

Copper CMP treatment using the Copper Select™ process

Michael W. Wismer & Richard E. Woodling, USFilter, Milpitas, CA, USA

ABSTRACT

The Copper Select™ process is being used at many semiconductor Fabs around the world to successfully treat copper-bearing CMP wastewaters. The patented process removes copper from wastewater without removing the CMP slurry particles. Studies have shown the process to be very successful with most commercially available copper slurry formulations.

Introduction

Advanced semiconductor device technology has driven several major process changes in the past few years. These include 300mm wafer platforms and the use of copper as the interconnect conductor. Prior interconnect technology had been based upon the use of aluminum and tungsten conductors for multilevel metal interconnects.

As a result, the industry must now treat wastewater generated by the various processes associated with the use of copper. Classical technology, such as precipitation and electrowinning, will provide an acceptable treatment method for most streams. However, precipitation technology generates a hazardous waste, copper hydroxide sludge, which must be hauled off to a permitted hazardous waste facility for treatment or disposal. Electrowinning, while viable for higher concentration waste streams, is less useful when copper concentrations are below 100–200 ppm, or when suspended solids are present.

USFilter has developed several methods for treating copper CMP wastewater. These include precipitation/clarification, CMP solids removal by microfiltration followed by regenerable ion exchange, and the patented “Copper Select™” process [1, 2]. This paper discusses the development and application of the Copper Select™ process treating copper-bearing CMP wastewaters.

Wastewater description

The majority of the copper CMP wastewaters produced have similar typical characteristics. These

TABLE 1: TYPICAL PROPERTIES OF COPPER CMP WASTEWATER

Component	Concentration (mg/l)
Dissolved copper	5–100
H ₂ O ₂	50–1000
Total solids	500–5000
Organic chelates	10–50
Total organic carbon	10–100
Alkyl/aryl triazole antitarnish	50–200

characteristics are presented in Table 1.

These ranges are representative of what is found typically at the wastewater liftstation or bulk collection tank where equalization has occurred. The higher concentrations are more representative of CMP tools with water recycling divert valves. Most wastewaters are characterized by total suspended solids (TSS) and total dissolved solids (TDS). Newer slurry formulations contain particles with sizes measured in the nanometer versus micrometer range. Standard testing methods for wastewaters typically use a 0.45-micrometer absolute filter for determining TSS. Particles retained by the filter are considered TSS and particles passing through the filter are classified as TDS. For this reason, we have used total solids (TS), which measures both TSS and TDS. The sample is placed in an oven at 110°C until dryness is obtained, after which the residual solids are weighed. Caution is taken not to burn organic components.

Copper Select™ process

The Copper Select™ process treats raw slurry wastewater by removing the dissolved copper without the need for solids removal or chemical addition other than slight pH adjustments. The pH is first adjusted to maximize the copper removal efficiency while simultaneously maximizing the resin capacity for copper. After pH adjustment is complete, removal of hydrogen peroxide is accomplished. Activated carbon is used to catalytically decompose the hydrogen peroxide to water and oxygen and achieves high removal efficiency of the hydrogen peroxide. The oxygen produced is vented to atmosphere. The peroxide-free

copper and slurry-bearing solution is then treated with a copper-selective ion exchange resin. The dissolved copper is removed without significant fouling to the ion exchange resin. The resin, once it has reached its copper-loading capacity, is sent offsite for regeneration using specialized regeneration processes. The system can be designed as a point-of-use treatment (POU) system in the sub-fab area of the facility to treat a small number of tools, or placed in the central utilities building (CUB) to treat an entire line of copper CMP tools. Capacities of three to 500 gallons per minute are easily achieved. As will be shown later in this paper, the process is also very robust and applicable to many slurry chemistries.

The patented Copper Select™ process has been previously described and was the subject of a Sematech funded study at a Motorola site generating copper CMP wastewater [2]. These studies showed Copper Select™ to be very effective at removing copper with minimal or no retention of CMP particles. Furthermore, they were able to discern that all of the copper in the waste water they tested was dissolved and not chemically or physically attached to the CMP particle. Similar verification has also been reported in a microfiltration/diafiltration process [3].

With the initial work in hand, USFilter began a longer-term laboratory based study. The goal of the laboratory studies was to better understand the performance of the Copper Select™ process with additives that could be found in CMP slurries. The initial testing was focused on the solution pH versus resin capacity. Next, we looked at the pH versus chelates added to the solution and how this affected copper loading on the ion

exchange resin. In addition, we examined copper and copper complex solubility versus solution pH. The addition of other compounds such as surfactants and wetting agents was also examined. Finally, the hydrogen peroxide destruction efficiency versus common additives was tested.

pH effect on resin capacity

Initial studies of the Copper Select™ process indicated that copper precipitated at a high pH value of 6.2-7.4 [1]. Our goal was to maximize the ion exchange resin capacity while minimizing precipitation of copper or a copper complex. The resin capacity for copper is directly related to the solution pH.

The testing of the resin capacity was conducted using a synthetic sample of the typical wastewater with the exclusion of the CMP slurry solids. The standard solution contained citric acid and an aryl triazole at greater than 100 mg/l each. Alkyl and aryl triazoles are typically used as anti-tarnish for the copper surface. The copper concentration of the standard solution

was approximately 40 mg/l. The solution was adjusted to the desired pH using sulfuric acid and sodium hydroxide. The system was operated at an empty bed contact time (EBCT) of three minutes. Table 2 lists the results we obtained from this testing.

These results are presented in pounds of copper per cubic foot of resin. It is clear that the system has to be operated above the pH of 1.5. Below this pH, the resin is essentially being regenerated. Operation at a pH of 3.5 shows a further increase in capacity over pH 3.0. These results are within expectations of typical ion exchange resins with chelating functionality.

pH versus copper and copper complex precipitation

We then focused on the possible precipitation of copper and copper complexes relative to the solution pH. It has been published in the literature that copper triazole complexes actually precipitate on and immediately following the CMP tool [4]. If copper precipitates during the wastewater treatment process, the larger solids would cause high differential pressures and channeling in both the activated carbon and ion exchange beds, rendering them ineffective. High levels of precipitate could completely block off the bed.

Standard solutions were prepared using 500 mg/l of an aryl triazole and 100 mg/l of copper sulfate. These solutions were prepared at an initial pH

of 2.0. The solutions were then raised to a higher pH value and allowed to stand overnight. A sample of the solution was then taken and analyzed for both copper and the aromatic triazole. The results of these studies are presented in Table 3. Synthetic solutions were prepared by combining equal volumes of solutions containing 200 ppm copper and 1000 ppm aryl triazole solutions at 4.0 pH. The combined solution had an ambient pH of 3.26 and immediately turned an olive green color, which intensified as the pH was raised. The strongest color change was observed at a pH of 3.45. All color disappears at a pH of 2.7. Complex formation is hindered due to the protonation of the triazole, which is responsible for the color changes observed.

The concentration levels shown in Table 3 are the levels of the species remaining in solution after pH adjustment. Triazole levels were monitored by UV absorption and a standardized curve. Copper levels were monitored using ICP-MS. In the pH region of 2.5 to 3.0, about 60% of the copper was precipitated. By pH of 4.0, 95% of the copper was precipitated. Previous reports have defined the copper aryl triazole complex as a 1:1 complex [5]. These results are based on examination of aryl triazoles on copper metal surfaces. Our results imply a 1:2 ratio in solution.

A second solution was prepared as above but spiked with citric acid to a concentration of 500 mg/l. Citric acid is a common additive to copper CMP slurries. Typically, it is considered a chelating agent with a binding constant $\log K_1$ of 4.35 for the CuL complex and $\log K_1$ of 14.2 for the CuL_2 complex for copper [6]. pH adjustment of the solution containing citric acid along with the aryl triazole and copper are presented in Table 4. In this circumstance we observed very little or no loss of the aryl triazole or copper. Furthermore, no green copper triazole complex color was observed as before. It is suspected that the citrate retarded complexation of the copper with the aryl triazole.

These results show that when citric acid is abundant in the wastewater, precipitation is of no concern. However, if citric acid, or other strong solubilizing chelate, is not present in the slurry formulation, precipitation should be of great concern. Testing should be considered if an alternative chelation agent is used.

TABLE 2: SOLUTION pH VERSUS COPPER CAPACITY OF RESIN

pH	Resin capacity at breakthrough (lbs/ft ³)
1.5	0.26
3.0	2.52
3.5	2.80

TABLE 3: PRECIPITATION OF COPPER TRIAZOLE VERSUS pH

Test condition	Cu ppm	Triazole ppm	Appearance
Cu+triazole pH 2.0	102	530	Colorless
Cu+triazole pH 2.5	100	530	Colorless
Cu+triazole pH 3.0	41.3	260	Purple/blue solids, green solution
Cu+triazole pH 3.5	22.1	195	Purple/blue solids, green solution
Cu+triazole pH 4.0	5.1	151	Purple/blue solids, green solution

TABLE 4: EFFECT OF CITRIC ACID ON PRECIPITATION OF COPPER TRIAZOLE

Test condition	Cu ppm	Triazole ppm	Appearance
Cu+triazole+citric pH 2.0	102	535	Colorless
Cu+triazole+citric pH 2.5	104	530	Colorless
Cu+triazole+citric pH 3.0	102	530	Light sky blue
Cu+triazole+citric pH 3.5	103	525	Bright sky blue
Cu+triazole+citric pH 4.0	102	520	Greenish blue

Effect of chelates on the Copper Select™ process

We initially ran a standard solution as a baseline for the process comparison. The solution contained no chelates and was spiked to approximately 35 ppm of copper. The results of this experiment are graphed in Figure 1. The effluent concentration of copper is plotted versus the empty bed volume (EBV). In

small-column testing, it is typical to see substantially reduced overall capacities. This is due, in part, to small column-wall effects and lack of good liquid distribution to the top of the packed column. Another contributor is the resin particle diameter to column diameter ratio. While the results are good for direct comparison, these results are substantially lower than one would expect in a full-scale system.

Breakthrough for these experiments was chosen as 30 mg/l of copper since this is typical of the lead column breakthrough point in a lead/lag dual column system. With a baseline in hand we looked at oxygen and nitrogen-based chelates. These are composed of organic hydroxy-acids, α , ω -diacids, amines, diamines and amine/oxygen-based chelates. Solutions were prepared with chelate concentrations of 170 mg/l, which is greater than 10 times the concentrations found in many CMP wastewaters. The purpose of operating at these high concentrations was to ensure that we would observe any long-term changes influenced by the presence of chelate compounds. The results for these tests are shown in Figure 2. We observed a good correlation between the conditional formation constant and the volume treated prior to breakthrough with an R^2 value of 0.85.

The formation constant, K_f , is defined by the following equation:



The conditional formation constant, K'_f , is the formation constant found at various pH values adjusted to correct for the test pH. This corrects the formation constant for the chelate in the acid, or protonated form, which is unavailable or minimally available for chelation. With polyprotic acids and bases, multiple formation constants, K_{fx} , exist. Likewise, multiple conditional formation constants exist that have been considered in the above calculations.

The activated carbon system was examined for interactions with organic chelates. Organic compounds are known to load on activated carbon. The rate of loading is dependent upon the concentration and solubility of the organic species. Organic loading could be related to the loss of catalytic activity as will be shown later. The chelates were again prepared in a solution concentration of 170 mg/l. This is 10 times or greater than the typical concentrations observed in copper CMP waste streams. The concentrations were raised to this magnitude to ensure that we would observe any detrimental long-term effect caused by these components. Figure 3 presents the results of the total organic carbon (TOC) and breakthrough for the activated carbon effluent. The activated

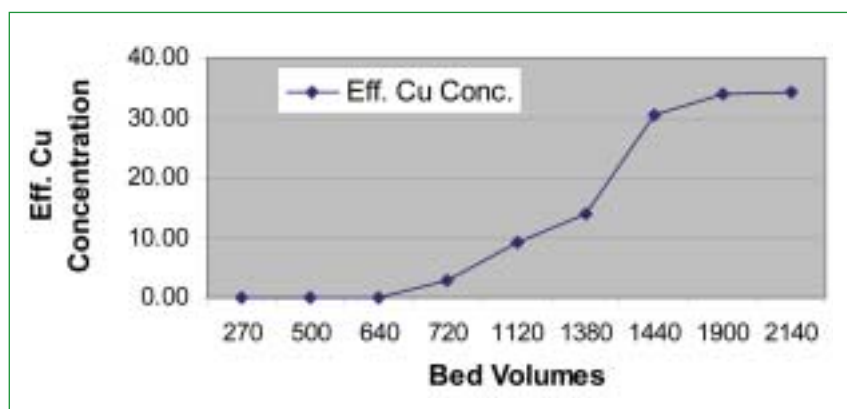


Figure 1. Baseline Resin Capacity Testing.

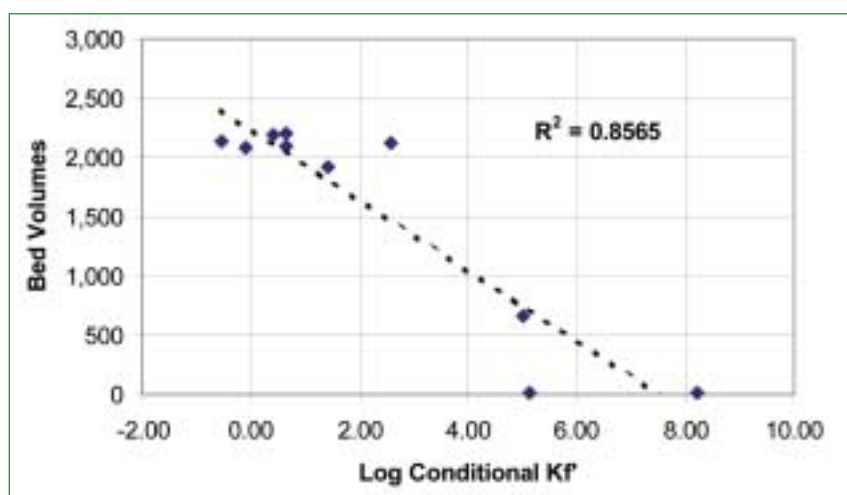


Figure 2. Chelate Conditional Formation Constant's effect on Resin Capacity.

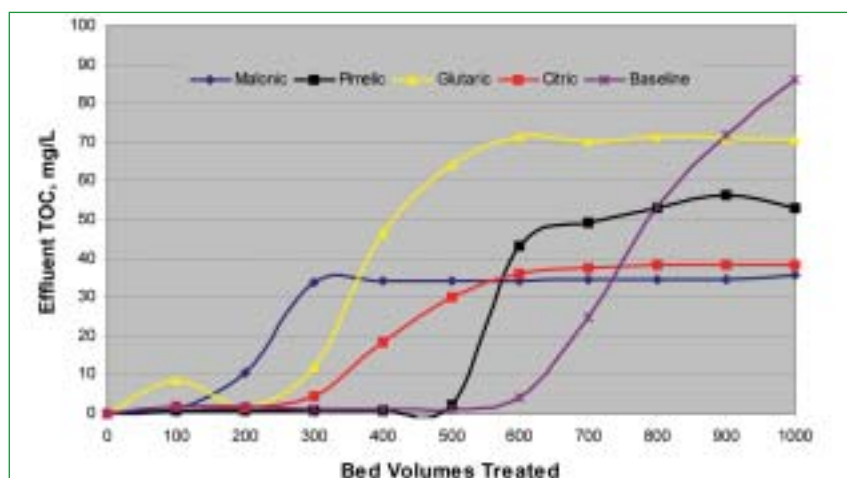


Figure 3. Organic Chelate Effect on Activated Carbon.

carbon was challenged with a solution containing the chelating organic compound while monitoring the effluent. Starting solutions were prepared based on compound concentration instead of TOC values; therefore, each solution had different starting TOC values. TOC that does not pass through the activated carbon is chemisorbed onto the carbon. The baseline solution contained aryl triazole as the TOC source. In all cases, the TOC breakthrough occurred before the baseline breakthrough. This is observed by examining the inflection point in the graph prior to increased TOC values.

Breakthrough sooner than baseline implies less interaction of the organic component with activated carbon than the baseline solution. A breakthrough occurring later than the baseline solution implies greater interaction of the organic component with the activated carbon. From these results we concluded that chelates did not load at a level as high as the baseline solution. To fully understand if chelates were affecting the activated carbon process, we looked at the hydrogen peroxide catalytic destruction efficiency. Chelating agents were added to a solution containing copper and hydrogen peroxide. The breakthrough point of the hydrogen peroxide was monitored and compared to a baseline solution containing copper and aryl triazole. The results from this experiment are presented in Figure 4. It is important to note that these small-bed experiments and observed breakthrough points are not indicative of full-scale systems. Typical carbon bed life ranges from 12,000 to 20,000 bed volumes in full-scale systems. The range is, of course, dependent upon additives in the solution and environmental conditions.

Effects of surfactants on Copper Select™ process

The portion of our experimentation that focused on surfactants looked at the effect on the ion exchange resin, as well as the activated carbon used for the destruction of hydrogen peroxide.

Testing on the ion exchange resin was conducted in a similar fashion as the chelate studies described above. The same baseline was used for the small-column testing. Trials were repeated several times to ensure consistency. We chose surfactants for testing that included representatives from different

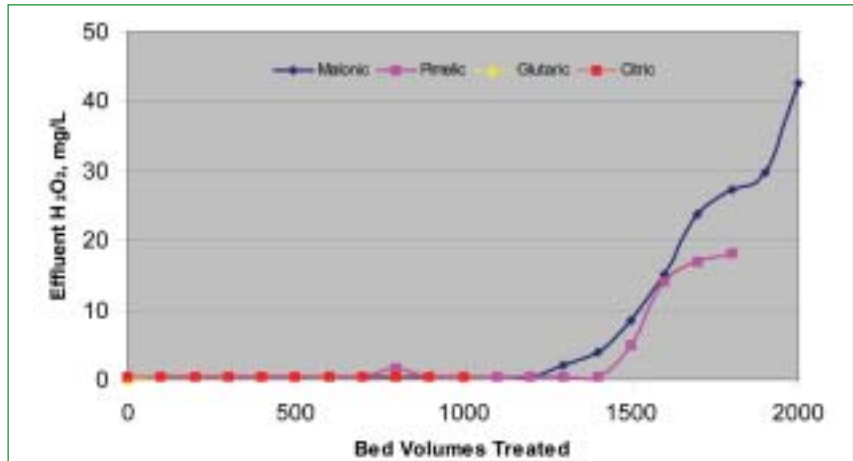


Figure 4. Organic Chelate Effect on Hydrogen Peroxide Destruction

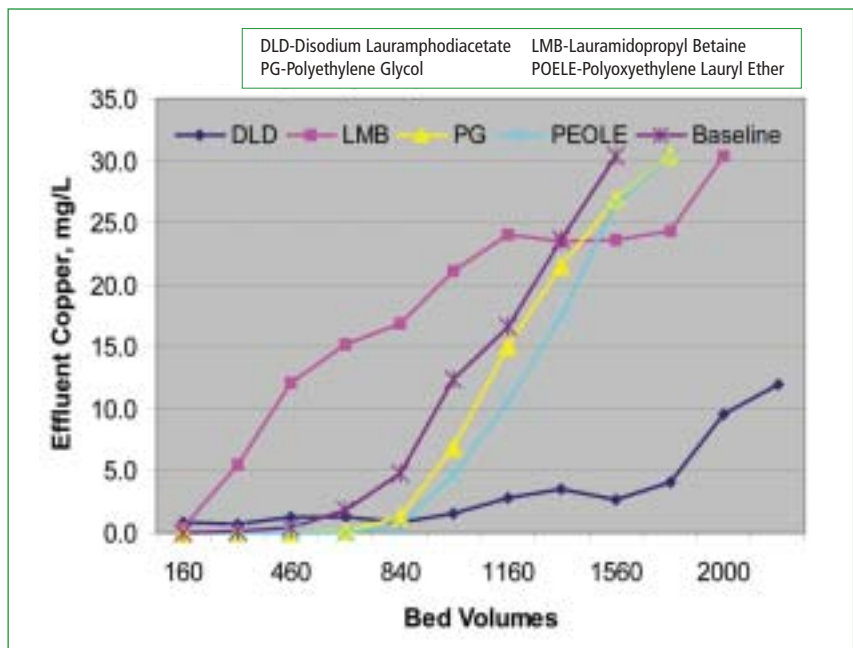


Figure 5. Surfactant Effect on Ion Exchange Resin Capacity

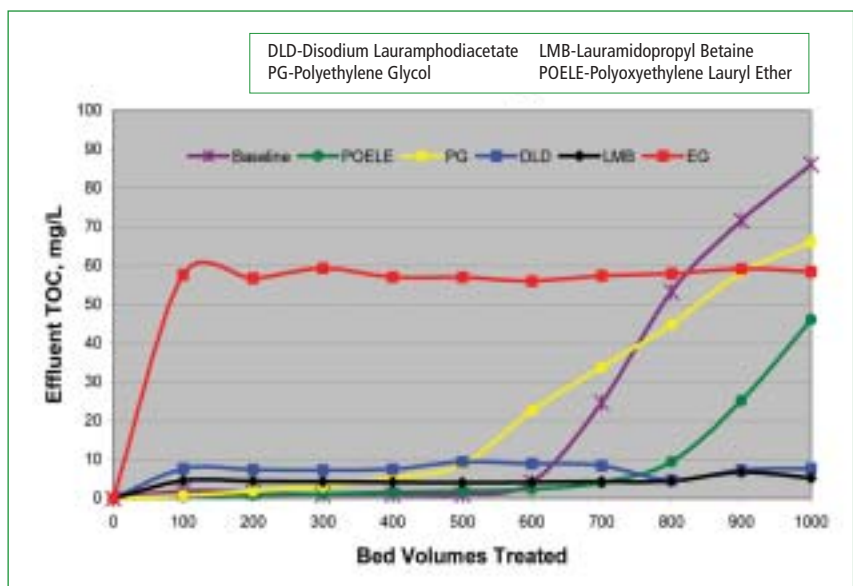


Figure 6. Surfactant Breakthrough on Activated Carbon as Measured by Effluent TOC.

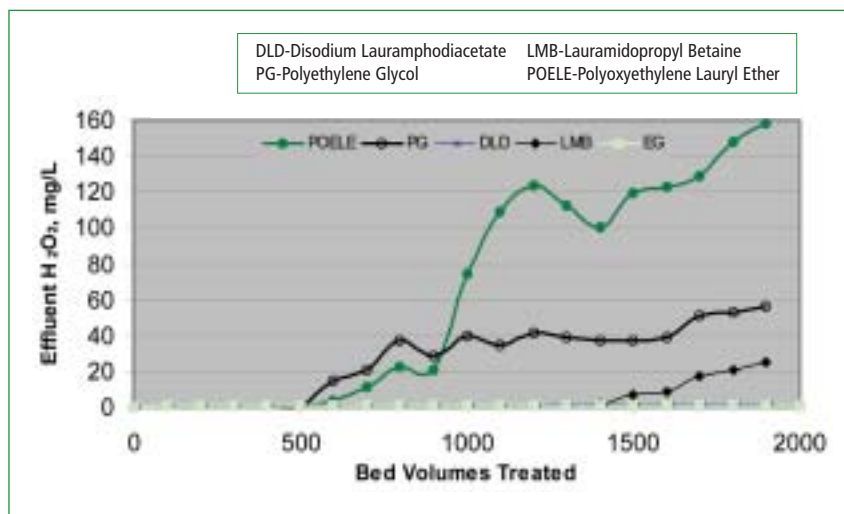


Figure 7. Surfactant Effect on Hydrogen Peroxide Destruction.

chemical families used in typical CMP slurry formulations. The results in Figure 5 illustrate the bed volumes treated prior to breakthrough. Breakthrough is considered to be the point at which the effluent copper concentration reaches 30 mg/l.

The LMB has a constant bleed of copper, which appears to begin around bed volume 160. All other surfactants had no detrimental effect on the ion exchange. An unexpected result is a slight improvement in the resin capacity.

The effect of surfactant on the activated carbon was also examined (see Figure 6). First, as with the chelates, a study was completed that examined the effluent TOC of the solution after treatment with activated carbon. TOC not passing through the column is chemisorbed onto the carbon. The smaller molecules such as ethylene glycol (EG) are seen to breakthrough at a rate faster than the baseline aryl triazole solution. Larger molecules, such as polyoxyethylene lauryl ether, take much longer until full breakthrough. This is expected based on the octanol/water partition coefficient values of these molecules. The octanol/water partition coefficient is used to predict adsorption of organic

molecules on hydrophobic media such as activated carbon.

The carbon efficiency to destroy hydrogen peroxide was then investigated. In Figure 7, the effluent hydrogen peroxide is plotted versus the bed volumes treated. All solutions were spiked with copper, hydrogen peroxide and surfactant. We were unable to make a direct correlation between the TOC breakthrough and the loss in destruction efficiency of the hydrogen peroxide. We examined the octanol/water partition coefficient, and the mass loaded on the carbon but were unable to see a statistical correlation. However, a general trend was noticed that implies that the hydrogen peroxide destruction efficiency drops as the activated carbon capacity for some molecules is achieved.

Conclusion

Studies have been completed on the Copper Select™ process, showing it to be a very robust system based on use of typical CMP chemicals. The control of the pH of the solution prior to activated carbon and ion exchange is important for both capacity and precipitation purposes. A copper aryl triazole complex precipitates if the solution does

not contain a strong chelator as the pH increases. The conditional formation constant can be used to predict the operating capacity trend of the ion exchange resin. No detrimental effects of chelates are observed on the ion exchange or activated carbon system in the concentrations we tested. Most surfactants have either no effect or a positive effect on the ion exchange resin capacity. Finally, no physical property correlation is observed between a variety of surfactants and the activated carbon process.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Mr. Jim Day for laboratory assistance during the course of these studies.

REFERENCES

- [1] United States Patent Number US6,346,195 B1 and 6,818,129; Patent Pending in China, European Patent issued; Patent issued in Israel and Mexico.
- [2] Riley, C.; Mendicino, L.; Brown, P.; Filson, J.; "Copper Removal from Chemical Mechanical Polishing" presented at The Electrochemical Society, 197th Meeting, Toronto, Canada.
- [3] Woodling, Richard; "Treatment of Copper CMP Wastewater", Semiconductor Fabtech, 14th Edition, pp 69-72.
- [4] Banerjee, G.; So, J.; Mikkola, B.; "Simultaneous Optimization of Electroplating and CMP for Copper Processes"; Solid State Technology, November, 2001.
- [5] Koeck, D.C.; "Microscopic Studies of Friction and Wear at the Benzotriazole/Copper Interface"; Tribology Letters, Vol. 14, #4, pp 261-268.
- [6] Lang's Handbook of Chemistry, 10th edition.

ABOUT THE AUTHORS

Richard Woodling is the Technical Director of the USFilter Microelectronics Group focusing on wastewater treatment and water-recycling methods. He was also a visiting scientist at IBM Almaden Research Center. He received his PhD in chemistry from the University of California, Riverside and a Bachelor in chemistry from the University of California Santa Barbara.

Michael Wismer is the Director of EH&S and Technical Services for USFilter Recovery Services, Inc., Roseville, MN, a RCRA Part B permitted TSDF. Employed by USFilter since 1988, he manages environmental compliance, R&D, and laboratory services for the company and provides technical support to customers. He received a B.S. in chemistry from Purdue University.

ENQUIRIES

Richard Woodling
USFilter
960 Ames Ave
Milpitas
CA 95035
USA

Tel: +1 (408) 935-6266
E-mail: woodlingr@usfilter.com