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

H.M. Krall, R.P. Renz, CEF, E.J. Taylor, Ph.D., & J.J. Sun
Faraday Technology, Inc., Clayton, OH 45315

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.

For More Information Contact:
Phillip Miller
Marketing Director
Phone (937) 836-7749
Fax (937) 836-9498
E-mail: phillipmiller@faradaytechnology.com
Introduction

The electronics industry is the second largest basic industry in the world, only surpassed by the agriculture industry.\(^1\) Virtually all electronics are mounted on printed wiring boards, or PWB.\(^2\) The PWB not only provides a structural surface for electronics components to be mounted onto, 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\(^3\):

1. Copper is relatively inexpensive when compared with other metals; copper is also in stable supply
2. Copper has a high electrical conductivity
3. Copper has a high plating efficiency, offers good plating coverage, and offers good throwing power, and
4. 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.\(^2\) 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.\(^2\) 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. 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 needs 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 known 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 as follows:

- 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 (Figure 1). The electrically mediated waveform consists of a cathodic voltage, applied for time $t_{c,on}$, 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 a time dependent process. Electrically mediated electrolysis causes concentration fluctuations near the electrode surface and reduces the effective

![Figure 1: Schematic of an Electrically Mediated Waveform.](image-url)
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 builds up. 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 Figure 2. The corresponding thickness of the Nernst diffusion layer, $\delta$, is also shown in Figure 2 for various time periods. 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:

$$i = nFD\frac{dC}{dx}\bigg|_{x=0} = - nFD\frac{(C_b-C_s)}{\delta}$$  \hspace{2cm} (1)

In steady state DC electrolysis, $\delta$ is a time-invariant quantity for given electrode geometry and hydrodynamics; this quantity is represented by $\delta_{\infty}$. In electrically mediated electrolysis, however, $\delta$ varies from 0 at the beginning of the process to a value of $\delta_{\infty}$ 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 $t = t_0$) before $\delta$ 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\textsuperscript{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\textsuperscript{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.

**In-Process Recycling of Rinse Water**

Our patented in-process recycling system* has proven to be an effective means for the treatment and recycling of copper rinse water from industrial plating lines. The inventiveness of this design lies in several fundamental features. It can “simultaneously” remove anionic and cationic contaminants, resulting in decreased metal concentration, TDS and a neutralized pH.

The treatment of rinse water from a copper plating line is illustrated in Figure 3. First, the rinse water contaminated with $\text{CuSO}_4$ is pumped into the cathode frame, where a cathodic electric field is applied. Under the influence of the electric field, $\text{Cu}^{2+}$ ions transmigrate to the integrated ion exchange cathode, which contains standard, off-the-shelf cation exchange resin mixed with graphite particles. The $\text{Cu}^{2+}$ ions are removed from the wastewater through 1) a cation exchange reaction and 2) an electrodeposition reaction. At the cathode, $\text{H}^+$ 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:

1. $2(R - SO_3^-)H^+ + Cu^{2+} \rightarrow (R - SO_3^-)\text{Cu} + 2H^+$
2. $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$
3. $2H^+ + 2OH^- \rightarrow 2H_2O$

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

![Figure 3: Schematic of Our In-Process Recycling Unit for the Treatment of Copper-Plating Rinse Water.](image-url)
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 oxygen evolution reaction occurring at the anode to form water, shown in the following reactions.

\[
2R - OH + SO_4^{2-} \rightarrow R_2 - SO_4^{2-} + 2OH^- \quad \text{(5)}
\]
\[
2H_2O \rightarrow 4H^+ + O_2(g) + 4e^- \quad \text{(6)}
\]
\[
2OH^- + 2H^+ \rightarrow 2H_2O \quad \text{(7)}
\]

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 build up. 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 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 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 followed 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 reversing the polarity of the electric field, the electrode previously functioning as the cathode now becomes

![Figure 4: Schematic of Cell Regeneration.](image-url)
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$^{2+}$.

$$2H_2O \rightarrow 4H^+ + O_2(g) + 4e^-$$  \hspace{1cm} (8)

$$\left( R-SO_3^- \right)_2 Cu + 2H^+ \rightarrow 2\left( R-SO_3^- \right)H^+ + Cu^{2+}$$  \hspace{1cm} (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.

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$$  \hspace{1cm} (10)

$$R_2 - SO_4^{2-} + 2OH^- \rightarrow 2R - OH + SO_4^{2-}$$  \hspace{1cm} (11)

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

**Experimental**

Experiments were conducted to treat copper rinse water generated from a commercial PWB manufacturing facility. Test conditions are summarized in Table 1, below. As seen in Table 1, 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) and height (30 cm), but varied in thickness. Anode frames of three thicknesses were used for testing: 11.5 mm, 22.3 mm, and 45.0 mm. 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. Volume of the cell, utilizing 11.5 mm anode frames, is approximately 1 L.
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 L min$^{-1}$, 0.8 L min$^{-1}$, and 2.4 L min$^{-1}$. For tests utilizing 22.3 mm and 45.0 mm anode frames, the flow was set to 2.4 L min$^{-1}$. Cell voltage was controlled at 10.5 V for 11.5 mm anode frames, and 26 V for 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. solution was split and simultaneously run through both 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, wastewater was first circulated through the cathode and then circulated through the anode. Figure 5 gives a schematic of solution flow during treatment.

The regeneration of the cell was accomplished by reversing the polarity of the cell. During regeneration, 30 liters of dilute sulfuric acid were circulated between the IIX cathode compartment and the catholyte holding tank. Thirty liters of tap water were circulated between

| Cell Parameters | Electrode Surface Area = 450 cm$^2$
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode Frames:</td>
<td>11.5 mm holds 350 g of resin</td>
</tr>
<tr>
<td></td>
<td>22.3 mm holds 600 g of resin</td>
</tr>
<tr>
<td></td>
<td>45.9 mm holds 1200 g of resin</td>
</tr>
<tr>
<td>Cathode Frame:</td>
<td>11.5 mm holds 250 g of graphite/70 g of resin</td>
</tr>
<tr>
<td></td>
<td>22.3 mm holds 500 g of graphite/140 g resin</td>
</tr>
</tbody>
</table>

| Cu$^{2+}$ Concentration ~24 ppm
| TDS: 1400 ppm
| pH ~2

| Experimental Parameters | Single-Pass Operation
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>--------------------------</td>
<td>-----------------------------</td>
</tr>
</tbody>
</table>
| Flow Rates:             | 11.5 mm Anode Frames - 0.2, 0.8, and 2.4 L min$^{-1}$
|                         | 22.3 and 45.0 mm Anode Frames - 2.4 L min$^{-1}$
| Control Voltage:        | 11.5 mm Anode Frame - 10.5 Volts
|                         | 22.3 and 45.0 mm Anode Frames - 26 Volts

Figure 5: Flow Schematic for Treatment.
the IIX anode compartment and the anolyte holding tank. The cell voltage was controlled at 10.5 volts and the current decreased from approximately 13 to 9 amps 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 TDS. Sulfate concentration was estimated by the difference between the TDS and copper concentration since TDS is the summation of cation and anion concentrations except H\(^+\) and OH\(^-\). Copper concentration was analyzed with Cyclic Voltammetry (CV) or Anodic Stripping Voltammetry (ASV) at Faraday Technology, Inc. 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 (Cole-Parmer, TDSTestr 10).

Tests were conducted to study the effects of 1) the flow pattern, 2) solution flow rate, 3) the Faradaic Process (FP) as compared to DC and 4) regeneration.

Results and Discussion

All results presented are from previous work conducted on the recycling of copper plating rinse water.\(^7\)

Effect of Flow Pattern

Initial tests were run in parallel flow for 60 minutes at a flow rate of 3.2 L min\(^{-1}\). The voltage was steady at 10.5 volts, resulting in a current of 5 Amps. During these tests, the color of the SBG1OH 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 speculated that the blue solid on the anion-exchange resin is a Cu(OH)_2 precipitate, and is formed when the copper ions come 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 the resin. 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$_2$SO$_4$ 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 L min$^{-1}$, 0.8 L min$^{-1}$, and 2.4 L min$^{-1}$.

The actual residence time may be calculated from the cell dimensions and the flow rate. The average area of the flow channel is approximately 17.25 cm$^2$. Consequently, the average flow velocities are 11.6, 46.4, and 139.1 cm min$^{-1}$ for the flow rates of 0.2, 0.8, and 2.4 L min$^{-1}$, respectively. Since the solution first flows through the cathode frame and then the two anode frames, the residence time in the anode frames is 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 is approximately 1 liter (for 11.5 mm anode frames), the average residence times for flow rates of 0.2, 0.8, and 2.4 L min$^{-1}$ are 5 min, 1.25 min, and 0.42 min, respectively; these values are also listed in Table 2.

<table>
<thead>
<tr>
<th>Flow Rate (L min$^{-1}$)</th>
<th>Average Residence Time (min)</th>
<th>Cathode Residence Time (min)</th>
<th>Anode Residence Time (min)</th>
<th>Total Residence Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>5</td>
<td>2.6</td>
<td>5.2</td>
<td>7.8</td>
</tr>
<tr>
<td>0.8</td>
<td>1.25</td>
<td>0.65</td>
<td>1.3</td>
<td>1.95</td>
</tr>
<tr>
<td>2.4</td>
<td>0.42</td>
<td>0.22</td>
<td>0.43</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Table 3 gives the effluent concentrations of sulfate and copper after 180 minutes of treatment at varying flow rates. From the results presented in Table 2, 0.8 L min$^{-1}$ 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$^{-1}$ optimal for testing conditions.
Table 3: Test Results for 11.5 mm Frame Treatment at Varying Flow Rates.

<table>
<thead>
<tr>
<th>Flow Rate (L min(^{-1}))</th>
<th>Mass Removed (mg)</th>
<th>Cu</th>
<th>SO(_4^{2-})</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 L min(^{-1})</td>
<td>932</td>
<td>0.1</td>
<td>9.8</td>
<td>0.1</td>
</tr>
<tr>
<td>0.8 L min(^{-1})</td>
<td>2148</td>
<td>0.8</td>
<td>50</td>
<td>4</td>
</tr>
<tr>
<td>2.4 L min(^{-1})</td>
<td>7992</td>
<td>4</td>
<td>130</td>
<td></td>
</tr>
</tbody>
</table>

Effect of the Electrically Mediated Process as Compared to Direct Current Treatment

The cell used for this phase of testing consisted of an 11.5 mm cathode frame and two 22.3 mm anode frames. Direct current tests were run for comparison purposes. DC tests were run at 10 Amps. Treatment with the electrically mediated process had the following waveform parameters: 10 Amps 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.

Regenerations 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 anode frames and a single 22.3 mm cathode frame. The solution flow was set to 2.4 L min\(^{-1}\) for all three tests. The current was held constant at 10 Amps for the first and third test, and was held at 6 Amps for the second test. The cell was regenerated between each treatment test described above. The copper and sulfate removal (in grams) was calculated for each test. These results are given in Table 4.
Table 4: Copper and Sulfate Removal for Evaluation of In-Situ Resin Regeneration.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Copper Removal (g)</th>
<th>Sulfate Removal (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.7</td>
<td>128</td>
</tr>
<tr>
<td>2</td>
<td>2.3</td>
<td>103</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>150</td>
</tr>
</tbody>
</table>

As shown in Table 4, test one and three are very comparable in the mass of copper and sulfate removed. Test two, however, shows 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 magnitude. Therefore, it appears that regeneration of the cell results 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 PEG is only additive in system) in which an electrically mediated process is used in place of other additives. To improve efficiency of the process, in-process recycling unit has been incorporated into the system. This recycling unit will clean the rinse water contaminated with copper sulfate, so that the water can be recycled back to 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 plating operation or dumped into the electrowinning unit, also incorporated into the system for heavy metal removal. Schematics of the system are given in Figures 9 and 10, and a photograph is given in Figure 11. Results from these investigations will be presented at a later date.

Figure 9: Schematic of Our In-House Copper-Plating Line with Recycling in Treatment Mode.
Figure 10: Schematic of Our In-House Copper Plating Line Recycling System in Regeneration Mode.

Figure 11: Photograph of In-House Copper Plating Line Including an In-Process Recycling System.
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 shows little degradation after regeneration;
- The regenerated solution contains a small volume of solution concentrated with the same chemical components as plating bath, which can be recycled to the plating operation.

References:

2 http://www.p2pays.org/ref/13/12023/pr_ptl-2.htm
3 http://www.pfonline.com/articles/pfd0014.html
4 http://www.pfonline.com/articles/030102.html