A Process for Efficient Treatment of Cu CMP Wastewater

Dustin James, Ph.D., Deon Campbell, Jereme Francis, Thuy Nguyen, and Daun Brady Koch Microelectronic Service Co. Inc. – 5/1/2000
Semiconductor International

A process for treating Cu CMP wastewater was conceived, designed, piloted and commercialized at a major semiconductor manufacturer's site. The following process units were used: pre-treatment chemistry, microfiltration and ion exchange. A design of experiment (DOE) series was conducted to determine which of the following experimental variables were critical: pH, inlet Cu concentration, inlet TSS concentration, flow and slurry type. It was found that inlet Cu concentration was most important in determining the Cu concentration in the MF product. None of the independent variables was statistically significant in determining the Cu concentration in the ion exchange product. The mean + 3 sigma total Cu concentration in the ion exchange product was 1.12 ppm, well below the target mean + 3 sigma value of 1.50 ppm total Cu. The process was commercialized and has been operating without any membrane cleaning cycles. Performance data from continuing operations will be presented.

At a Glance

The introduction of copper has meant enhanced system speed but has also faced challenges in various areas from copper contamination and abatement issues in disposing of copper silicides to CMP waste products. Cu CMP wastewater typically contains from 5 to 100 ppm soluble Cu^{+2} and large amounts of suspended silica and/or alumina particles. Federal regulations limit soluble copper in rivers, streams and groundwater to 1.50 ppm. This article describes a process for treating Cu CMP wastewater.

Introduction

When metallic copper (Cu) layers are introduced into semiconductor circuits, one method of reducing topography interferences with subsequent imagery is to perform a chemical mechanical planarization (CMP) step. In the Cu CMP process, an aqueous slurry of silica and/or alumina particles is used in conjunction with a rotating pad to polish the surface of the Cu layer, in much the same way as "wet sanding" is used to form a very smooth painted surface on automobiles. Oxidizing chemicals are added to the Cu CMP slurry so that metallic Cu is converted to soluble Cu^{+2}. This is the "chemical" part of the CMP process. The wastewater produced as a result of the Cu CMP process typically contains from 5 to 100 ppm soluble Cu^{+2}. Large amounts of suspended silica and/or alumina particles also are present, sometimes with solid metallic Cu particles if the oxidation chemistry is not completely successful.

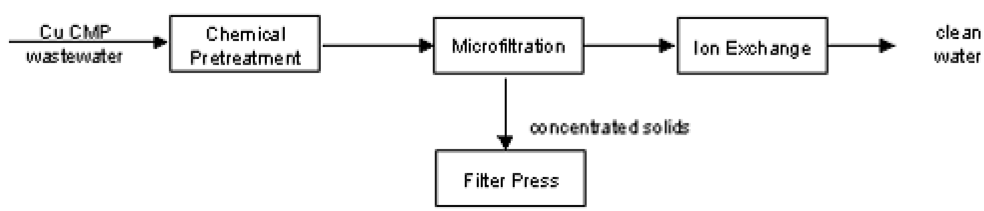


Figure 1

The federal limitation on soluble Cu^{+2} in water discharged to rivers, streams and groundwater is 1.50 ppm. Some state and European limitations are more stringent. At the present time there is no federal limit on soluble Cu content of solid wastes; however, some states, such as California, do have such limits.

An additional problem is that many localities have regulations concerning the total suspended solids (TSS) content of discharged water. Therefore, in addition to removing Cu, the treatment process should include a TSS reduction step. This step also is necessary to reduce the cost of operation for the copper removal step.

Analytical Results of Cu CMP DOE Study

Exp. #	A pH	B Inlet [Cu] ppm	C Inlet TSS, ppm	D Inlet Flow, gpm	E Slurry Type	Response Variable System Effluent [Cu] ppm
1	High	3.19	129	Low	A	0.01
2	High	508	458	High	A	35.40
3	Low	133	8,630	Low	A	1.16
4	Low	3.57	6,030	High	A	0.40
5	Low	142	320	Low	A	0.35
6	Center	69.9	10,900	Center	B	1.45
7	Low	13.2	180	Low	B	0.19
8	Low	140	102	High	B	7.60
9	High	17.9	18,200	High	B	0.21
10	High	166	15,500	Low	B	0.04
11	Center	62.8	8,080	Center	B	0.43

Table 2

DOE for Cu CMP Pilot Operation

Variables			
B ppm	C TSS, ppm	D Inlet, gpm	E slurry type
10	500	Low	A
120	500	High	A
120	20,000	Low	A
10	20,000	High	A
120	20,000	Low	A
65	10,250	Center	B
10	500	Low	B
120	500	High	B
10	20,000	High	B
120	20,000	Low	B
65	10,250	Center	B

capable of meeting the 1.50 ppm Cu discharge limitation. At the same time, the filter cake produced from removal of the suspended solids needed to have minimal soluble Cu content. A process that met the required discharge specifications was designed, piloted and commercialized at the customer's site.

Process design

A process was designed that would meet the criteria for removing soluble copper and yielding product water with low TSS. The process flow diagram (PFD) is shown in Figure 1. The Cu CMP wastewater first was passed through a chemical pretreatment process where proprietary chemistry took place, including pH adjustment and oxidant neutralization. The chemically pretreated stream then was treated using a cross-flow microfilter to remove TSS. The concentrated solids were sent to a filter press for dewatering. The product water was pumped through the ion exchange bottle, where the soluble copper was removed to achieve a concentration below the discharge limit. The clean water then was discharged to the appropriate facility.

A pilot unit was configured as shown in the PFD for operation at the customer site.

In carrying out process development optimization, one important independent variable was retention time or residence time – i.e. in a continuous process, the amount of reaction time that was allowed for each reaction step. The retention time was determined both by the flow rate through the system and the volume of the reaction vessels. For a reaction tank with a volume of 100 gallons and a flow rate of 10 gpm, the average retention time was 10 min. If the flow rate were increased to 20 gpm, the retention time would be 5 min.

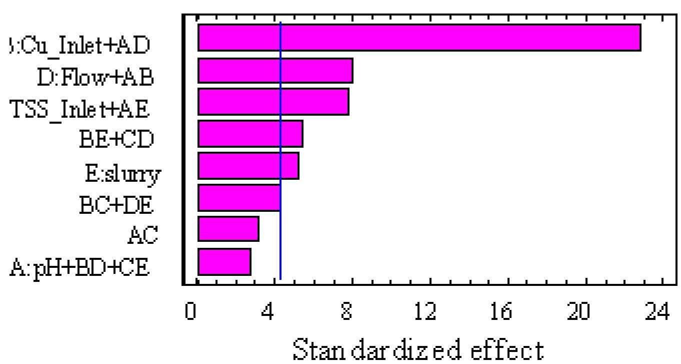


Fig. 2. Standardized Pareto Chart for MFProdCu

Design of experiment (DOE)

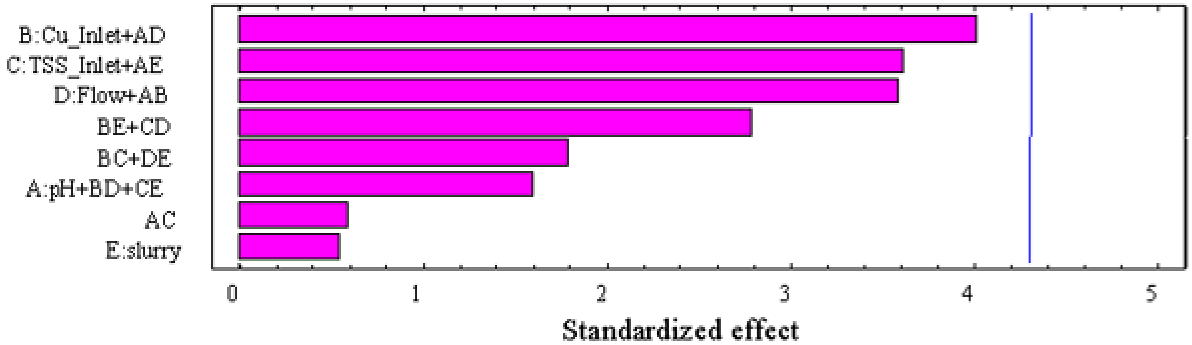


Fig. 3. Standardized Pareto Chart for IXProdCu

Design of experiment (DOE) is a method of using statistics to determine the best conditions for conducting processes[1]. Several computer programs exist that are helpful in DOE[2]. These programs contain useful features that allow one to construct the DOE, analyze the results and display the analyses in graphical formats that can be pasted into reports.

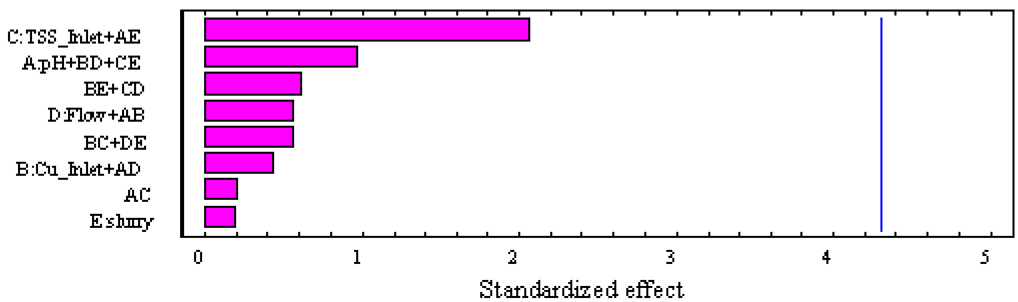


Fig. 4. Standardardized Pareto Chart for TSSMFConc

Initially it was thought that several independent variables could be important in determining the best operating conditions for a Cu CMP wastewater treatment process. These variables were pH, inlet Cu concentration, inlet TSS concentration, flow rate (retention time) and slurry type. The variable values for the design of experiment (DOE) series carried out at the customer site are shown in Table 1.

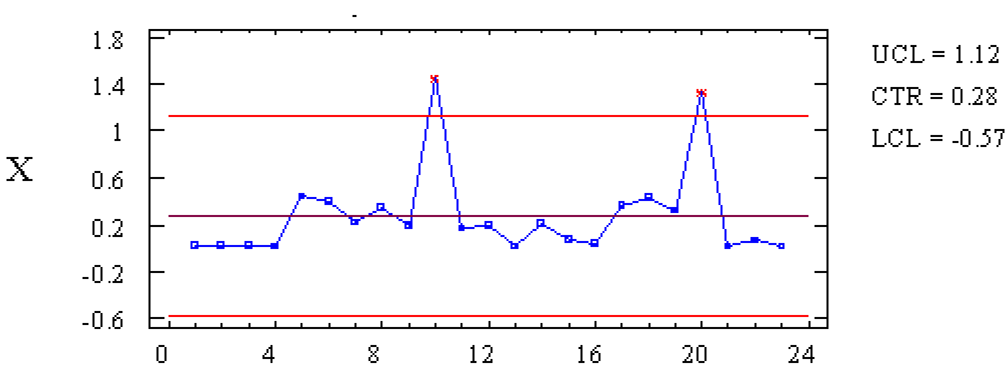


Fig. 5. X Chart for IX_Prod_Cu_Conc

Since there are five variables, a full factorial design would have required 32 experiments plus center points. Due to time constraints the number of experiments was reduced to 8 (quarter-fractional) with two center points and one duplicate. The 11 experiments were completed in about two weeks.

The pH was varied due to the differing solubility of Cu compounds at differing pH values. The pH could potentially affect the performance of the pretreatment chemistry, performance of the membrane and performance of the ion exchange system. Preliminary work in the lab narrowed the pH window to a proprietary range that was easily studied in a DOE.

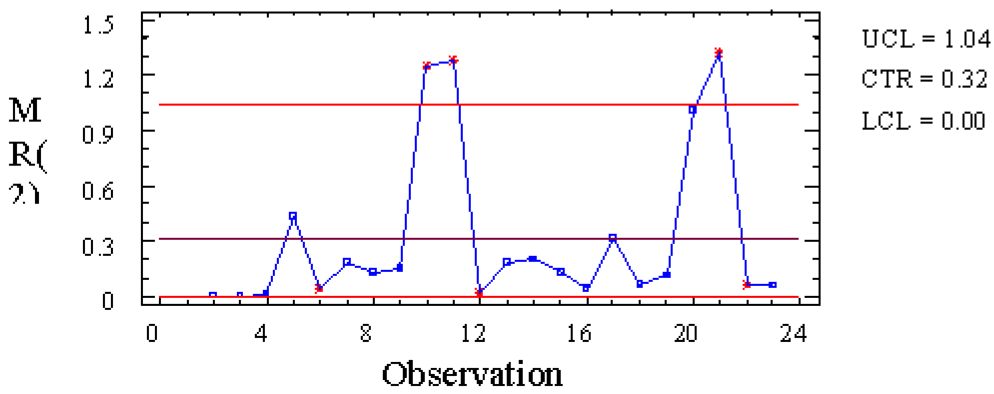


Fig. 6. MR(2) Chart for IX_Prod_Cu_Conc

It was important to determine if the system could handle the wide variation of expected Cu concentrations in the wastewater. Therefore the DOE was constructed so that the highest expected Cu concentration in the inlet was set as one of the independent variable values, at 120 ppm. The low setting of the inlet Cu concentration was 10 ppm.

Since removal of the solids via microfiltration was a key unit operation, it was necessary to challenge the system with the highest expected TSS content. The high value of the inlet TSS independent variable was therefore set at 20,000 ppm, and the low value was set at 500 ppm.

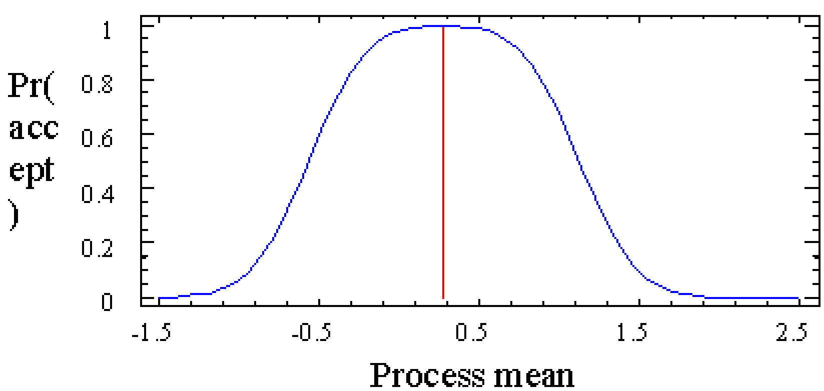
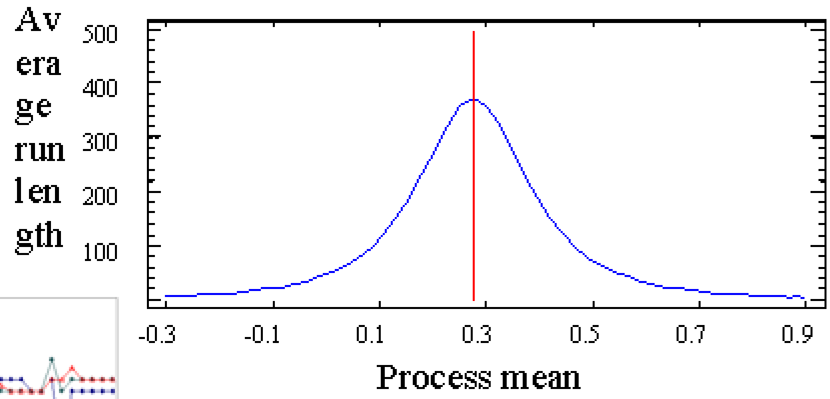


Fig. 7. OC Curve for X

To determine if retention time was an important variable the flow rate was set at "high" and "low" values. This flow rate was maintained throughout the system, including the ion exchange beds. As a result, the empty bed contact time was varied at the same time as the retention time.

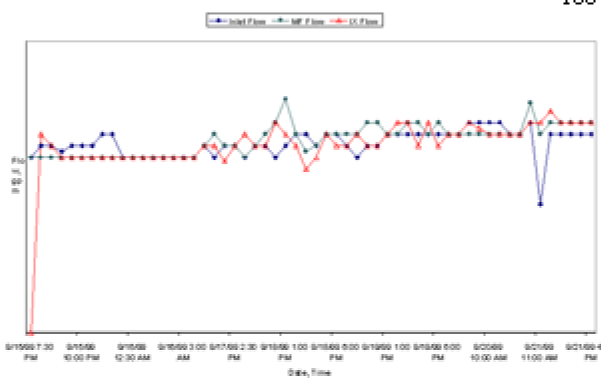
As earlier discussed, slurries could contain alumina, silica or a mixture of both. They also could contain different oxidants and chelants. The customer had settled on two slurry formulations: A and B. In the DOE the slurry type was varied between A and B because it was important to ensure that the wastewater treatment system could handle both formulations.

To achieve the desired concentrations of Cu and TSS in the feed, a base wastewater was analyzed and charged to a feed mix tank. The base wastewater usually contained 10-20 ppm Cu and 100-500 ppm TSS. The mix tank was not well marked, and the volume of base wastewater in the tank had to be estimated. To increase the Cu concentration, known amounts of copper sulfate were added to the mix tank; to increase the TSS concentration, known amounts of concentrated slurry were added. The remainder of the volume in the tank was then made up with clean water. As will be seen in the following section, this method of producing the feed wastewater led to an aggregate experimental error that was quite large.



L Curve

DOE results



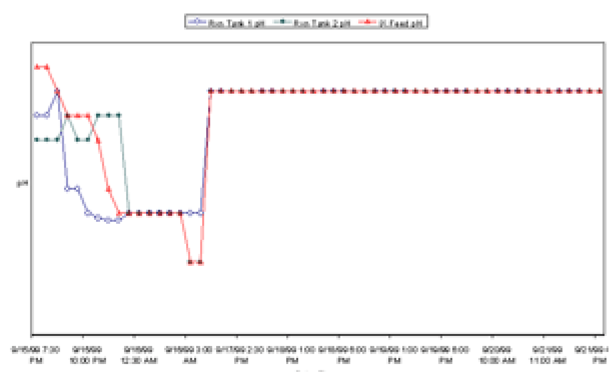
[Click for full size image]

Fig. 9. Cu CMP Pilot Flows-Marathon

the DOE are shown in [Table 2]. These results were obtained by analysis of samples at Columbia Analytical Services Co. (Kelso, Wash.). Analyses of the streams were done at the midpoint and the end of each experiment. However, only the results of the second analysis from each experiment are shown. As discussed above, it was difficult to hit the desired independent variable values with any degree of accuracy. For Experiment 2 an error was made in calculating the amount of copper sulfate to add to the feed tank, leading to the high 508 ppm Cu concentration in the feed for that experiment.

All Cu concentrations were obtained by total Cu analysis, so that both dissolved and precipitated Cu species along with metallic Cu were detected and reported.

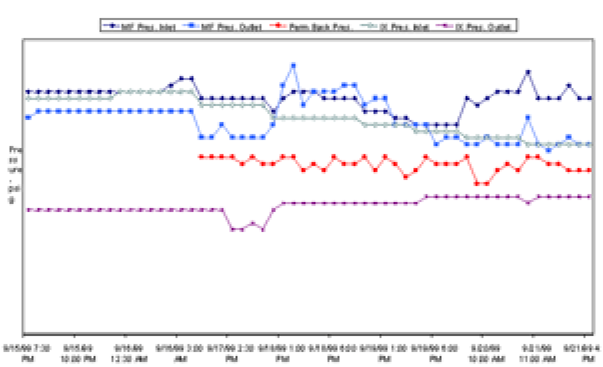
One method of displaying the important independent variables is to use a Pareto chart. The Pareto chart for Cu concentration in the MF Product is shown in [Figure 2]. The Pareto chart shows each of the estimated effects in decreasing order of magnitude. The length of each bar is proportional to the standardized effect, which is the estimated effect divided by its standard error. This is equivalent to computing a t-statistic for each effect. The vertical line can be used to judge which effects are statistically significant. Any bars that extend beyond the line correspond to effects that are statistically significant at the 95.0% confidence level. In this case, five effects are significant.



[Click for full size image]

Fig. 10. Cu CMP Pilot pH Control--Marathon

It can be seen that the most important independent variable for determining the response variable MF Product Cu was a combination of Inlet Cu concentration and the cross term AD, which was a combination of both pH and Inlet Flow Rate. Several other of the most important independent variables also contain cross terms. To determine the value of these cross terms, and perhaps eliminate them from the analysis, more experiments would need to be done. Time constraints did not allow for further study.



[Click for full size image]

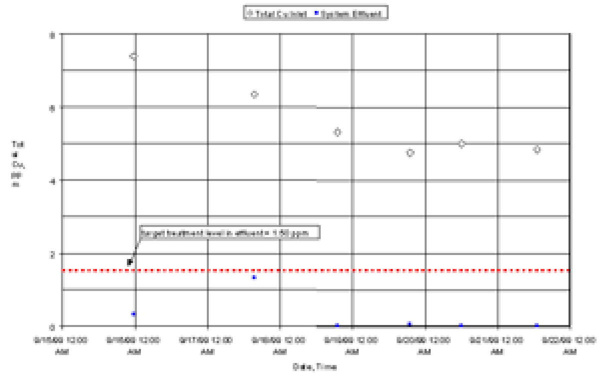
Fig. 11. Cu CMP Pilot Stream Pressures-Marathon

In contrast, there were no statistically important variables for determining the value of the Cu concentration in the IX product (Fig. 3). This was the hoped-for result, since it was desirable that the Cu concentration in the IX product be unaffected by any changes in the feed wastewater.

There also were no statistically important variables for determining the value of the TSS in the MF Concentrate, as shown in Figure 4.

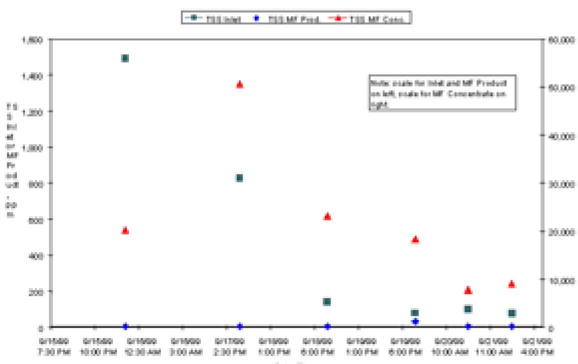
Control charts on IX product Cu concentration

The analytical data from the DOE was used to construct control charts for the IX Product Cu concentration (Fig. 5). Note that 23 data points were plotted, with the calculated mean 0.27 ppm, and the +3 Sigma upper control line (UCL) at 1.12 ppm. When the Cu concentration in a sample was undetectable at the limits of the analytical method, the Cu concentration was set at 0.01 ppm. The two points at 1.45 and 1.33 ppm were considered beyond control limits. A pilot operation consisting of 11 different experiments would not be expected to be in control due to the purposeful variations in the feed to the system. The Cu CMP wastewater treatment system was shown to be fully capable of meeting the discharge limitation imposed by the customer even during this experimental phase.



Click for full size image

Fig. 12. Cu CMP Pilot-Marathon Cu Levels



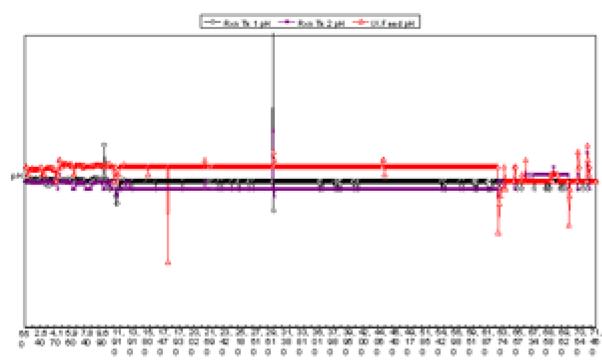
Click for full size image

Fig. 13. Cu CMP Pilot TSS Levels -- Marathon

Figure 6 shows the moving ranges for each of the 23 measurements. Three points were beyond the control limits.

The operating characteristic curve (Fig. 7) shows the probability that the next point plotted on the control chart will remain inside the control limits as a function of the true process mean. It therefore plots the probability that you will not get a signal from the chart, even though the process is not at the assumed center. It is useful in judging the effectiveness of the control chart in detecting drifts in the process away from the target. For example, suppose the true mean moved to 0.6. The probability that the next point plotted on the chart will be within the control limits equals 0.967941.

Figure 8 shows the average run length (ARL) for the selected control chart as a function of the process mean. For example, if the process is actually running at the centerline, the chart would generate an out-of-control signal on average approximately every 370 samples. If the process moved away from the centerline, the ARL would change as shown. This plot could be used to help select an adequate sampling plan to monitor the process.



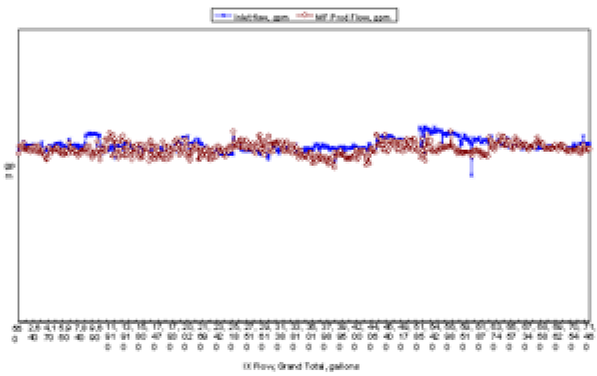
Click for full size image

Fig. 14. pH Control of KMSC Cu CMP Treatment

Ten-day marathon

To prove the long-term viability of the process, a 240-hr marathon was conducted using actual Cu CMP wastewater as the feed to the pilot skid. Figure 9 shows the consistency of flows achieved with the pilot skid.

After initial problems caused by bad pH probes, pH control was very steady throughout the marathon (Fig. 10). Pressures throughout the system also were maintained fairly consistently (Fig. 11).



Click for full size image

Fig. 15. Flow Control of KMSC Cu CMP Treatment System

The Cu concentration in the System Effluent stayed below the specification limit. The analytical data in Figure 12 is from analytical work at the pilot, not from Columbia Analytical.

The microfilter performed very well during the marathon, removing the TSS to acceptable levels without the necessity for a single cleaning cycle (Fig. 13).

Commercialization of the process

Due to the success of the process, it was quickly scaled up to meet the intermediate wastewater treatment goals of the customer. Figure 14 shows the solid and consistent pH control that was achieved with the process.

The flow control was also quite consistent (Fig. 15).

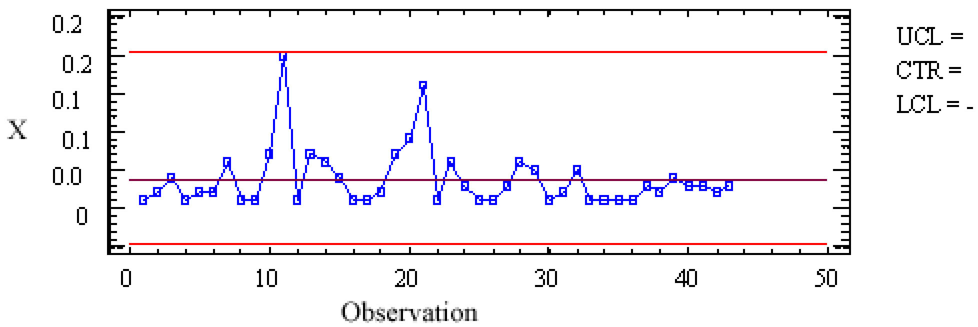


Fig. 16. Chart for CulXProduct

Forty-four samples of System Effluent were taken and analyzed for total Cu content by Columbia Analytical. A control chart was constructed from the data and is shown in Figure 16. The UCL was at 0.20 ppm, well below the 1.50 specification. The center line (mean) is at 0.04 ppm.

The moving ranges chart (Fig. 17) has a UCL of 0.17 ppm, with a center at 0.03 ppm.

Summary

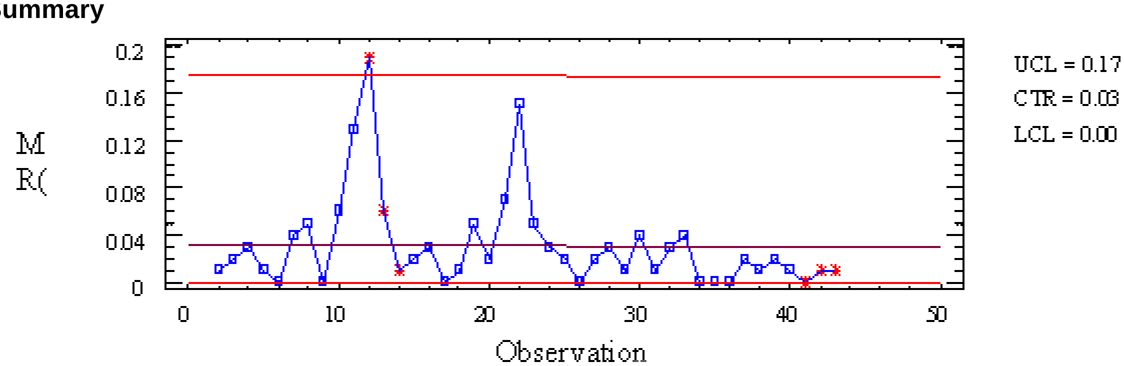


Fig. 17. MR(2) Chart for CulXProduct

The advent of copper metalization in the semiconductor industry requires a new Copper CMP fab wastewater treatment method, robustly designed to accommodate slurry changes, process changes and varying effluent characteristics. The data from the DOE, marathon and continuous operations at KMSC's customer site demonstrate that such a process has been developed and commercialized.

Contact the authors at JamesD@kochind.com.

REFERENCES

1. Box, Hunter, and Hunter, "Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building" John Wiley and Sons, New York, 1978. Douglas C. Montgomery "Design and Analysis of Experiments, 4th Edition" John Wiley and Sons, New York, 1996. Douglas C. Montgomery, Raymond H. Myers "Response Surface Methodology: Process and Product Optimization Using Designed Experiments" John Wiley and Sons, New York, 1995.

2. The following web pages can be consulted for more information: STATGRAPHICS Plus , CARD by S-Matrix, Smart Solutions, DOE by multi-simplex methods

<<< Back | Print