Tests of Iron-Oxide-Coated Sand For Treatment of Plating Rinsewaters

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As discharge limits for metals tighten, alternative technologies. such as adsorption and filtration become increasingly attractive for high-level treatment of metal-bearing wastes. Adsorption onto iron oxides is capable of removing many metals from solution. and, when combined with appropriate regeneration steps, may allow recovery of the metals, reducing or eliminating the need for sludge disposal. In theory, freely suspended iron oxides could be used in a batch treatment process, but it would be difficult to achieve the necessary solid/liquid separation required to meet discharge limits. It would be equally impractical to use iron hydroxides as the media in a filter column, since they would likely form a plug, limiting the flow of water. The following describes a process developed to overcome these problems.

n an effort to eliminate some of the more common problems associated with the treatment of plating wastewater, a process has been developed by which iron oxide can be coated onto sand filter media for the successful treatment of metal etching wastes. The process involves the passage of pH-adjusted wastewater through a column packed with this media, providing filtration of particulate metals and adsorption of soluble metals. Thus, the potential exists for excellent contaminant removal and solid/liquid separation in a single step. In addition, continuously operated packed columns tend to occupy much less space than comparably successful batch systems.

Precipitation & Adsorption Onto Free Ferrihydrite

Copper removal by (1) precipitation and (2) adsorption was evaluated in batch tests. The copper-containing solution was adjusted to the desired pH and mixed for two hr. The pH was then re-measured, and the samples were passed through a filter* with 0.45 μ m pores, acidified and saved for

analysis. The tests were identical, except that iron hydroxide (Fe(OH) $_{\rm s}$) was added to the solution during the adsorption tests.

The Effect

Of Ammonia Concentration

Ammonia-complexed copper-containing wastes are generated in a variety of plating operations. Ammonia (NH₃) is added during bath makeup to prevent copper from precipitating out of the process solution or, as part of an etchant solution, to strip unmasked copper from circuit boards. The formation of complexes interferes with the precipitation processes employed in conventional waste treatment for metals removal.

With this in mind, the influence of ammonia concentration on copper adsorption was also evaluated in batch tests. Concentrated ammonium hydroxide (NH₄OH) was added in increments to a solution containing 10^{3} M iron hydroxide and a 1:10,000 dilution (by volume) of ammoniated copper etchant. The final ammonia concentration ranged from 0.01 to 0.1 M. At each ammonia concentration, pH was adjusted to the target value (8.0 or 10.2). After the samples were mixed for two hr, the final pH and ammonia concentration were measured. The samples were then filtered (0,45 µm pore size) and saved for analysis.

Continuous-Flow Column Tests Of Adsorptive Filtration

Preparing Synthetic Waste water

Three kinds of synthetic wastewater were used in the column tests:

1. Soluble copper solutions for *adsorption* tests were prepared by diluting raw ammoniated copper etching solution 10,000:1 by volume with ammonia and deionized water to yield a final solution containing 0.04M ammonia and 14 mg/Lcopper. Solution pH was adjusted to the target value of 8.0. Copper solutions prepared in this way were completely soluble.

2. Particulate copper solutions for *filtration* tests were prepared by diluting the etching solution as described previously, but without ammonia addition. In these solutions, 97 percent of the copper was present in particulate form.

3. To some of the suspensions containing particulate copper, small doses of anionic polyacrylamide flocculent** were added.

^{*}Millipore Corp., Bedford, MA.

Preparation & Characterization

Of Iron-oxide-coated Sand

The filter media used in most of the experiments was 20-30 mesh Ottawa sand to which a coating of iron oxide had been applied. The iron coating solution was prepared by adding 120 mL of a 2.0M Fe(NO₃),solution to 400 g clean sand. The solution was heated at 110 °C for 12 hr. during which time, the liquid evaporated and the coating formed. After the sand cooled to room temperature, it was rinsed with deionized water, dried and saved for use without further processing.

Column Operation

Two 1/2-in. ID plexiglas filter columns were constructed and run either in parallel or in series. Each column was packed with 30 mL of media (gross volume, including void space). Influent entered the top of the columns, and effluent samples went either to a waste line or an autosampler.

Column operation involved four distinct stages: treatment, backwash, regeneration and re-equilibration. In the treatment stage of a typical run, wastewater was pumped through the column, and effluent was collected and analyzed for copper concentration. Hydraulic loadings of 6 and 10 mL/min were used in column runs, corresponding to empty bed detention times of five and three rein, respectively. Both un-coated and iron-oxide-coated sand beds had porosities of 0.34 ± 0.03 , so the hydraulic detention times within the beds were 1.7 and 1 rein, respectively. Unfiltered effluent samples were taken to determine total copper, and filtered samples were collected to determine soluble copper. Headloss across the bed was recorded throughout the run.

At the end of the treatment stage, the column was taken off line. If the particulate copper trapped during the treatment stage could not be dissolved in the regeneration phase, such as when real ammoniated copper etching rinsewater was being treated, a backwashing stage was included. However, if all the copper being treated was soluble or if particulate copper retained in columns could be dissolved at a low pH, backwashing was eliminated from the column operation. This was the case in some adsorption tests, filtration tests using synthetic influent and tests using real cuprous chloride wastewater. If the column was to be backwashes, the bed was fluidized with an expansion of approximately 40 percent. The backwash fluid was 200 mL of deionized water (about seven bed volumes).

After backwashing, an acidic solution was circulated in a closed loop through the column at a flow rate of 45 mL/min to release the adsorbed soluble metals and regenerate the adsorbent. By the addition of nitric acid (HNO₃), pH was maintained at 2.0. After 30 rein, circulation was terminated. Regenerant solution was collected and analyzed after each run.

The bed was fluidized briefly after regeneration to release trapped bubbles. Finally, to assure the media would not alter influent pH in the subsequent run, the filter media was equilibrated to that pH by circulating 200 mL of a pHadjusting solution through the column in a closed loop. Solution pH was measured and maintained at the target (the influent pH of the next run). In some cases, the solution contained 0.04M ammonia. Flow rates were generally the same as in the regeneration stage. Circulation was stopped after the pH had stabilized and could be maintained at the target without the base addition for three to four min.

Analytical Methods

All influent and effluent samples were acidified with 2.5 volume percent nitric acid. Metal analysis was conducted by atomic absorption spectrophotometry (AAS) in the flame mode. Ammonia concentrations were measured with an ammonia-selective electrode after adjusting the samples to pH > 12.

Comparison of Precipitation & Adsorption

As shown in Fig. 1, copper in the waste could be removed by precipitation only when the pH was greater than 11.5. The addition of iron oxides improved removal of copper over the pH range of 6.5 to 11.5. Thus, it appears that the complexation of copper by ammonia interfered with copper precipitation, but that those complexes could be adsorbed by iron hydroxide solids. This indicated adsorption maybe an effective treatment process.



Fig. I—Batch tests for Cu removal by precipitation (no Fe added) and by adsorption (10 M Fe added) from synthetic (solution 1) and real (solution 2) etching rinsewaters.

Table 1

	Regeneration	Performance		
Run #	Efficiency, % pH 8.0	Iron loss, 0/0		
1	73	0.11		
2	79	0.53		
3	85	0.46		
4	99	0.44		
5	94	0.41		
6	95	0.39		
7		0.26		
		Avg. 0.37		

Adsorption of Copper In Packed Columns

An initial evaluation of copper adsorption and filtration was conducted with rinsewater prepared by dilution of a *proprietary* etching solution. In the first of such tests, the solution was adjusted to pH 8.0, and ammonia was added to maintain most of the copper (12.4 mg/L) in soluble form.

During the first three runs using this solution, the removal capacity decreased, and copper recovery during regeneration was incomplete (Table 1). However, the removal capacity stabilized and the breakthrough curves were quite

^{**}Magnifloc 1820-A, American Cyanamid Corp., Wayne, NJ.



Fig. 2—Breakthrough curves for treatment of synthetic waste at $\,_{\text{PH}\,6.0}$ in six consecutive runs.

reproducible in runs four through six (Fig. 2). One possible explanation for the initial deterioration of removal capacity is the heterogeneity of surface binding sites on iron-oxidecoated sand; that is, perhaps some binding sites with higher affinity for copper were occupied first and were not regenerated during the initial runs. In any case, it appeared that the process could be operated successfully to remove soluble, complexed copper from the rinsewater.

Regeneration

The purposes of regeneration are to (1) recover the copper in a reasonably concentrated solution and (2) reactivate the coated media. The recovery of copper from the iron-oxidecoated sand during regeneration was evaluated by sequential exposure to three batches of regenerant solution at pH 2.0 with regeneration times of 60, 30 and 30 rein, respectively. Most of the adsorbed copper was recovered in the first two batches; in the first batch, most of the recovery occurred within 30 to 45 min (Fig. 3). The copper concentration of the second regenerant solution was about 1/5 that of the first batch. In an actual application, the second batch could be used as the first batch for the next run. Operation in this way can maximize copper concentration in the regenerant solution.

Using Two Columns In Series

Treatment Efficiency

The treatment system was altered so the influent passed through two columns in series. To run the system continuously during regeneration, the first column (A) was taken off line at the end of a run (about 22 hr), and the influent flow was switched to the second column (B). After column A was regenerated and re-equilibrated, it was placed in the downstream position. Column operation in this manner utilized the maximum removal capacity of the

packed media while maintaining low effluent concentration. The system was run successfully at a flow rate of 6 mL/min for approximately 40 days, during which time the treatment was interrupted occasionally to replenish the influent solution. The longest uninterrupted run lasted 10 days, corresponding to runs 13 through 22.

In general, the breakthrough curves of the first column were quite reproducible with respect to the amount of copper removed (Fig. 4). This indicated that the removal capacity of the coated media did not deteriorate over the course of one month of treatment. Furthermore, the effluent concentration of the downstream column typically ranged from 0.02 to 0.05 mg/L, corresponding to 99.6 percent to



Fig. 3—Cumulative regeneration efficiency, using three batches of regenerant solution for Cu recovery from exhausted media.

99.8 percent removal efficiency. The downstream column was, thus, very effective at removing the copper passing through the upstream column,

Regeneration, Re-equilibration

During the regeneration process of these experiments, 40 mL of regenerant solution, maintained at pH 2.0 by acid addition, was circulated through the columns for 30 min at a flow rate of 45 mL/min. An identical batch was applied for another 30 min. The concentrations of copper in the regenerant solutions are listed in Table 2. The average and standard deviation for 18 runs were 1576 and 256 mg/L, respectively, corresponding to a concentration factor of 127 in the first batch compared to the influent.

The average copper recovered for the first 20 runs was only 82 percent. That is, an average 18 percent of the copper was retained in the column after each regeneration. If this retained copper had blocked the surface, the capacity of both columns would have been depleted after about 12 runs. However, the reproducibility of the breakthrough curves indicates either the retained copper formed a surface precipitate that was, itself, able to adsorb copper, or the retained copper was present in a way that did not block access of copper in subsequent batches to the iron oxide adsorption sites. For the last 10 runs, the average copper recovery efficiency Increased to 96 percent.

To summarize, these tests demonstrated the potential of iron-oxide-coated sand packed in columns as an adsorbent for the treatment of plating wastewaters containing soluble ammonia-complexed copper. The process can be used intermittently and/or continuously over a period of at least a month with excellent treatment efficiency, no deterioration in performance, and good recovery of the removed metal in a reasonably concentrated solution.



Fig. 4—Breakthrough curves for the upstream column during treatment of synthetic rinsewater at pH 8.0 in 30 consecutive runs.

Table 2					
Regeneration Efficiencies					
And Regenerant Concentration in Selected Runs					
	EBDT, Regen. #1*, Regen. #2*, Efficiency,				
Run #	min	mg/L Cu	mg/L Cu	%	
6	3.75	1750	412	77	
7	3.75	1428	932	85	
8	5	1713	363	76	
13	5	1500	332	90	
14	5	1508	340	86	
15	5	1400	304	85	
16	5	1260	680,	80	
17	5	1536	368	80	
18	5	1320	664	79	
20	5	1040	856	82	
21	5	1556	380	82	
22	5	2060	585	109	
23	5	2130	560	111	
24	5	1800	500	94	
25	5	1650	550	86	
28	5	1670	380	100	
29	5	1480	410	94	
30	5	1560	360	94	
Avg		1576	500	88	
s.d.		280	180		

*mg/L Cu

Treatment of Particulate Cu

In Packed Columns

Background

Filtration of a waste stream through a sand bed to remove small, difficult-to-settle particles is a common polishing step following conventional precipitation/settling. A small dose of polyelectrolyte is often applied to improve results. As particles are removed, the filter clogs and headless through the bed increases. Filtration continues until either the particles of interest are no longer effectively removed (breakthrough) or until the headless reaches some predetermined limiting value.

Although polyelectrolytes or other coagulant can increase the tendency for suspended particles to attach to the filter media and, thus, increase the time-tobreakthrough of a filtration run, headloss often increases when coagulant are used because of improved removal efficiency and poor bed penetration, Increasing media size and fluid flow rate can increase bed penetration and, thus, decrease development of headless. Therefore, optimization of the filtration process requires the correct choice of bed, velocity and coagulant to achieve efficient removal of suspended particles with an acceptable headloss.

Direct filtration (i.e., the application of effluent to the filter without a prior settling stage) often has several advantages over conventional precipitation/settling processes, including lower chemical costs, better solid/liquid separation and limited space requirements. In the tests described in this paper, the potential to treat the plating rinsewaters by direct filtration was evaluated. The filtration capacity and head loss of a treatment column packed with iron-oxide-coated sand were compared with those of a control column containing uncoated sand (i.e., in which conventional sand filtration was occurring).

Effect of flocculation

The first experiments used a mixing period of two hr between preparation of the waste and initiation of the column run. In three sequential treatment cycles, particulate removal efficiency was significantly better when ironoxide-coated sand was used than when uncoated sand *was* used (Fig. 5). In spite of retaining less particulate matter, the column with uncoated sand had higher headless than the column with coated sand (Table 3).

Even though the performance of the column containing the coated sand was better than that of the uncoated sand, it was still judged unacceptable. Allowing 24 hr to lapse before applying the wastewater to the columns (in hopes the particles would grow and become more efficiently removed) improved performance dramatically. No particulate breakthrough occurred for the coated sand column; and the uncoated sand column also removed particles effectively for 130 bed volumes (Fig. 6). Headloss decreased, despite more particles being retained in the columns (Table 3). Aggregation of small floes during the flocculation period is the most likely explanation for this observation.



Fig. 5—Breakthrough curves for particulate Cu at pH 8.0 in three consecutive runs, with a flocculation time of two hr prior to treatment.

Table 3Headloss Characteristics of Column RunsWith Particulate Cu Influent

	Bed volumes treated until headless = 100 cm		
Conditions during run	Uncoated	Coated	
Figure 5, Run 1	47	63	
Figure 5, Run 2	19	40	
Figure 5, Run 3	18	20	
Figure 6	130	>150	
Figure 7	20	28	



Fig. 6—Breakthrough curves for particulate Cu at pH 8.0 with a flocculation time of 24 hr prior to treatment.

Sample #	рН	Tot Cu, mg/L	Soluble Cu, mg/L	Soluble Cu at pH of treatment, mg/L	Flowrate, mL/min	
1	6.05	3.9	3.2	0.55	10	
2	3.93	3.2	3.2	0.42	6	
3	7.6	25.3	8.3		6	
4	8.35	15.6	2.1		6	
5	7.8	69.5	6.0	3.5	6	





Fig. 7—Breakthrough curves for particulate Cu at pH 8.0 with a flocculation time of two hr and with addition of 1 mg/L anionic polymeric coagulant.

In the next tests, 1 mg/L of an anionic polymer^{**} was applied to the influent, which was adjusted to pH 8.0 in an effort to enhance the aggregation of small particulates and, thus, improve the filtration efficiency. The performance of both columns is shown in Fig. 7. Using the coated sand column, no particulate breakthrough was observed at all for about 150 bed volumes treated. Unfortunately, substantial headloss developed quite quickly in both columns (Table 3). This headloss might be reduced by using higher influent flow rates and/or larger-grain media. However, a larger diameter sand would also decrease the surface area per unit volume of filter column for ferrihydrite attachment, reducing the quantity of ferrihydrite within the column and the column capacity.

Treatment of Real Wastewater

It was demonstrated that coated sand outperformed uncoated sand in terms of removal efficiency for both soluble and particulate copper in *simulated* rinsewaters from an ammoniated copper etching process. Next, on-site tests were conducted to evaluate the applicability of this new technology for treating *real* rinsewater from ammoniated copper and cuprous chloride etching processes. The treatment system consisted of two columns in series, each packed with 30 mL coated sand. The flow rate was 6 or 10 mL/min, corresponding to 288 and 480 bed volumes treated in 24-hr continuous cycles.

Prior to entering the columns, rinsewater from an ammoniated copper etching line was pumped into a bottle and detained for five rein, during which time the pH was adjusted to 8.0. The test lasted for six days. The composition of five grade composition of five grade complex from the singulated line during the



Fig. 8—Influent and effluent Cu concentrations in on-site pilot tests for treating the ammoniated Cu rinsewater. Arrows indicate the end of each daily run, at which time the upstream column was backwashes and regenerated.

first five days of the test is shown in Table 4. Influent samples were collected semicontinuously during the last two days of the test in order to monitor the fluctuation of the influent copper concentration. These data are shown in Fig. 8 along with the effluent concentrations throughout the test period. The copper concentration in the effluent was usually below 0.1 mg/L, despite extensive fluctuation of the influent concentration. Occasional breakthroughs were observed during each run, but did not persist. In addition to copper, the influent and effluent concentrations of zinc and lead were analyzed. The coated sand was very effective in removing these metals as well (Fig. 9).



Fig. 9—Removal of Zn and Pb from the ammoniated CU rinsewater during the on-site pilot tests.

tion of five grab samples from the rinsewater line during the **Magnifloc 1820-A, American Cyanamid Corp., Wayne, NJ.

Because the particulate copper trapped in the column did not dissolve at low pH, the first column was backwashes after the treatment stage using 200mL deionized water. The copper concentrations of backwash waters were 61, 169, 102 and 207 mg/L in runs three through six, respectively.

Next, the treatment unit was moved to the cuprous chloride etching line. The only change in the treatment process was the elimination of the backwash step because of the ease with which the particulate copper could be solubilized. The amount of copper recovered is listed in Table 5. Despite the extremely high loading of copper and more frequent breakthrough, the copper concentration of most effluent samples was below 0.,7 mg/L (Fig. 10). A complete breakthrough in the last run apparently resulted when a slug of acid entered the columns during cleaning of the rinsewater line. This acid overwhelmed the capacity of the pH controller, allowing low pH water to enter the column during the run. In a full-scale system, precautions would be taken to prevent such an occurrence.

Although the treatment efficiency was almost always quite good (other than when the capacity of the neutralizer was exceeded), there were a few samples for which the extent of copper breakthrough was unacceptably large as a result of a very large copper spike in the influent. During full-scale operation, such fluctuations could be dealt with either by employing a third column in series, or by using an equalization basin upstream of the two-column setup to reduce the magnitude of the variation in in fluent concentration

Trea	Table 5Treatment Conditions for On-Site TreatmentOf RinsewaterFrom Cuprous Chloride Etching Process*				
	Bed volumes treated	Cu in Regenerant			
1	380	5720			
2	340	4281			
3	300	1670			
4	460	4625			

*Treatment pH: 8.0; Flowrate: 10 mL/min.



Fig. 10-Influent and effluent copper concentrations in on-site pilot tests for treating the cuprous chloride rinsewater. Arrows indicate the end of each daily run, at which time the upstream column was regenerated. No backwashing was required, since the particulate trapped in the column dissolved in the regenerant solution.

Further Studies Will Increase Applications

In general, the new media performed well, being capable of removing ammonia-complexed divalent copper and

chloride-complexed monovalent copper from solution under conditions in which conventional precipitation failed. In addition, the coated sand showed promise as a filter media, capable of removing particulate copper more efficiently and with less headless than uncoated sand, either with or without the addition of a polymeric flocculent.

The treatment of real rinsewaters was evaluated in both laboratory and on-site tests. The coated sand was effective at removing zinc and lead simultaneously with copper from these wastewaters. When two columns were used in series, the treatment system was able to handle fluctuations in copper concentration up to several hundred mg/L.

The limited tests of the process on line at a plating facility indicated application of the coated sand technology is feasible. The process was able to treat real wastewaters with reasonably high metal removal efficiencies (95 to > 99 percent). Although factors such as detention time, treatment pH and backwashing/regeneration frequency would have to be determined individually for each application, the overall performance is sufficiently encouraging to support further development of the process. Furthermore, recent modifications in the sand preparation procedure have led to an increase of about a factor of 3 in the capacity of the coated sand to adsorb copper.

While additional tests are required to investigate the ability of coated sand to handle the wastewaters of more complex metal finishing operations, this study has shown that adsorptive filtration using coated sand has potential for use in treatment processes at plating facilities, especially in systems for which both soluble and particulate removal are important.

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