

MICROELECTRONICS

AN APPROACH FOR COPPER AND HYDROGEN PEROXIDE REMOVAL FROM COPPER CMP AND SOLAR CELL WASTEWATER

The advent of copper integrated circuits in semiconductor manufacturing in the late 1990s led to the need for an efficient, environmentally compliant way to remove copper from wastewater generated from copper chemical mechanical planarization/polishing (CuCMP) processes. CuCMP chemistry involves oxide slurry solids, chelators and other components that complicate traditional precipitation wastewater treatment methods that create a waste solid (i.e., sludge) considered to be hazardous waste by federal and state environmental regulations.

To meet this need, an alternate CuCMP wastewater treatment system was developed^A, using selective ion-exchange (IX) resin to remove copper and allow for its recovery. This treatment system was commercialized^B in the early 2000s and has been successfully used to treat CuCMP wastewaters in the United States, Europe, and Asia.

Manufacturing processes for solar photovoltaic devices (i.e., solar cells) use chemistry with characteristics similar to those of CuCMP, and continued development of the treatment system has extended its use to solar cell manufacturing wastewater. Table A shows the typical composition of wastewater from CuCMP and solar cell manufacturing processes. This article focuses on the primary

TABLE A
TYPICAL WASTEWATER COMPOSITION

Copper CMP		Solar Cell	
Component	Range	Component	Range
Copper	5–100 mg/L	Copper	10–100 mg/L
Hydrogen peroxide	50–1,000 mg/L	Cadmium	5–15 mg/L
Total solids	500–5,000 mg/L	Oxidizer	10–1,000 mg/L
Organic chelators	10–50 mg/L	Thiourea	400–3,000 mg/L
TOC	10–100 mg/L	Organic chelators	10–50 mg/L
Alkyl/aryl triazole	50–200 mg/L	Conductivity	1,000–5,000 μ S/cm
pH	2–6	pH	1–7

Notes:
1. Source for copper CMP composition is Reference 8.
2. mg/L = milligram per liter; μ S/cm = microSiemens per centimeter.

components of the CuCMP treatment system—specialized activated carbon and selective IX resin—and discusses methods for choosing and optimizing these components for best performance in treatment applications.

Description of the CuCMP System

The treatment system was developed to deal with the specific chemistry of CuCMP wastewater and more recently, wastewater generated in solar cell manufacturing (1-4). It uses activated carbon with catalytic activity to decompose oxidizers such as hydrogen peroxide, which is decomposed to water and gaseous oxygen, and peroxysulfates, which are reduced to sulfates. The process uses IX resin to remove copper and other metals.

The treatment system eliminates the sludge problems of traditional precipitation-based treatment. It also has an advantage over conventional chemical treatment for oxidizers and metal precipitation in that the silica, alumina, ceria, or other CuCMP abrasive solids pass through the catalytic carbon and IX resin tanks without being removed or plugging the tanks. If necessary, the abrasives can be removed or recovered

later in the process, free of metal contamination.

Developed through Testing

Extensive laboratory and pilot tests were conducted on the copper-removal treatment system before commercialization, including multiple Design of Experiment tests to explore process operating variables and CuCMP chemistry, extended pilot runs to evaluate treatment process stability, and intentional excursions to process variables in order to evaluate the effects on treatment efficacy and the ability of the treatment system to recover. These tests were conducted using actual and synthetic CuCMP wastewater. Among variables explored were operating pH and chemistry such as oxidizers, surfactants, and chelators. Results of these tests have been previously reported (5-9).

System Configuration

A schematic representation of the primary components of the copper-removal treatment system is shown in Figure 1.

Following pH adjustment, CuCMP wastewater enters the first, or lead, catalytic carbon treatment tank. Catalytic

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carbon and IX resin tanks are arranged in a lead-lag configuration to allow complete or near-complete use of the media in lead tanks with polishing of untreated oxidizer and metal by media in the respective lag tanks. Treated CuCMP wastewater flows to additional downstream treatment; for example, slurry solids removal by membrane or precipitation and possible water reuse or to the facility's final waste neutralization system. Oxygen gas, produced when hydrogen peroxide decomposes, is vented from the tank directly to atmosphere or through an exhaust vent or scrubber system. A gas/liquid valve at the high point of the tank opens when oxygen gas builds in the top of the tank, allowing it

to escape. Oxidizers that do not form oxygen gas when catalytically reduced do not require venting.

Figure 2 is a photograph of a 25-gallon-per-minute (gpm) copper-removal treatment system installed at a semiconductor manufacturing facility. The three tanks inside the containment area (foreground, left) are catalytic carbon tanks. Two are in operation and the third is an "installed spare" that can be easily brought online by switching valves on the manifold system at the right. A gas/liquid separator for venting is fitted to the top of each tank but essentially all oxygen is released from the lead carbon tank. The three IX tanks, just visible behind the carbon tanks, use the same "installed spare" configuration.

The manifold houses the influent flow control valve, tank pressure gauges, and system influent and effluent lines. While not shown here, copper and hydrogen peroxide multipoint on-line monitoring systems can be included.

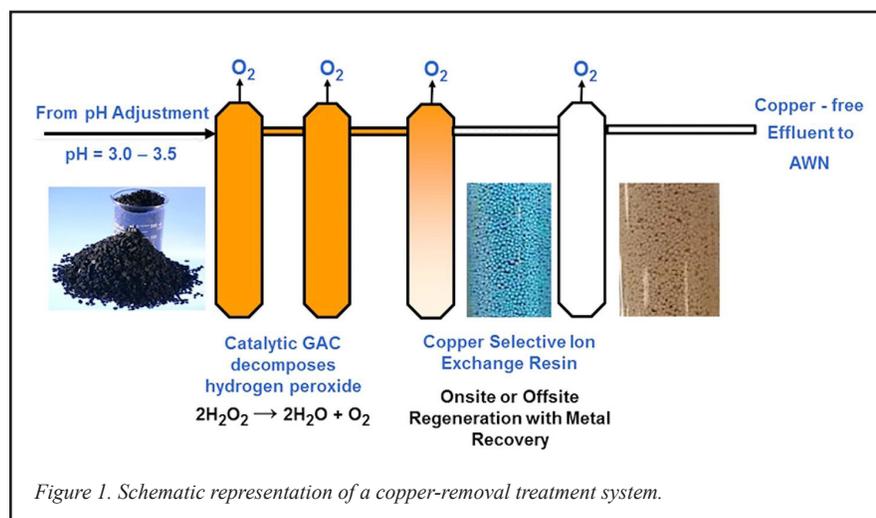
Venting Oxygen Protects IX Resin

The hydrogen peroxide decomposition reaction is rapid. Only three-to-five minutes of contact with the catalytic carbon is required to reduce peroxide to water and oxygen gas. Unless oxygen gas is removed from the catalytic carbon tank, it will accumulate and soon dewater the tank as it seeks to find a way to escape to the atmosphere. When tanks are dewatered, the peroxide no longer comes into contact with catalytic carbon, preventing further decomposition and allowing untreated peroxide to contact the IX resin. As an example, catalytic carbon treating 25 gpm of CuCMP wastewater at 77°F (25°C) and containing 250 milligrams per liter (mg/L) of hydrogen peroxide generates 0.3 cubic feet per minute (CFM) of gaseous oxygen. That is 18 cubic feet per hour (ft³/hr), more than enough to dewater the head space and interstitial space in the carbon and resin beds of all the on-line tanks in the photograph.

Catalytic Activated Carbon

Oxidizers damage IX resins by degrading IX sites and/or breaking divinylbenzene (DVB) crosslinks that bind the resin polymer strands together. Degradation of IX sites means that the IX resin will treat less wastewater volume between regeneration cycles, removing less metal with each cycle. Unless something is done to protect the IX resin, it will need to be replaced more often and will significantly increase operating costs.

Activated carbon is the conventional choice for this task. It is a well-established treatment for residual chlorine in IX processes, and is also useful in removing low concentrations of hydrogen peroxide. However, standard activated carbon becomes ineffective at peroxide concentrations exceeding 1 or 2 mg/L because the oxygen gas accumulates (binds) in the carbon bed and disrupts further peroxide treatment.



Treatment of the high concentrations of peroxide and other oxidizers found in CuCMP and solar cell wastewaters requires an alternative to standard activated carbon. During development of the copper-removal treatment system, it was demonstrated that activated carbon with catalytic activity was effective for decomposing hydrogen peroxide and, for reasons not totally known, the oxygen formed would not bind in the bed.

How Much Hydrogen Peroxide?

After catalytic carbon treatment, how much residual hydrogen peroxide can the IX resin tolerate without excessive damage? To answer this question a long term test was conducted by exposing IX resin to synthetic CuCMP wastewater, containing hydrogen peroxide at concentrations of 0, 50, 100, 500, and 1,000 mg/L through repeated loading and regeneration cycles. Figure 3 shows the number of hours of exposure required for a 25% loss of IX capacity as a function of hydrogen peroxide concentration. Based on these data and other considerations, a target maximum peroxide concentration of 20 mg/L entering the IX resin tanks was determined to sufficiently protect the IX resin while allowing efficient and economical removal of copper and other metals.

IX Resin Test Results

Figure 4 is a photograph of the resins used in the oxidation study. The top row shows new, unused resin on the left and three samples exposed to no peroxide during the test. Visually, the resins are opaque and there is no apparent difference among the four. The IX capacity of these resins was unchanged over the course of the test. The lower row shows resin at the four hydrogen peroxide concentrations tested. The resins darken as concentration increases from 0 to 1,000 mg/L. Not readily noticed in the photo is that the IX resin beads shrank on exposure to peroxide, became increasingly granular in appearance and lost their spherical shape. They did not soften or swell but became increasingly translucent and brittle with higher peroxide concentration. This suggests that hydrogen peroxide degrades the IX resin by damaging the IX sites rather than breaking DVB crosslinks.

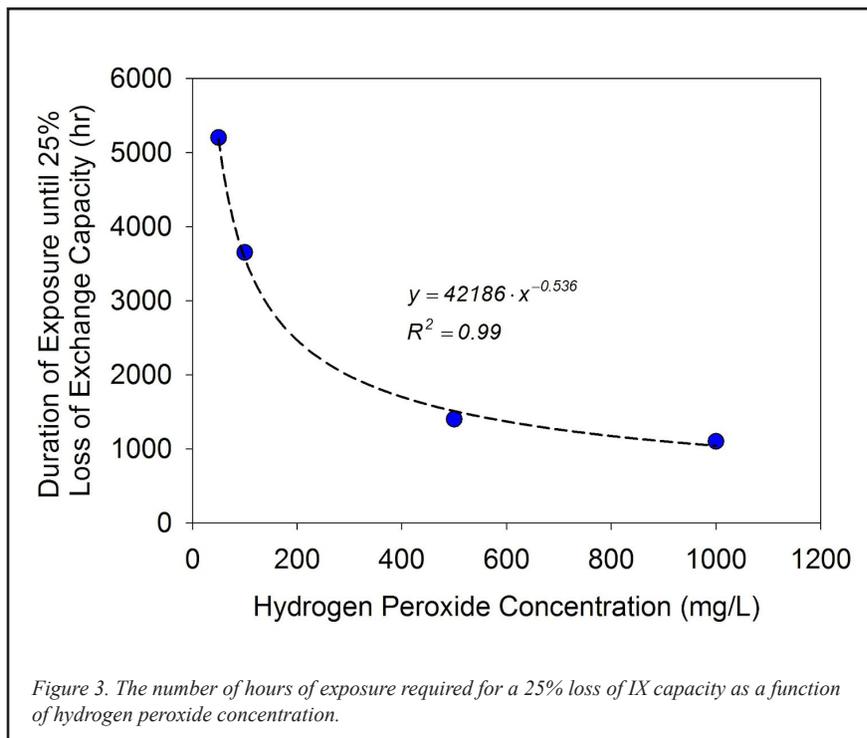


Figure 3. The number of hours of exposure required for a 25% loss of IX capacity as a function of hydrogen peroxide concentration.

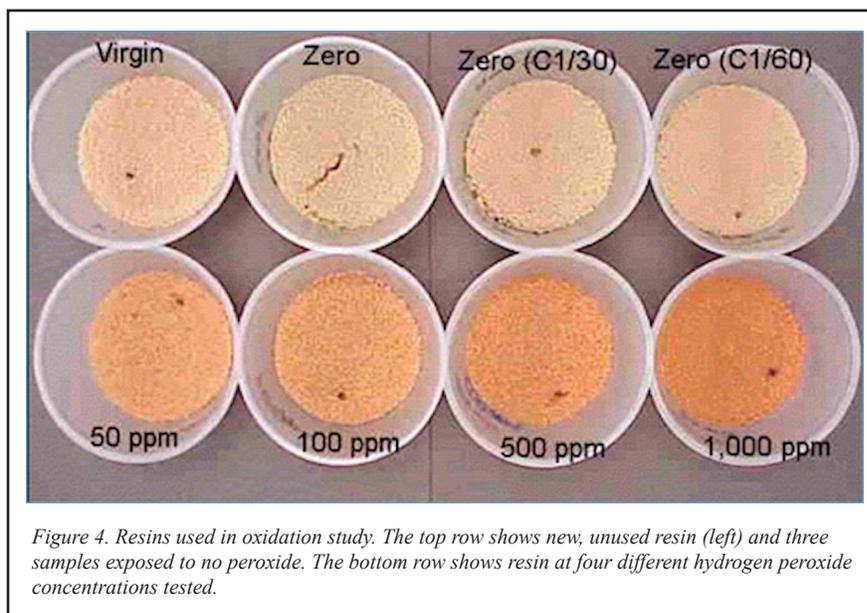


Figure 4. Resins used in oxidation study. The top row shows new, unused resin (left) and three samples exposed to no peroxide. The bottom row shows resin at four different hydrogen peroxide concentrations tested.

Finding the Right Carbon

Jar tests were conducted to evaluate three commercially-available catalytic activated carbons. Figure 5 shows the relative hydrogen peroxide decomposition rate of catalytic and non-catalytic activated carbons. The test was conducted by adding the same amount of dry activated carbon to 1 L of solution containing 1,000 mg/L of hydrogen peroxide. Samples were taken at preset

time intervals and analyzed for residual peroxide. Residual hydrogen peroxide results show that decomposition by catalytic carbon is a first-order kinetic reaction and that activated carbon from different sources produce varying rates of decomposition. By contrast, non-catalytic carbon decomposed little peroxide over the period of the test.

Figure 6 shows peroxide removal from synthetic CuCMP wastewater in a

flow-through pilot test comparing two of the catalytic activated carbons in tanks with a hydrogen peroxide influent concentration of 225 mg/L, later increased to 275 mg/L. Both catalytic carbons decomposed essentially all of the peroxide through 10,000 bed volumes (BV). (A BV is a dimensionless number

equal to the volume of solution treated divided by the volume occupied by the carbon bed.) The residual peroxide from both carbons was below the 20 mg/L target until 25,000 BV had been treated. At 25,000 BV, the influent hydrogen peroxide concentration was increased and resulted in higher residual peroxide

concentration in the effluent from each carbon tank.

Carbon 2 showed a greater increase and exceeded the target concentration before leveling off. Carbon 1 remained below the target until 40,000 BV had been treated. In an operating treatment system, Carbon 2 would have been exchanged at about 27,000 BV and Carbon 1 at about 42,000 BV. Based on the data, variation in performance can be expected, depending on the source of catalytic carbon. Since two catalytic carbon tanks are placed in series (lead-lag configuration), any residual peroxide in excess of the 20 mg/L target concentration is polished by the lag tank, eliminating the danger of oxidative damage to downstream IX resin.

Treating Other Oxidizers

Hydrogen peroxide is only one oxidizer that can be decomposed or reduced by catalytic carbon. Others include chlorine or hypochlorite, peroxymonosulfate, and peroxydisulfate. Like hydrogen peroxide, peroxydisulfate reduction is consistent with a first-order kinetics reaction. Figure 7 shows results of a jar test using catalytic carbon to reduce potassium peroxydisulfate. The test was conducted in the same manner described for Figure 5 and, once again, shows a difference in the rates of reaction for catalytic carbon from different sources. Non-catalytic carbon, while more effective in reducing potassium peroxydisulfate than hydrogen peroxide, still lags far behind the performance of catalytic carbons.

Catalytic Carbon versus Chemical Treatment

In addition to its demonstrated effectiveness in reducing/decomposing oxidizers in CuCMP and solar cell wastewaters, catalytic activated carbon has other advantages over alternate treatment methods. One is that no additional total dissolved solids (TDS) are added to the wastewater. Hydrogen peroxide decomposes to water and oxygen gas, and peroxydisulfates reduce to sulfate.

By contrast, when a chemical reducing agent like sodium metabisulfite is used to treat oxidizers, the TDS load increases in proportion to the concentration of the oxidizer. For example, in the 25 gpm of CuCMP wastewater in the treatment

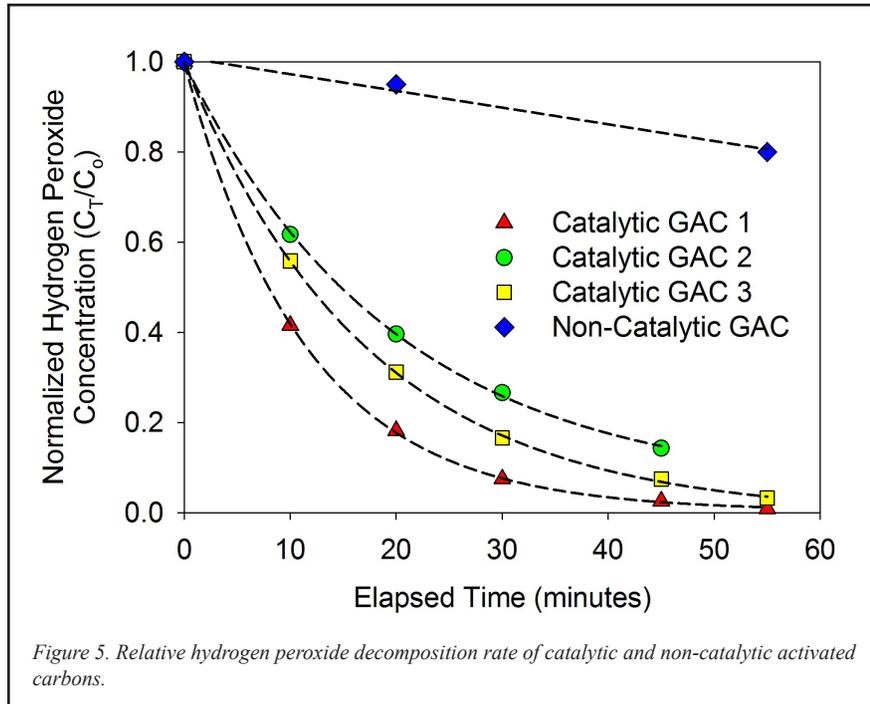


Figure 5. Relative hydrogen peroxide decomposition rate of catalytic and non-catalytic activated carbons.

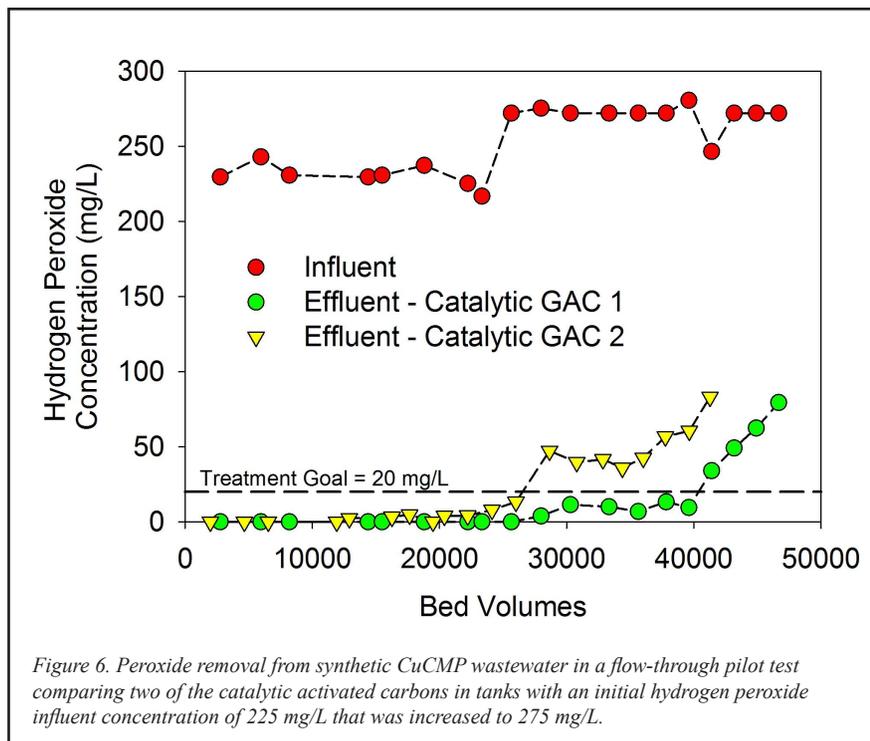


Figure 6. Peroxide removal from synthetic CuCMP wastewater in a flow-through pilot test comparing two of the catalytic activated carbons in tanks with an initial hydrogen peroxide influent concentration of 225 mg/L that was increased to 275 mg/L.

system discussed earlier, treating hydrogen peroxide with sodium metabisulfite or liquid sodium bisulfite solution (40% by weight) would add more than 1,000 mg/L of TDS to the background TDS.

Chemical reduction of oxidizers requires feed-and-control systems, chemical containment for the reagent used and makeup of dry chemical or replacement of liquid reagent as it is consumed. It is easy to over- or under-dose the reducing agent when treating hydrogen peroxide using an oxidation-reduction potential (ORP) controlled chemical feed system because the ORP response signal changes little over a broad peroxide concentration range (9). By contrast, catalytic activated carbon self-adjusts to variability in oxidizer concentration and only requires simple monitoring of the effluent for residual oxidizer. Monitoring can be done automatically using an in-line analyzer or manually by simple titration. Ease of use with catalytic activated carbon is favored over chemical addition systems.

Economics of Carbon Exchange

Catalytic carbon is not a catalyst in the classical sense. Functional-based sites on the surface of the activated carbon responsible for catalytic activity are altered over time by contact with the oxidizer and eventually the catalytic effect is lost. Exposure to higher concentrations of oxidizers speeds this loss but does not appear to do so in direct proportion to oxidizer concentration. Tanks of catalytic activated carbon need to be exchanged more frequently when used to treat higher concentrations. Of course, in a chemical reduction system, higher oxidizer concentration would also require adding more chemical reducing agent to the wastewater, and in this case is directly proportional to the oxidizer concentration (i.e., twice as much sodium metabisulfite is required when the oxidizer concentration doubles).

All activated carbons adsorb certain organic compounds and catalytic activated carbon is no exception. This may be beneficial if the wastewater is reused after treatment; however, some organic compounds at higher feed concentrations may load onto the carbon at a rate that shortens the useful life of the carbon for

oxidizer reduction. An economic evaluation would need to be done in such cases to determine whether catalytic activated carbon, treatment with reducing agents, or TOC pretreatment followed by catalytic activated carbon offers the most favorable operating cost.

Optimizing IX Resin

Removing metals from water and wastewater with IX resins is well established. The copper-removal technology discussed in this article uses cation resins to remove cationic metals, including copper, nickel, cadmium, cobalt, and zinc. Because CuCMP and solar cell wastewaters contain one or more chelating compounds, chelating IX resins are more effective in selectively removing copper and other metals from them. However, even chelating resins have difficulty removing metals when certain chelating compounds are present.

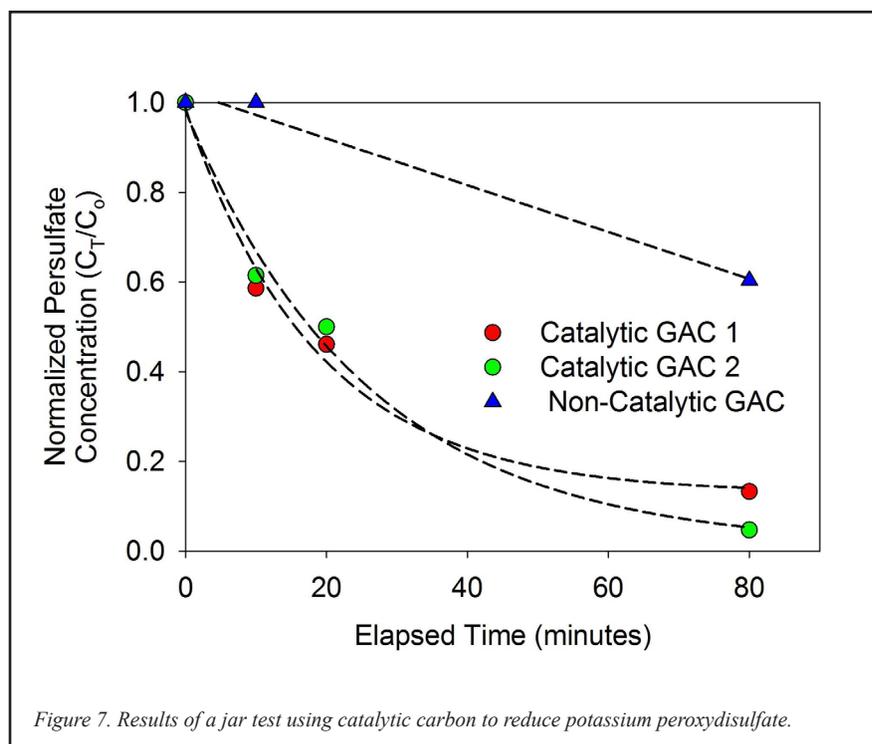
Thus, to optimize resin performance, copper-removal tests were conducted using CuCMP wastewater spiked with a variety of chelating compounds. The results demonstrated that the presence of aminocarboxylic acid chelates (for example, ethylenediaminetetraacetic acid [EDTA]) greatly reduced copper removal (8). Such chelating agents also negatively

impact metal removal by traditional precipitation treatment systems. It is important to review both process and wastewater chemistries to ensure that the copper-removal treatment approach will be effective.

Best Operating Parameters

In addition to wastewater chemistry, other factors are useful in optimizing the performance of IX treatment systems. The two most important, and the easiest to control, are influent pH and flowrate. The pH of the wastewater greatly affects the ionic form of copper and other metals in solution and their removal by the functional groups on the IX resins. For CuCMP wastewater, the best operating pH is in the 3.0 to 3.5 range. In this range, copper in the wastewater remains soluble so that the resin exchange group can pull copper out of the chelate and sorb it onto the resin. Differences in solar cell wastewater chemistry allow a wider operating pH range of 3.0 to 5.5.

With regard to treatment system influent feedrate, metal loading on IX resin is best when the feedrate is slow. To balance the system size against capital and operating costs, it is recommended that the feedrate not exceed 2.5 gallons per minute per cubic foot of resin (gpm/



ft³). Using a faster influent feedrate may reduce metal loading and allow the use of smaller equipment, reducing footprint and capital costs; but it has consequences. With faster influent feedrates, operating costs will be higher because more frequent resin regeneration will be required. Using the optimal operating pH and system feedrate allows optimal metal loading on the resin and optimal operating cost.

Service Exchange or On-Site Regeneration?

An important consideration is whether to regenerate spent IX resin on-site or off-site. Regenerating IX resin off-site (the service exchange model) minimizes the amount and sophistication of on-site equipment needed for the treatment system. When the resin becomes saturated with metal or the catalytic activated carbon exceeds the target oxidizer concentration, spent tanks are exchanged with fresh tanks. The spent tanks are returned to the service facility where they are emptied and refilled with freshly regenerated IX resin or new catalytic carbon.

In the service exchange model, resin quality, tank maintenance, and handling are the responsibility of the service facility. The only dedicated on-site equipment needed is a tank to collect and equalize wastewater from the CuCMP or solar cell manufacturing tools, a pH adjust tank to ensure that the pH is within the optimal operating range, and suitable pumps, hoses, controls, and monitoring equipment.

By contrast, in addition to the equipment necessary for service exchange, on-site regeneration requires that IX resin tanks be designed to operate correctly during both metal loading and regeneration cycles. Such tanks are larger and significantly more mechanically complicated. On-site regeneration also requires tanks to store regeneration chemicals and metering systems to ensure that regeneration is done properly with the correct volume and concentration of chemicals.

These chemicals must be collected and treated after regeneration, requiring additional tanks, chemicals, and control systems. Neutralization of the waste re-

**TABLE B
TYPICAL EFFLUENT METAL AND OXIDIZER RESULTS**

Copper CMP Wastewater		Solar Cell Wastewater	
Component	Result	Component	Result
Effluent copper	< 0.05 mg/L	Effluent copper	< 0.05 mg/L
Effluent peroxide	ND–20 mg/L	Effluent cadmium	< 0.01 mg/L
Slurry solids	pass through	Effluent oxidizer	ND–50 mg/L
TOC	5–50 mg/L	Thiourea	pass through
Effluent pH	2.0–3.5	Effluent pH	4.0–5.5

generation acid with sodium hydroxide also precipitates the copper and other metals as metal hydroxide solids. More equipment is needed to filter the treated wastewater, leaving a solid or semisolid metal hydroxide filter cake that needs to be handled in an environmentally responsible manner. In addition, skilled labor is required on-site to ensure all these operations are effectively performed. Unlike in the service exchange model, resin quality and replacement, system maintenance, and overall upkeep are the responsibility of the on-site system owner.

Waste filter cake often meets the definition of the Resource Conservation and Recovery Act (RCRA) hazardous waste under U.S. Environmental Protection Agency (EPA) regulations, and must be disposed of in a hazardous waste landfill to comply with those regulations. Alternately, metal-rich filter solids may be acceptable by metal recovery facilities if they meet certain requirements.

Summary and Conclusions

Table B shows typical effluent results for CuCMP and solar cell wastewater when treated in a copper-removal treatment system. Oxidizers and metals are effectively treated and removed with little or no change in organics (TOC and thiourea) since most organics in these wastewaters are not well adsorbed by activated carbon.

One key benefit of using a copper-removal approach such as discussed is that abrasive slurry solids used during CuCMP do not need to be removed before treatment. With conventional precipitation methods, metal hydroxides and abrasive solids are intermixed

in the treatment sludge, making it more difficult to cleanly remove and recover the metals. An IX resin-based copper-removal system favors metal recovery so that, ultimately, no hazardous waste and no environmental liability remain for the generator. This is a more sustainable, “greener” treatment process compared to precipitation-based systems in which solid wastes are mixed with other wastes, making them more likely to require disposal in hazardous waste landfills.

Catalytic activated carbon is clean, simple, effective, and rapidly decomposes hydrogen peroxide and other oxidizers in microelectronics manufacturing wastewater, especially when compared to treatment using chemical reducing agents such as sodium bisulfite. Unlike chemical treatment, catalytic carbon treatment adds no TDS to the treated water and is self-adjusting to varying oxidizer influent concentrations that are inherent in any manufacturing schedule. The ability of catalytic activated carbon to remove oxidizers may make it more broadly applicable to other waste streams in addition to those discussed in this article.

Users of a copper-removal system may use service exchange of spent IX resins and catalytic carbon tanks, or opt for on-site regeneration and tank handling. When selecting the appropriate treatment approach, factors to consider include available space, labor resources, capital, and operating costs, ease of use, treatment capacity flexibility, resource recovery and recycling, hazardous waste handling, and decisions concerning span of control.

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Endnotes

^AEvoqua Water Technologies LLC, Warrendale, PA, is the developer of the copper-removal CuCMP wastewater treatment technology discussed in the article.

^BCopper Select™ is the trademarked copper-removal treatment system owned by Evoqua Water Technologies LLC. It removes copper prior to particle flocculation and precipitation. In the article, this process is referred to as the "copper-removal" treatment or technology.



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