (I), salts. Two approaches are used to keep copper in solution, by the formation of copper-chloride or copper-ammonia complexes. Replenishing agents are also present that oxidize the cuprous salts formed back to the cupric salts used for etching. Copper-chloride baths require the addition of chemical oxidizers, such as chlorine, acidified chlorate or hydrogen peroxide. Copper-ammonia baths use the oxygen in the air for oxidation. Depending on the type etching solution used, the rinse water will be either an acidic copper solution (copper-chloride etch) or a basic copper solution (copper-ammonia etch).

Resist stripping

At this point, photo-resist still covers the image on the etched boards, and must be removed. A combination of either inorganic or organic caustics and solvents, somewhat similar to paint-stripping products used for furniture, is used to remove the photo-resist. The remaining copper has the same image as that of the removed photo-resist. This rinse water will be basic and contain solvents.

Laminating and fusing

Sandwiching together the etched CCL, insulating plastic pre-preg, and copper foil forms the multi-layer assembly, which is the basis of the printed circuit board. This assembly is then thermally bonded. No water is used in this process.

Machining

Machining is the first step in forming electrical connections between the different copper layers in the board. Consequently, correct registration is critical to this operation. A poorly registered hole can cause a bad connection. The only water used in this step is a high-pressure spray used to remove debris.

Deposition (Electroless Plating)

Once the holes are drilled through the various layers of the laminated board, electroless deposition is used to copper-coat the drilled holes, providing electrical connections between the different copper layers of the board. Since electroless copper is very fragile, electroplating follows this step, which forms a much more durable copper surface. This process is a much more difficult process than electroplating, and is aided by first applying a very thin layer of noble or transition metal such as palladium or nickel. The deposition of copper then follows. Irrespective of the type of metal deposited, all deposition baths and their rinses contain chelated metals and reducing agents.

Electroplating

Now that the various copper layers are electrically connected, electroplating is possible. Copper or other materials, or masking agents such as tin, are electrodeposited on exposed metal surfaces. This builds up these surfaces and in the case of solder deposition, masks the copper against subsequent etching. Since these baths are acidic, chelating agents are usually not necessary. Consequently electroplating rinses contain non-chelated metals in acidic solution.

Masking

This process uses imaging and developing to apply an image that is the negative of the original photo-resist image. Electroplating then applies a metallic mask, typically a lead-tin solder-type alloy, to uncovered copper surfaces. This protects the underlying copper during subsequent etching. Rinses from this process will be similar in composition with developing and electroplating rinses.

Lead and tin stripping

Once the lead-tin mask is no longer needed to protect copper against etching, a nitric acid-iron (III) solution is used to remove it from copper surfaces. The resulting rinse water will contain these metals in dilute nitric acid solution.

Contaminant removal processes

Contaminant removal processes may be classed into two types: (1) physical removal processes and (2) chemical removal processes. Physical removal processes avail themselves of a contaminant's physical properties to remove it. Filtration is a typical physical removal process. Chemical removal processes use chemical reactions to modify either the chemical identity or the physical properties of a contaminant. When its chemical identity is changed, the contaminant is said to be destroyed. For example, oxidation-reduction reactions destroy contaminants. Changing the water's pH or adding a polymer will change the solubility, a physical property, of the contaminants. In this case chemical treatment must be used in conjunction with physical treatment.

Physical processes

Cartridge filtration processes

Cartridge filtration (Fig. 1) typically removes particles down to one micron in size. The particles that are removed by this process are referred to as suspended solids. Filters of this type use normal (perpendicular) flow, and flow completely through the filtering media. This creates a single filtered effluent stream.

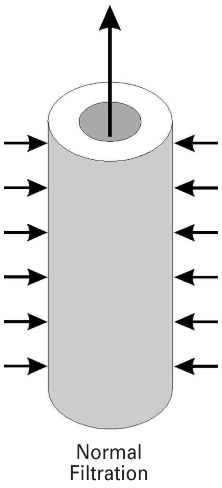

Figure 1—Cartridge filtration.

Crossflow filtration processes

In crossflow filtration (Fig. 2), the main water flow is along the surface of the membrane instead of into the filtering media. A high crossflow velocity keeps the pores of the membrane from being plugged. This is critically important since these pores are much smaller than those used in cartridge filtration. Microfiltration removes particles larger then 0.1 microns, such as all bacteria. Ultra-filtration removes particles larger than 0.01 microns, such as viruses and organic macromolecules. Nanofiltration removes particles larger than 0.001 microns, such as low molecular weight organic compounds like sugar. Finally, reverse osmosis removes particles smaller than 0.001 microns such as dissolved

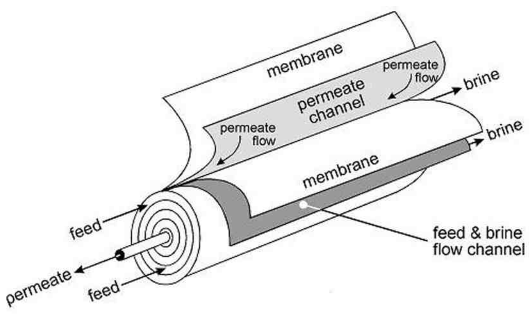

Figure 2—Crossflow filtration.

inorganic salts. Unlike normal filtration processes, crossflow filtration produces two effluent streams: (1) a very pure water stream that had permeated (passed through) the filter membrane and (2) an even more concentrated stream that is rejected by the membrane. Unfortunately, many membranes are vulnerable to chemical compounds that coat their surface, and oxidizing agents, which, in some instances, can destroy them.

Chemical processes

Ion exchange

Unlike filtration processes, which remove contaminants by physical means, ion exchange removes contaminants by chemical reaction between an insoluble media and a dissolved ionic species. The dissolved ionic species are attached to the media and rendered insoluble. Two general types of ion exchange media may be used: (1) a cation exchange resin that absorbs positively charged ions, and (2) an anion exchange resin that absorbs negatively charged ions. Like membranes, resins are vulnerable to organic compounds, which coat their surfaces, and oxidizing agents, which can destroy them.

Bath #	Designation	Volume	Flow	Composition
.				
5	Cleaning Bath			Nitric acid
6	Rinse			
.				
.				
8	Deposition			Basic chelated copper
9	Rinse			
.				
.				
13	Catalyst			Noble Metal
14	Acid Rinse			Sulfuric Acid
15	Rinse			
.				
.				
19	Microetch			Persulfate
20	Rinse			
.				

Figure 3—Sample of a Process Analysis Sheet.

Treatment with reactive chemicals

Two types of chemical reactions are used to remove metals from rinse waters. Both reactions have the same objective: to decrease metal solubility so that it precipitates and can be removed by one of the physical filtration processes. For chelated metals, chemical treatment is required.

One frequently-used reaction forms insoluble sulfides by adding organic sulfur compounds called carbamates, or inorganic sulfur compounds such as mono- or poly-sulfide salts. Another method is to use oxidizing agents to convert the metals to an insoluble form. Both of these approaches require balancing the amount of chemical added to the amount of metals to be removed.

Selecting the right process for rinse water recovery

Conceptually, the approach for selecting the appropriate removal processes for process rinse waters is simple. Match the removal process capability and requirements to the rinse water characteristics. In practice this can be difficult, because the characteristics of the various rinse waters are not well defined. In the worst case, the various streams entering the waste treatment facility are not known. Significant detective work is required. One must first identify the various rinse waters to be treated, and then define their characteristics. The tools of the trade are Process Analysis Sheets, which identify all sources of rinse water, and process chemicals, and Material Safety Data Sheets, which provide information on rinse water composition. A Process Analysis Sheet lists each bath for a given process line and the chemicals present in each. Rinse waters may be assumed to contain dilute solutions of the bath that precedes them. A simplified example of a Process Analysis Sheet is shown in Fig. 3.

The details of the bath's chemical composition are determined from the Material Safety Data Sheets. These sheets are divided into different sections as set down by the federal government. The second section of the sheet contains chemical information on the product. An excerpt for a pH 7 buffer is shown in Fig. 4 as an illustration. The CAS (Chemical Abstract Service) number provides a path to detailed information about each component.

MSDS SECTION II COMPOSITION

Chemical Identity	CAS #	Exposure Limits			%
		PEL	TLV	other	
Potassium Phosphate, Monobasic	7778-77-0				<1%
Sodium Phosphate, Dibasic	7558-79-4				<1%
Water	7732-18-5				Balance

Figure 4—Sample of a Material Safety Data Sheet section.

Once the chemistry of each rinse stream is understood, a treatment scheme is developed. This scheme is tested first in the laboratory, and then in an onsite pilot study. Each of these steps is used to ensure the successful implementation of a treatment scheme.

Laboratory Studies

Laboratory studies may check the chemistries of different rinse waters, evaluate precipitation and settling schemes or as in the study shown in Fig. 5, evaluate ion exchange as a removal process for a dissolved contaminant. Here, representative water from the white bucket on the bench is pumped through two cartridge filters, a carbon column and finally an ion exchange resin column. Samples, which are collected after the exchange column, are analyzed for the species that must be removed. Three types of information are gained from these studies: (1) the resin's leakage (species concentration in the effluent) for each species that must be removed, (2) the resin's exhaustion point and (3) the repeatable removal performance of the resin after successive regenerations. The first result defines how low a concentration can be achieved, the second determines how frequently the resin must be regenerated and the third determines whether this performance is sustainable.

Figure 5—Laboratory study setup for evaluating ion exchange as a removal process.

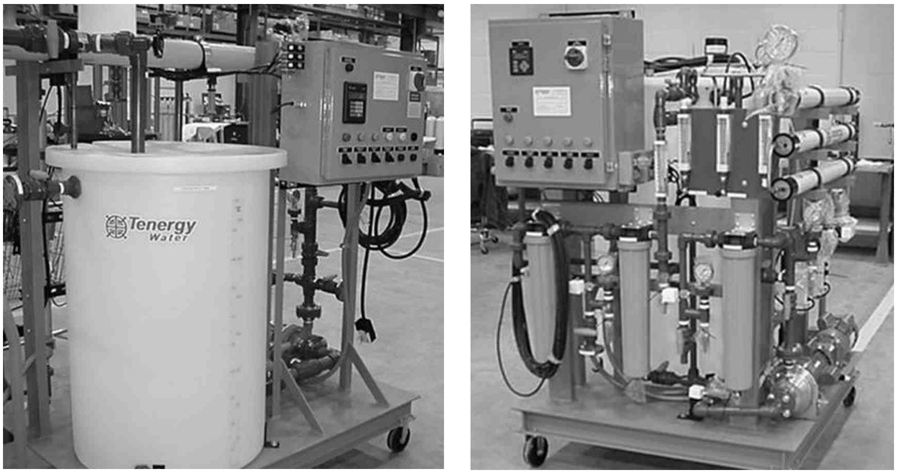

Figure 6—Onsite pilot setups for (a) microfiltration and (b) reverse osmosis evaluations.

Onsite pilot studies

Since dynamic processes such as the operation of cross-flow filtration equipment, cannot be evaluated in the laboratory, onsite pilot studies are required. Examples of pilot study setups, specifically for evaluating microfiltration and reverse osmosis, are shown in Fig. 6. Skid-mounted pilot units are shipped to the study site and connected to a small portion (~1 gpm) of the waste stream whose treatment is to be studied. During the study, which typically lasts for two to four weeks, equipment operation and waste stream characteristics are closely monitored. By the end of this study, the suitability of the process for treating the waste stream is established. In addition, performance data, which aids in the design of full-scale equipment, has been gathered.

Wastewater Recycle Case History

Original conventional wastewater treatment: 200-gpm discharged, no recycle.

The developmental approach discussed above was used to great success at a New England printed circuit board manufacturer. At the outset of the project, conventional wastewater treatment, shown in Fig. 7, handled plant's entire 200-gpm flow. No water was recycled. During conventional treatment, chemicals were added to precipitate the metals. Ferric chloride and magnesium hydroxide were added to Reaction Tank 1 to produce insoluble metal hydroxides. This was followed by the addition of a carbamate to Reaction Tank 2 to produce even more insoluble sulfides. Polymer was then added at the clarifier to speed the precipitation of these insoluble salts. The sludge was de-watered by a filter press and wastewater was pH adjusted, then discharged to a publicly-owned treatment works (POTW).

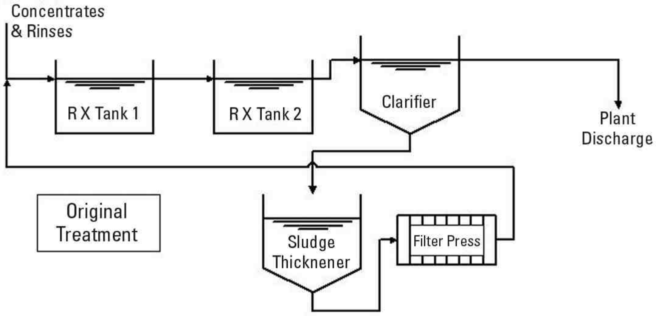

Figure 7—Conventional treatment system.

Phase I wastewater treatment: 135-gpm discharged, 65-gpm recycled.

The first step in developing a wastewater recycling system treated only process rinse water. The conventional wastewater treatment system shown in Fig. 7 continued to treat concentrates and bath dumps. The rinses after the manufacturing steps listed below were combined in an equalization tank:

Conditioner	Copper plating
Neutralizer	Tin plating
Catalyst	Rack strip (acid)
Anti-tarnish	Ammoniacal etchants
Rack strip (persulfate)	Acid cleaner (black oxide)
Electroless copper	Microetch (black oxide)
Acid cleaner	Oxide bath (black oxide)
Acid pre-dip	Gold line rinse

From the equalization tank, the wastewater was pumped through a bag and carbon filters, to a UV sterilizer, to a cartridge filter and through a reverse osmosis (RO) unit. Of the total flow of 100-gpm treated by the RO unit, 65-gpm of filtrate was returned to the manufacturing process as rinse water. The remaining 35-gpm RO reject was directed to the conventional wastewater treatment system. The system diagram is shown in Fig. 8.

Phase II wastewater treatment: 65-gpm discharged, 135-gpm recycled (estimated).

The next step in the development of the wastewater recycling system treated the additional streams listed below:

Tin strip rinse
Black oxide rinse
Stannous sulfate rinse
Surface cleaning rinse
Deburring rinse
Pumice scrub rinse
Pre-coat cleaning rinse
Cupric etch rinse

These streams were combined and treated with ferric chloride and magnesium hydroxide to form insoluble hydroxide salts. This stream was evaluated in a microfilter pilot study. The objective of this study was to determine if a second RO unit could treat the filtrate produced by the microfilter. In a similar manner, the

35-gpm reject stream from the Phase I RO unit was pre-treated by ion exchange. The performance of the combined pilot system shown in Fig. 9 will be the basis of the remaining discussion in this paper. The flow for the combined pilot study is as follows. The pH adjusted, ferric chloride- and magnesium hydroxide-treated streams from Reaction Tank 1, after being filtered by the pilot microfilter, were combined with the ion exchanged-treated reject of RO #1 in the filtrate tank. This tank then fed the Pilot RO unit (#2), whose permeate became an additional rinse water source.

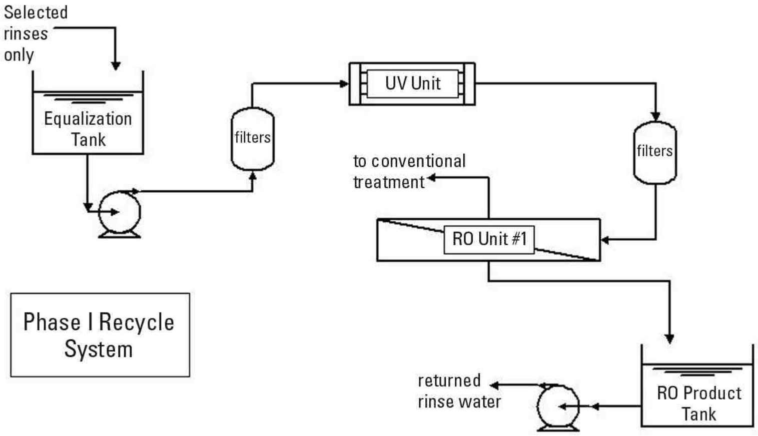

Figure 8—Integration of the recycle system into the wastewater treatment system.

Key pilot performance parameters

Note: For Figs. 10 through 13 the solid lines represent actual data points. The dotted lines represent a normalized trend line from the data.

The single, most important parameter in any membrane filtration process is the flux, or product flow, passing through the membrane. For microfiltration, this flow is called the filtrate. For RO units it is called the permeate. Membrane filtration devices are usually taken out of service for cleaning when flux drops below 70% of its initial value. It is obvious that the longer the interval between required cleaning, the more usable a treatment process will be. As can be seen in Fig. 10, with the exception of some spikes, the microfilter flux was fairly constant, with a very slow decline. This demonstrates the compatibility of the microfilter and the wastewater.

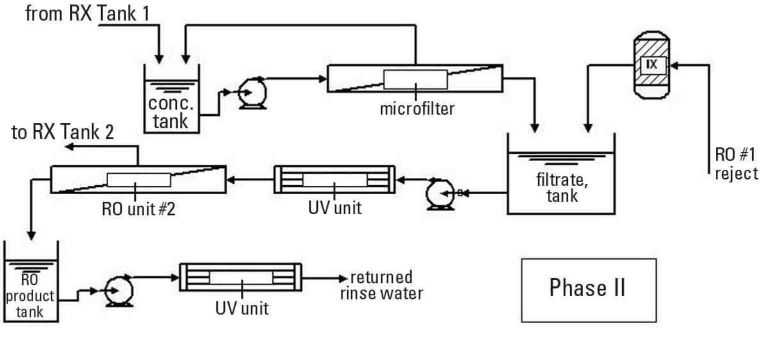

Figure 9—Phase II wastewater treatment system.

The RO performance parameters are a bit more complex. Flux and produced water quality are the most important parameters. The restoration of flux after cleaning is very important. The RO flux shown in Fig. 11 is quite steady and slowly increasing, which demonstrates the increasing compatibility of the RO unit with this waste stream. Salt rejection and salt passage are different sides of the same coin. The defining equations for these two parameters are:

Salt Rejection =	$\frac{(\text{Feed TDS} - \text{Reject TDS}) \times 100\%}{\text{Feed TDS}}$	(1)
Salt Passage =	$\frac{(\text{Feed TDS} - \text{Permeate TDS}) \times 100\%}{\text{Feed TDS}}$	(2)
100 % =	*Salt Rejection + Salt Passage*	(3)

where TDS is total dissolved solids or conductivity.

Salt rejection (Fig. 12) is a measure of RO performance from the equipment perspective. Salt passage (Fig. 13) is a measure of RO performance from water quality perspective. The slow increase in salt rejection and the coupled decrease in salt passage indicate that there is slow, but manageable build up of solids on the membrane. This is quite normal. Chemical analysis of the produced water or permeate, show that very high quality water was obtained for use as recycled rinse water (Table 1).

Summary and Conclusions

The treatment scheme presented here was compatible with the wastewater produced by the customer's manufacturing process. The paybacks can be significant. In Phase I, which successfully treated the plant's wastewater for six years, the average flow recycled as rinse water was 65-gpm, or nearly 94,000-gpd. Based on the results of this pilot study, the projected recycled water more than doubled to 135-gpm or 194,000-gpd. The economic incentive for using this approach is clearly shown in Fig. 14. These series of curves are based solely on the cost of discharging wastewater.

Table 1
Quality of RO-Produced Water

Parameter	Expressed as	Result	Detection Limit
Calcium	mg/L Ca	none detected	2.5
Magnesium	mg/L Mg	none detected	2.5
Sodium	mg/L Na	none detected	2.5
Potassium	mg/L K	none detected	2.5
Iron, total	mg/L Fe	none detected	0.1
Nickel	mg/L Ni	none detected	0.04
Copper	mg/L Cu	0.07	
Tin	mg/L Sn	none detected	0.25
Chloride	mg/L Cl	11.0	
Sulfate	mg/L SO_4	none detected	7.0
Phosphate	mg/L PO_4	0.07	
Silica	mg/L SiO_2	0.07	

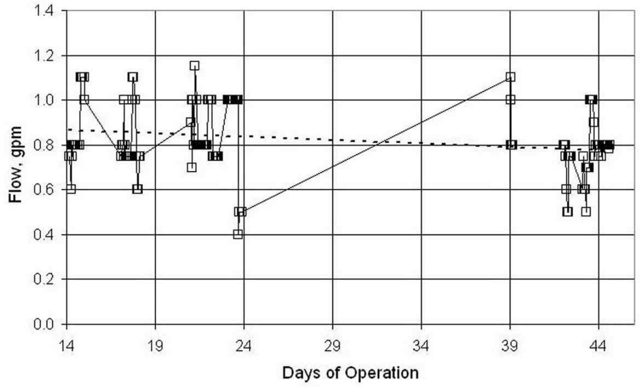

Figure 10—Pilot microfilter flux.

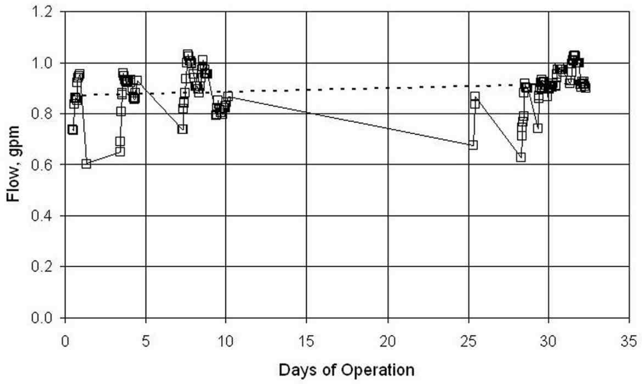

Figure 11—Pilot reverse osmosis flux.

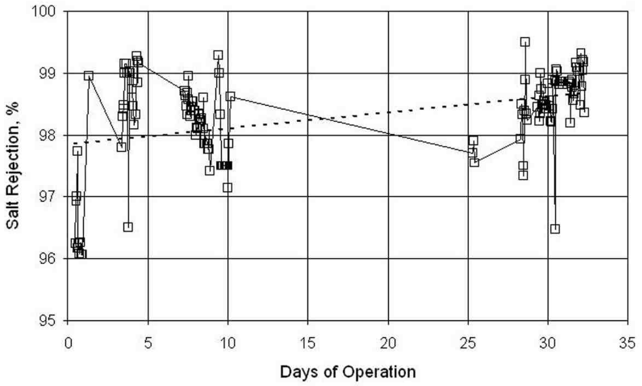

Figure 12—Pilot salt rejection.

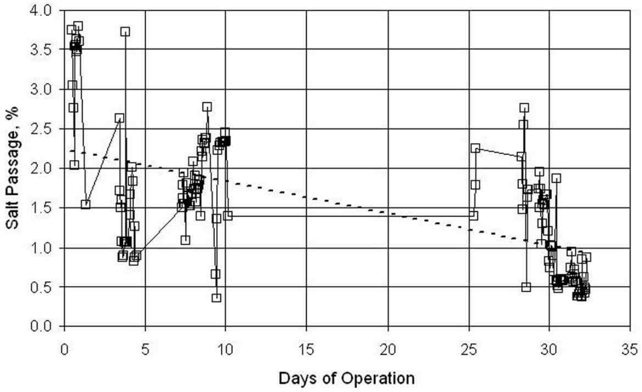

Figure 13—Normalized salt passage.

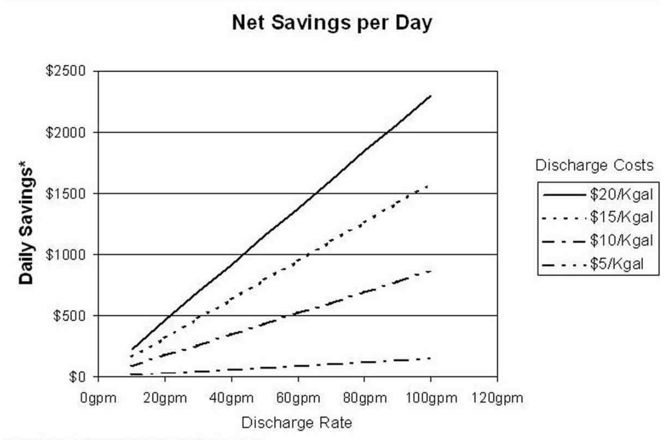

Figure 14—Net cost savings per day (Note: For the PC board industry, the average cost to chemically treat, use and discharge water is $13/1,000 gallons.

The fact that less water will need to be purchased and conditioned to meet the plant's rinse water requirement is yet another savings. The final saving has to do with the energy required to adjust the temperature of the water to the desired level. Frequently, recycled water does not need additional adjustment. During this study, two of the three stages of the plant's gas-fired boiler used to temper water could be turned off.

The key to success was using an ordered wastewater treatment development process. The steps of this process were the following:

1. Know sources, volumes and composition of the rinse waters to be treated.
2. Know the weaknesses and capabilities of treatment processes.
3. Match the waste streams to be treated to the appropriate process.
4. Conduct laboratory studies on the proposed waste streams.
5. Conduct onsite pilot studies on the proposed waste streams.

Printed circuit board rinse water can be successfully treated for recycle, but it is accomplished by hard work, not by magic, requiring the close partnership between the manufacturing plant and the equipment manufacturer. ***P&SF***