In-Process Recycling of Rinse Water From Copper Plating Operations Using Electrical Remediation

by H.M. Garich, R.P. Renz, CEF, E.J. Taylor, & J.J. Sun*

The copper plating industry generates large amounts of contaminated rinse water. A novel system has been developed to recycle the spent rinse water back to the rinsing operation. This system integrates electrowinning and ion-exchange for the efficient removal of metal contaminants, such as copper. The system utilizes integrated ion-exchange electrodes for the simultaneous removal of anions and cations in solution. After treatment, heavy metal concentration and TDS are reduced, and the pH is neutralized. Consequently, treated water can be recycled back to the rinse operation. As an added benefit, the cell has the ability to be regenerated *in-situ.*

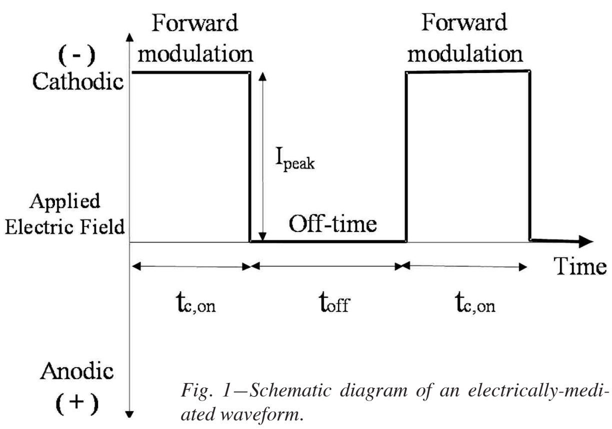

Fig. 1—Schematic diagram of an electrically-mediated waveform.

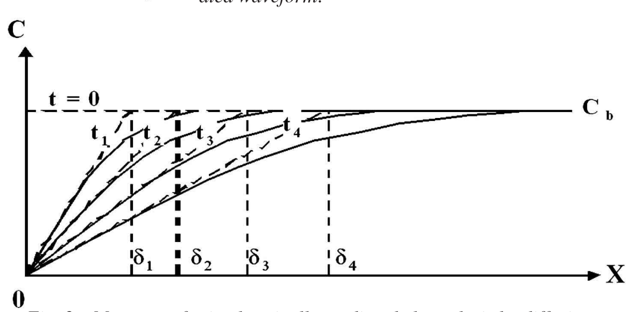

Fig. 2—Mass transfer in electrically-mediated electrolysis by diffusion.

Nuts & Bolts: What This Paper Means to You

The electronics industry generates large amounts of contaminated rinse water from copper plating operations. Here, a novel system is described to recycle the spent rinse water, combining electrowinning and ion-exchange for the efficient removal of metal contaminants, such as copper. Heavy metals and dissolved solids are reduced, the pH is neutralized and treated water is recycled back to the rinse.

Introduction & Background

The electronics industry is the second largest basic industry in the world, surpassed only by the agriculture industry.[1] Virtually all electronics are mounted on printed wiring boards (PWB).[2] The PWB not only provides a structural surface for electronics components on which to be mounted, but also provides an electrical connection for the components. A PWB is formed by placing a patterned conductive layer of metal atop of an inert substrate. The conductive surface is often composed of copper for several reasons:[3]

- Copper is relatively inexpensive when compared with other metals; copper is also in stable supply;
- Copper has a high electrical conductivity;
- Copper has a high plating efficiency, offers good plating coverage and offers good throwing power and
- Copper is less stringently regulated by the EPA than some other plating metals.

There are seven basic markets that employ printed wiring boards: automotive, communication, consumer electronics, computers/business equipment, government/military, industrial electronics and instrumentation.[2] With such a high demand, there are over 750 PWB manufacturers in the United States alone. States with the greatest number of PWB manufacturers include California, Minnesota, Texas, Illinois, Massachusetts and Arizona, although there are PWB manufacturers in virtually all fifty states. Therefore, there are large quantities of copper being plated at PWB manufacturers, and large amounts of copper-laden rinse waters are being generated as a consequence. This illustrates the need for an efficient treatment technology to remove the copper ions from the rinse water and recycle the rinse water back to the rinse operation.

Best available treatment technologies for this application include precipitation, ion-exchange, reverse osmosis and electrowinning. Precipitation has conventionally been the most extensively used treatment technology for the removal of heavy metals from solution.[4] However, in the face of further reduction of discharge limits, treatment of wastewater by precipitation alone does not adequately meet compliance. Ion-exchange works well for this type of treatment when contaminant concentrations are relatively low.

*For more information contact:
Phillip Miller
Marketing Director
Phone (937) 836-7749
Fax (937) 836-9498
E-mail: phillipmiller@faradaytechnology.com

In order to optimize the ion-exchange process, two columns, one cation- and one anion-exchange, are run in series. Once the resin has been exhausted, the resin must be regenerated for further treatment. This requires application of a strong acid or base to the resin, for cation- and anion-exchange resins respectively, followed by rinses with deionized water. The result of resin regeneration is volumes of contaminated water that need further consideration. As previously stated, ion-exchange works best for lower concentrations, and would be limited for waste streams with high contaminant concentrations. Additionally, conventional resin regeneration is a time-consuming process and often requires a large footprint. Another decontamination technology, reverse osmosis, requires a membrane to separate pure water from ionic and other contaminants. Membrane fouling is a common problem associated with reverse osmosis that leads to reduced process efficiency.

Wastewater may also be freed of heavy metal ions by electrodepositing metals in metallic form at the cathode, in a process know as electrowinning. Some of the advantages of electrowinning are:

- Metal ions can be recovered in metallic form;
- No additional chemicals are needed and
- No secondary waste stream is generated.

The major challenges of electrowinning dilute metal-bearing wastewater are:

- Low current efficiency,
- High power consumption and
- High effluent concentration due to hydrogen evolution at the cathode.

In dilute metal-laden aqueous streams, such as plating rinse water, the decontamination process is limited by the transport of the ions in solution to the electrode surface. Therefore, the efficiency of the process is dependent upon the coefficient of mass transport and the surface area of the electrode. An increase in both leads to an increase in process efficiency. The surface area of the electrode may be maximized by using a metal mesh or expanded metal electrode. The mass transfer coefficient is usually limited by the Nernst diffusion layer, which becomes depleted of ions as electrolysis progresses. Through the use of an electrically-mediated process, the transport rate may be enhanced by greatly decreasing the effective diffusion layer thickness.

Electrically-mediated Processes

It is possible to enhance the performance of the proposed technology by use of an electrically-mediated waveform (Fig. 1). The electrically-mediated waveform consists of a cathodic voltage, applied for time t_{on}, followed by zero voltage for a period of time t_{off}. The sum of the on-time and off-time is the *period* and the inverse of the period is the *frequency*. The percent cathodic on-time is defined as the cathodic *duty-cycle*. The voltage during the on-time is known as the *peak voltage* and the *average voltage* is defined as the time-average of the instantaneous voltage over a period. It should be noted that in electrically mediated electrolysis, the peak voltage, duty cycle and frequency are additional parameters available to control the mass transfer process and current distribution, as compared to DC electrochemical processes.

Unlike DC electrolysis, the mass transfer characteristics of charge-modulated electric field electrolysis are time dependent. Electrically-mediated electrolysis causes concentration fluctua-

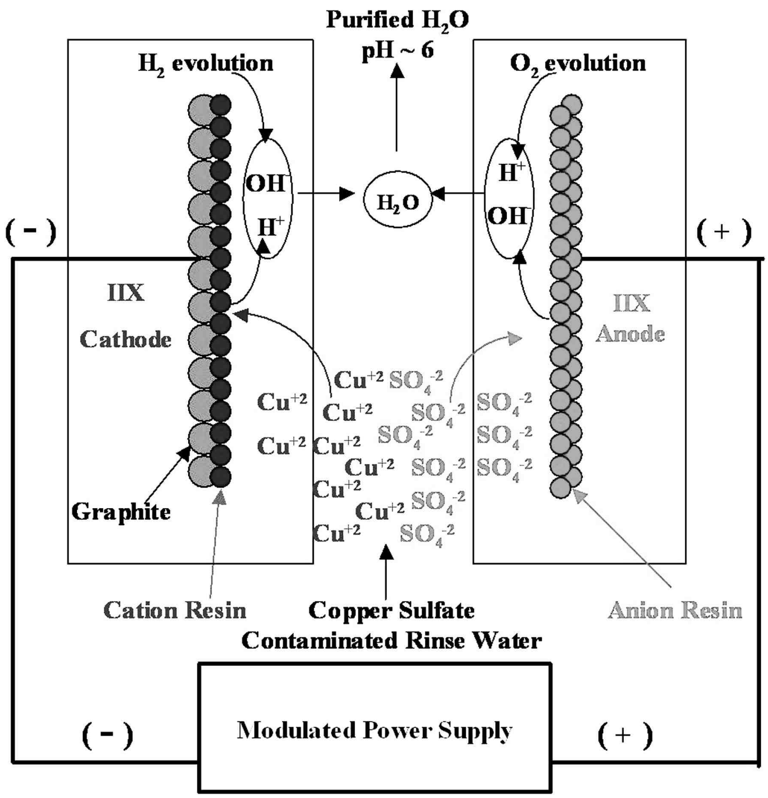

Fig. 3—Schematic diagram of the in-process recycling unit for the treatment of copper-plating rinse water.

Table 1
Treatment Test Conditions

Cell Parameters	Electrode surface area = 450 cm^2 (69.8 in^2) Anode frames: 11.5 mm (0.45 in.) holds 350 g (12.3 oz) of resin 22.3 mm (0.88 in.) holds 600 g (21.2 oz) of resin 45.9 mm (1.81 in.) holds 1200 g (42.3 oz) of resin Cathode frame: 11.5 mm (0.45 in.) holds 250 g (8.8 oz) of graphite and 70 g (2.5 oz) of resin 22.3 mm (0.88 in.) holds 500 g (17.6 oz) of graphite and 140 g (4.9 oz) of resin
Copper Plating Rinse Water	Cu^{+2} concentration = ~24 ppm TDS = 1400 ppm pH = 2.0
Experimental Parameters	Single-pass operation Flow rates: 11.5 mm (0.45 in.) anode frame = 0.2, 0.8, 2.4 L/min (0.05, 0.21, 0.63 gal/min) 22.3 and 45 mm (0.88 and 1.81 in.) anode frames = 2.4 L/min (0.63 gal/min) Control voltage: 11.5 mm (0.45 in.) anode frame = 10.5V 22.3 and 45 mm (0.88 and 1.81 in.) anode frames = 26V

tions near the electrode surface and reduces the effective Nernst diffusion layer thickness. Consequently, very high instantaneous limiting current densities can be obtained with electrically-mediated electrolysis as compared to DC electrolysis.

To qualitatively illustrate how electrically-mediated electrolysis enhances the instantaneous mass transfer rate, consider the case of a single rectangular cathodic current modulation. Before the current is turned on, the concentration of the diffusing ion is equal to the bulk concentration, C_b. After the current is turned on, the concentration near the cathode drops and a diffusion layer forms. Using the non-steady-state Fick's law of diffusion, this concentration profile as a function of the distance from the electrode surface, X, is depicted in Fig. 2. The corresponding thickness of the Nernst diffusion layer, □, is also shown in Fig. 2 for various time periods.

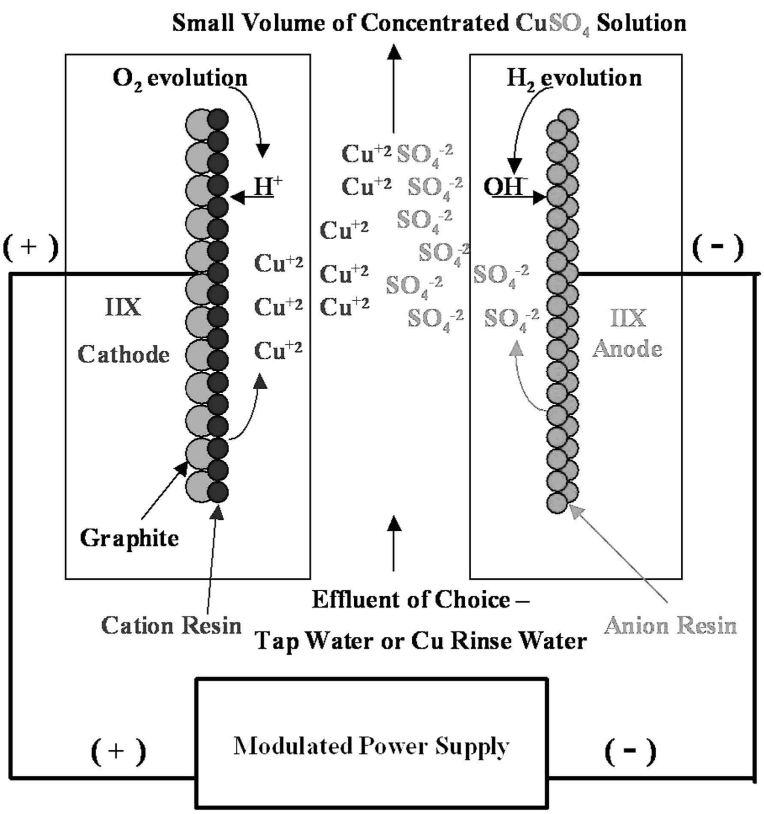

Fig. 4—Schematic diagram of cell regeneration.

The mass transfer limited current density is related to the concentration gradient at the electrode surface and to the thickness of the Nernst diffusion layer by:

$$i = nFD[dC/dx]_{x=0} = -nFD[(C_b - C_s)/\delta] \qquad (1)$$

In steady state DC electrolysis, □ is a time-invariant quantity for a given electrode geometry and hydrodynamics. This quantity is represented by $□_\infty$. In electrically-mediated electrolysis however, □ varies from 0 at the beginning of the process to a value of $□_\infty$ when the steady state Nernst diffusion layer is fully established. The corresponding diffusion current density would then be equal to an infinite value at t = 0 and decrease to a steady state value of the DC limiting current density at $t = t_\infty$. The advantage of electrically-mediated electrolysis is that the current can be interrupted (*e.g.*, at $t = t_a$) before □ has a chance to reach the steady-state value. This allows the reacting ions to diffuse back to the electrode surface and replenish the surface concentration to its original value before the next current modulation. In this way, one obtains a diffusion-controlled modulated current density greater than the steady-state limiting current density. This diffusion-controlled modulated current density can be made very large if one employs a current modulation of very short duration followed by very long relaxation time to permit the surface concentration to recover to the bulk value. Modeling work by Chin[5] has indicated that limiting current densities obtained under pulse reverse current (PRC) conditions of low duty cycle and high frequency can be two to three orders of magnitude greater than the DC limiting current density. Vilambi and Chin[6] confirmed the earlier modeling work with experimental studies for a copper sulfate bath for selected pulse periods and duty cycles in PRC electrolysis. They reported peak current densities as high as several hundred A/cm^2 for PRC electrolysis, while the corresponding values for DC electrolysis were less than 1 A/cm^2.

The electrically-mediated process may be coupled with our in-process recycling system to enhance the removal of ionic contaminants from an aqueous stream. Our innovative recycling system integrates ion-exchange with electrowinning for the simultaneous removal of cations and anions. Treatment with our unit results in decreased metal and anion concentrations, decreased TDS, and neutralized pH, for consequent water recycle. Additionally, the unit has the ability to be regenerated *in-situ* under the influence of an electric field. This eliminates the need for strong chemical species required for conventional ion-exchange regeneration.

Table 2
Residence Time at Varying Flow Rates

Flow rate (L/min; gal/min)	Average Residence Time (min)	Cathode Residence Time (min)	Anode Residence Time (min)	Total Residence Time (min)
0.2; 0.05	5.00	2.60	5.20	7.80
0.8; 0.21	1.25	0.65	1.30	1.95
2.4; 0.63	0.42	0.22	0.43	0.65

Table 3
Test Results for 11.5 mm (0.45 in.) Frame Treatment at Varying Flow Rates

	0.2 L/min (0.05 gal/min)		0.8 L/min (0.21 gal/min)		2.4 L/min (0.63 gal/min)	
	Cu	SO_4^{-2}	Cu	SO_4^{-2}	Cu	SO_4^{-2}
Mass removed (mg)	932	48747	2148	135852	7992	100620
Concentration (ppm)	0.1	9.8	0.8	50.0	4.0	130.0

In-process Recycling of Rinse Water

While our patented in-process recycling system** has never been implemented into an industrial plating line, it has proven to be an effective means for the treatment and recycling of copper rinse water generated from industrial plating lines. The inventiveness of this

*** E-CHANGE®, Faraday Technology, Inc., Clayton, OH*

Table 4
Copper & Sulfate Removal for Evaluation of *in-situ* Resin Regeneration

Test #	Copper Removal (g)	Sulfate Removal (g)
1	3.7	128
2	2.3	103
3	3.0	150

design lies in several fundamental features. It can "simultaneously" remove anionic and cationic contaminants, resulting in decreased metal concentration, total dissolved solids (TDS) and a neutralized pH. The treatment of rinse water from a copper plating line is illustrated in Fig. 3.

First, the rinse water contaminated with $CuSO_4$ is pumped into the cathode frame, where a cathodic electric field is applied. Under the influence of the electric field, Cu^{+2} ions transmigrate to the integrated ion exchange cathode, which contains standard, off-the-shelf cation exchange resin mixed with graphite particles. The Cu^{+2} ions are removed from the wastewater through (1) a cation exchange reaction and (2) an electrodeposition reaction. At the cathode, H^+ is generated from the cation exchange reaction; this combines with the OH^- generated at the cathode via water electrolysis to form water, shown by the following reactions:

$$2(R - SO_3^-)H^+ + Cu^{+2} \square (R - SO_3^-)_2\, Cu + 2H^+ \quad (2)$$

$$2H_2O + 2e^- \square H_2\,(g) + 2OH^- \quad (3)$$

$$2H^+ + 2OH^- \square 2H_2O \quad (4)$$

From the cathode the water is then circulated through the anode frames, where SO_4^{-2} ions migrate toward the integrated ion exchange anode, and are removed through the anion exchange reactions. The OH^- generated via the anion-exchange reaction combines with H^+ generated via the oxygen evolution reaction occurring at the anode to form water, shown in the following reactions.

$$2R - OH + SO_4^{-2} \square R_2 - SO_4^{-2} + 2OH^- \quad (5)$$

$$2H_2O \square 4H^+ + O_2(g) + 4e^- \quad (6)$$

$$2OH^- + 2H^+ \square 2H_2O \quad (7)$$

The small volume of gases produced as a consequence of water electrolysis may be "burped" with a special valve to ensure there is no pressure buildup. After treatment, the concentration of Cu^{+2} and SO_4^{-2} ions is greatly reduced and the pH is neutralized, enabling the water to be recycled back to the rinse operation. A typical treatment in the electrochemical cell results in a reduction in copper concentration from 24 to 0.1 ppm. Once the ion-exchange resin ceases to remove Cu^{+2} and SO_4^{-2}, the cell can be electrochemically regenerated, restoring it to its initial state. The result of cell regeneration is a small volume of highly concentrated copper sulfate, which then can be used as a starter plating solution.

In-situ *Cell Regeneration*

The ingenuity of this design resides in the ability of the system to be regenerated *in-situ* without the need of strong chemical species. Figure 4 shows a schematic diagram of the regeneration process. Conventionally, ion-exchange resin must be regenerated through treatment with a strong chemical species. This process involves slowly flowing a strong acid through cation-exchange resin fol-

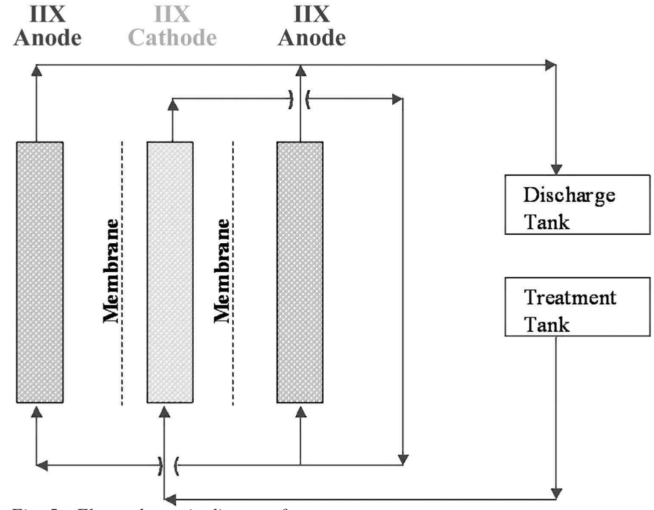

Fig. 5—Flow schematic diagram for treatment.

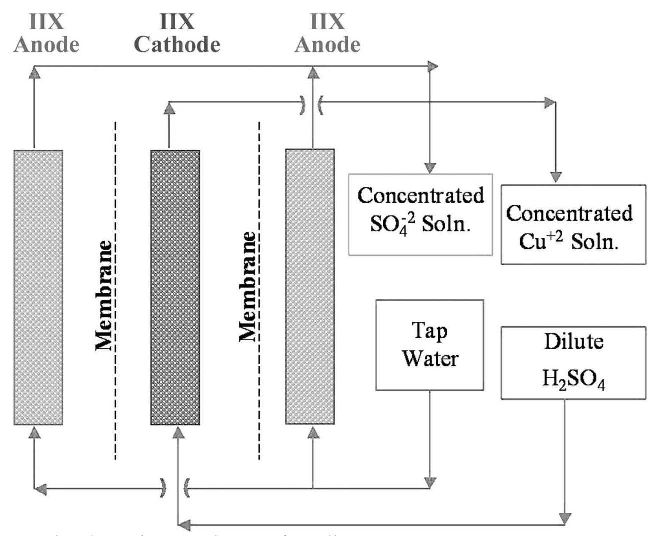

Fig. 6—Flow schematic diagram for cell regeneration.

lowed by several slow rinses with water, all steps requiring a relatively long period of time. The use of chemical species and time requirement translate into higher capital costs. Another disadvantage of chemical regeneration is the large required footprint. Our system does not require the addition of chemicals or multiple water rinses, but instead utilizes the applied electric field for the regeneration of ion-exchange resin. This is achieved simply by reversing the polarity of the applied electric field. Upon doing so, the electrode previously functioning as the cathode now becomes the anode. At this terminal, water is electrolyzed, producing oxygen gas and H^+ ions. The cation-exchange resin preferentially absorbs the H^+ ions, liberating copper ions back into solution and fully regenerating the cation-exchange resin. These reactions are shown in Equations 8 and 9. The copper metal that is plated will be oxidized to Cu^{+2}.

$$2H_2O \square 4H^+ + O_2\,(g) + 4e^- \quad (8)$$

$$(R - SO_3^-)_2\, Cu + 2H^+ \square 2(R - SO_3^-)H^+ + Cu^{+2} \quad (9)$$

Similarly, the electrode functioning as the anode in the treatment step becomes the cathode when the electric field polarity is reversed. Water electrolysis at this terminal yields hydrogen gas and OH^-. The anion-exchange resin will absorb the OH^- generated, releasing the anions absorbed onto the anion-exchange resin and fully regenerating the anion-exchange resin, as illustrated by Equations 10 and 11.

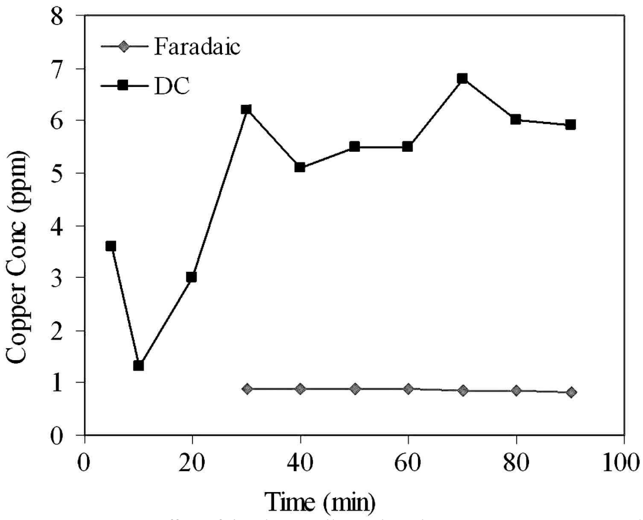

Fig. 7—Effect of the electrically-mediated process on copper removal as compared with DC treatment.

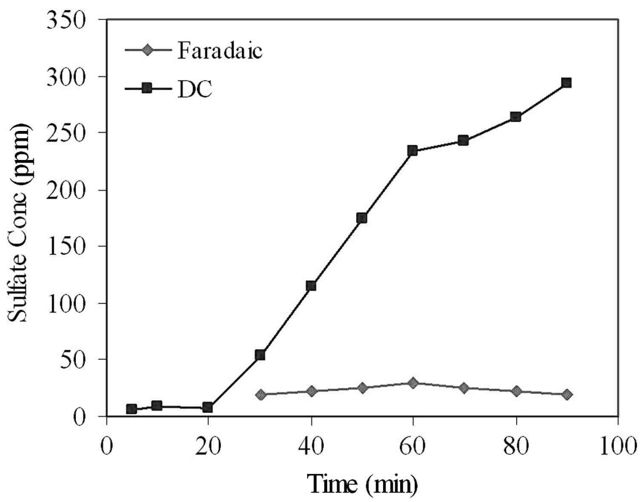

Fig. 8—Effect of the electrically-mediated process on treatment as compared to DC treatment.

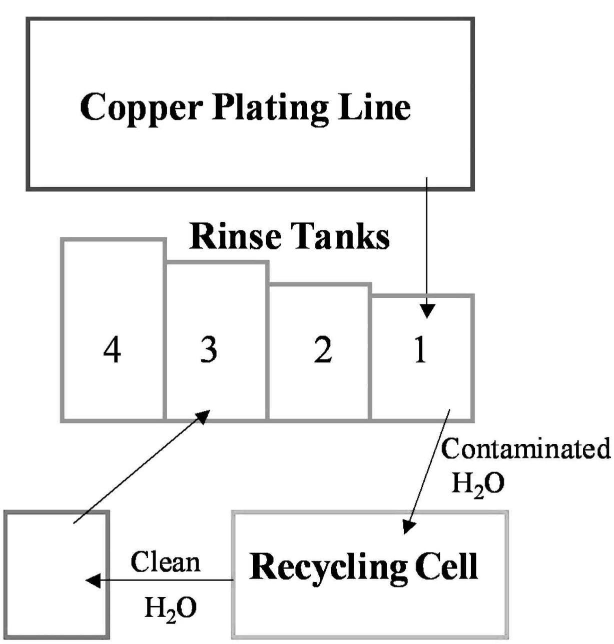

Fig. 9—Schematic diagram of the in-house copper-plating line with recycling in treatment mode.

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad (10)$$

$$R_2 - SO_4^{-2} + 2OH^- \rightarrow 2R - OH + SO_4^{-2} \quad (11)$$

The result of this process is a small volume of concentrated solution, which can be recycled back to the plating operation or disposed of properly.

Experimental

Experiments were conducted to treat copper rinse water generated from a commercial PWB manufacturing facility.[7] Test conditions are summarized in Table 1. As seen, from the cell parameters in the table, the cell consists of one cathode and two anodes in alternating arrangement. The cathode was isolated from each anode by the presence of a Nafion® membrane. Every electrode frame used in this study had the same length [15 cm (~6 in.)] and height [30 cm (~12 in.)], but varied in thickness. Anode frames of three thicknesses were used for testing: 11.5 mm, 22.3 mm and 45.0 mm (0.45, 0.88 and 1.77 in.). For tests utilizing 11.5 mm and 22.3 mm anode frames, an 11.5 mm cathode was used. Cells built with 45.0 mm anode frames contained a 22.3 mm cathode frame. The volume of the cell, utilizing 11.5 mm anode frames, was approximately 1 L (0.26 gal).

Experiments were run to explore the effect of solution flow rate. Three flow rates were tested with the 11.5 mm anode frames: 1) 0.2, 0.8 and 2.4 L/min (0.05, 0.21 and 0.63 gal/min). For tests utilizing the 22.3 mm and 45.0 mm anode frames, the flow was set to 2.4 L/min (0.63 gal/min). Cell voltage was controlled at 10.5V for the 11.5 mm anode frames, and 26V for the 22.3 mm and 45.0 mm anode frames. All treatment tests were run in single-pass operation. Initial tests were run in parallel flow, *i.e.*, the solution was split and simultaneously run through both the cathode and anode frames. Treatment in this manner leads to undesirable side reactions, as discussed in the Results section. Consequent tests were run in series flow, where wastewater was first circulated through the cathode and then circulated through the anode. Figure 5 gives a schematic diagram of the solution flow during treatment.

Cell regeneration was accomplished by reversing the polarity of the cell. During regeneration, 30 L (~8 gal) of dilute sulfuric acid were circulated between the IIX cathode compartment and the catholyte holding tank. Thirty liters of tap water were circulated between the IIX anode compartment and the anolyte holding tank. The cell voltage was controlled at 10.5V and the current decreased from approximately 13 to 9A during the regeneration. Figure 6 schematically shows the flow scheme of the cell during regeneration.

Samples were taken every 5 to 10 minutes from the outlet tube to measure pH, copper concentration and total dissolved solids (TDS). The sulfate concentration was estimated by the difference between the TDS and copper concentration, since TDS is the summation of cation and anion concentrations except for H^+ and OH^-. Copper concentration was analyzed by cyclic voltammetry (CV) or anodic stripping voltammetry (ASV) at our laboratory. To ensure accuracy, several samples were sent to a local EPA-approved lab to analyze copper concentration by atomic absorption spectroscopy (AAS). TDS was measured with a TDS meter***.

Tests were conducted to study the effects of 1) the flow pattern, 2) solution flow rate, 3) electrical-mediation as compared to DC and 4) regeneration.

Results & Discussion

All results presented are from previous work conducted on the recycling of copper plating rinse water.[7]

*** *Cole-Parmer TDSTestr 10, Cole-Parmer Instrument Co., Vernon Hills, IL.*

Effect of Flow Pattern

Initial tests were run in parallel flow for 60 min at a flow rate of 3.2 L/min (0.84 gal/min). The voltage was steady at 10.5V, resulting in a current of 5A. During these tests, the color of the anion resin**** changed from yellow to blue. In previous studies, when the anion exchange resin was mixed with graphite particles, this was not observed. It is possible that the blue solid on the anion exchange resin was a $Cu(OH)_2$ precipitate, and was formed when the copper ions came into contact with the hydroxide ions generated via anion exchange reactions. The H^+ generated via the oxygen evolution reaction only occurred on the DSA current collector. It took a certain period of time for the H^+ to transport to the top layer of anion resin and neutralize the OH^- there. Therefore, with this type of IIX anode, a high pH layer was generated on the anion resin, which precipitated blue $Cu(OH)_2$ on it. In contrast, with a mixture of graphite particles and anion resin, the OH^- generated via the anion exchange reaction would be neutralized immediately with H^+ generated via oxygen evolution reaction on the graphite particles. Therefore, no high local pH would be generated in this case and no blue $Cu(OH)_2$ would precipitate on the resin.

The approach taken to solve this problem was to switch electrolyte flow from a parallel pattern to a series pattern. Specifically, the electrolyte would flow through the cathode frame first, to remove the copper, and then flow through the anode frames to remove anions present in the waste stream. In this way, when the rinse water flowed through the anode compartment, the copper concentration was considerably reduced in the cathode compartment, which would minimize the precipitation of $Cu(OH)_2$. All subsequent tests were conducted using series flow.

Regeneration utilizes two separate regenerate streams, dilute H_2SO_4 was circulated through the cathode and tap water through the anode frames. Previous studies have also shown that copper rinse water and tap water are catholyte alternatives.[8]

Effect of Flow Rate

The removal of contaminants with our unit is limited by the metal deposition reactions as well as the accompanying anion-exchange reactions. This limitation may be overcome by a longer residence time, and thus a lower flow rate. However, the mass transfer rate is low at a low solution flow rate, which will have an adverse effect on the removal efficiency. Therefore, there is an optimum flow rate that balances the residence time and mass transfer rate. Experiments were run at three different flow rates: 0.2, 0.8 and 2.4 L/min (0.05, 0.21 and 0.63 gal/min).

The actual residence time may be calculated from the cell dimensions and the flow rate. The average area of the flow channel was approximately 17.25 cm^2 (2.67 $in.^2$). Consequently, the average flow velocities were 11.6, 46.4 and 139.1 cm/min (4.6, 18.3 and 54.8 in./min) for the flow rates of 0.2, 0.8 and 2.4 L/min, respectively. Since the solution first flowed through the cathode frame and then the two anode frames, the residence time in the anode frames was twice as long as in the cathode frame. The actual residence time in the cathode and anode frames is shown in Table 2. Since the cell volume was approximately 1 L (for the 11.5 mm anode frames), the average residence times for flow rates of 0.2, 0.8 and 2.4 L/min are 5, 1.25 and 0.42 min, respectively. These values are also listed in Table 2.

Table 3 gives the effluent concentrations of sulfate and copper after 180 min of treatment at varying flow rates. From the results presented in Table 2, a flow rate of 0.8 L/min appears to enhance the removal of both copper and sulfate in terms of overall efficiency as compared to the other flow rates. While more copper was removed at the highest flow rate, the removal of sulfate was compromised, therefore making flow at 0.8 L/min optimal for testing conditions.

Effect of Electrically-mediated Process As Compared to DC Treatment

The cell used for this phase of testing consisted of an 11.5 mm (0.45 in.) cathode frame and two 22.3 mm (0.88 in.) anode frames. Direct current tests were run for comparison purposes. DC tests were run at 10A. Treatment with the electrically-mediated process had the following waveform parameters: 10A average current, 50% duty cycle and 10 Hz frequency. Figure 7 shows the concentration of copper after treatment as a function of DC and electrically-mediated treatment. Figure 8 gives the concentration of sulfate ion after DC and electrically-mediated treatment. In both instances, the contaminant concentrations are lowered after electrically-mediated treatment.

Regeneration studies were also conducted to explore the ability of the unit to be regenerated *in-situ*, under the influence of an electric field. The cell utilized for these tests contained two 45.0 mm (1.77 in.) anode frames and a single 22.3 mm (0.88 in.) cathode frame. The solution flow was set at 2.4 L/min (0.63 gal/min) for all three tests. The current was held constant at 10A for the first

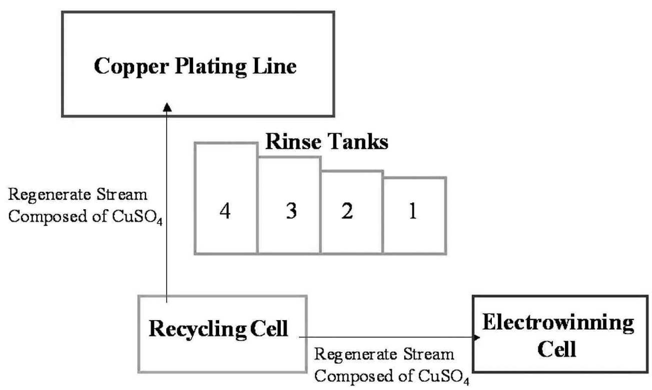

Fig. 10—Schematic diagram of the in-house copper plating line recycling system in regeneration mode.

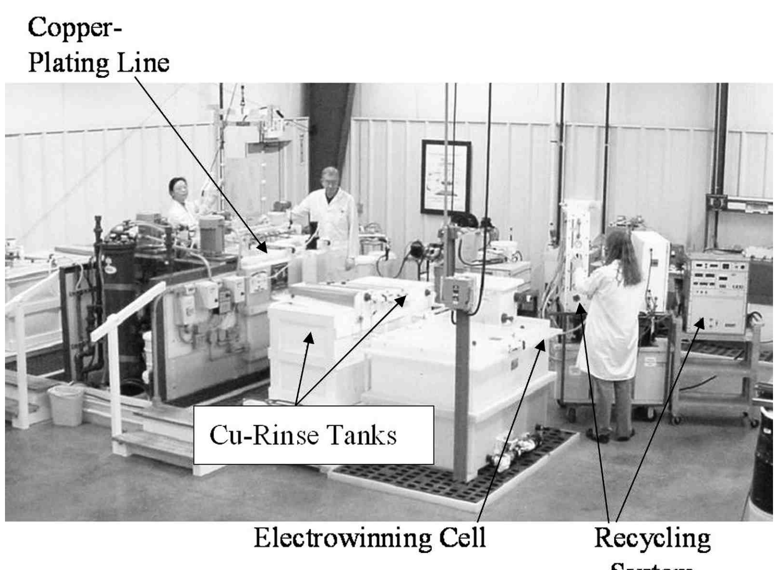

Fig. 11—Photo of the in-house copper plating line including an in-process recycling system.

****SBG1-OH Anion Exchange Resin, ResinTech, Inc., West Berlin, NJ.

and third test, and was held at 6A for the second test. The cell was regenerated between each treatment test as described above. The copper and sulfate removal (in grams) was calculated for each test. These results are given in Table 4.

As shown in Table 4, Tests 1 and 3 were very comparable in the mass of copper and sulfate removed. Test 2, however, showed significantly lower removal of both copper and sulfate. This is most likely attributed to the lower treatment current, specifically the lower removal efficiency at this current level. Therefore, it appears that regeneration of the cell resulted in a fairly complete regeneration of the ion-exchange resins present in the integrated ion-exchange electrode.

Currently, our facility has built a pilot scale, easily-controlled copper plating line for PWB applications. The process utilizes an essentially additive-free plating bath [350 ppm polyethylene glycol (PEG) is only additive in the system] in which an electrically-mediated process is used in place of other additives. To improve efficiency of the process, an in-process recycling unit has been incorporated into the system. This unit cleans the rinse water contaminated with copper sulfate, so that the water can be recycled back to the rinse operation. Once the cell is saturated with copper and sulfate contaminants, it is regenerated, resulting in a small volume of concentrated copper sulfate solution. This regenerate stream can either be recycled back to the plating operation or dumped into the electrowinning unit, also incorporated into the system for heavy metal removal. Schematic diagrams of the system are given in Figs. 9 and 10, and a photograph is given in Fig. 11. Results from these investigations will be presented at a later date.

Conclusions

Our experimental work successfully demonstrated the technical and economic feasibility of in-process recycling plating rinse water with our in-process recycling system process. Specifically,

- After treatment of Cu plating rinse water with our in-process recycling system, the treated water can be recycled to the rinsing operation;
- There exists an optimal flow rate in our in-process recycling system to balance residence time and mass transfer rate;
- The contamination removal rate and removal efficiency were higher with an electrically-mediated compared to the direct current (DC) process;
- The cell performance showed little degradation after regeneration;
- The regenerated solution contained a small volume of solution concentrated with the same chemical components as the plating bath, which can be recycled to the plating operation.

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About the Authors

Holly Garich is a project engineer at Faraday Technology, Inc. Garich received her BS and MS degrees in chemistry at Wright State University, Dayton, OH in 1999 and 2001, respectively. Currently, she is leading Faraday's environmental recycling efforts including build-up and testing of reactors for (1) acid copper rinse water, (2) trivalent chromium plating bath chemistry maintenance, (3) anodic process electrolyte maintenance and (4) a hybrid system for decontaminating CMP slurry waste from silicon wafer processing. She is a member of the American Chemical Society and AESF.

Robert Renz, PE, CEF, is the engineering manager at Faraday Technology, Inc. He has published numerous papers and holds several US Patents with several more pending. Renz received his BS degree in metallurgical engineering from the University of Cincinnati. He has nearly 30 years of industrial metal finishing and waste treatment experience prior to joining Faraday. Renz's experience at General Motors Corp., Delphi Chassis Division includes chromium plating, tin plating and zinc phosphating. He is a member of AESF, where he serves as a member of the Hard Chromium Plating Committee.

E. Jennings Taylor is the chief technical officer at Faraday Technology, Inc., Clayton, OH. He founded the company to develop and commercialize innovative electrochemical technology using sophisticated charge-modulated electric fields. The company's intellectual property has been successfully transferred both to government agencies and large manufacturers in the form of process engineering technology and products. He holds a BA in chemistry from Wittenberg University, an MA in technology strategy and policy from Boston University, and MS and PhD degrees in materials science from the University of Virginia. He has published more than 70 technical papers and articles and holds many patents. He serves on the AESF Pulsed Electrodeposition Processes Committee and is chairman of the Research Board.

Jenny J. Sun is a project engineer at Faraday Technology, Inc. She has worked on numerous projects to establish the feasibility of using charge-modulated electric fields for electrode position and electrochemical machining technology. She holds a BS in materials science from the University of Science and Technology, Beijing and an MS in materials science from Wright State University. She is a member of AESF and the Electrochemical Society, has published several papers in the areas of electrode position and electrochemical machining, and is co- inventor on several patents.