Recovery of Cadmium and Cyanide Using a Combination of Ion Exchange And Membrane Extraction

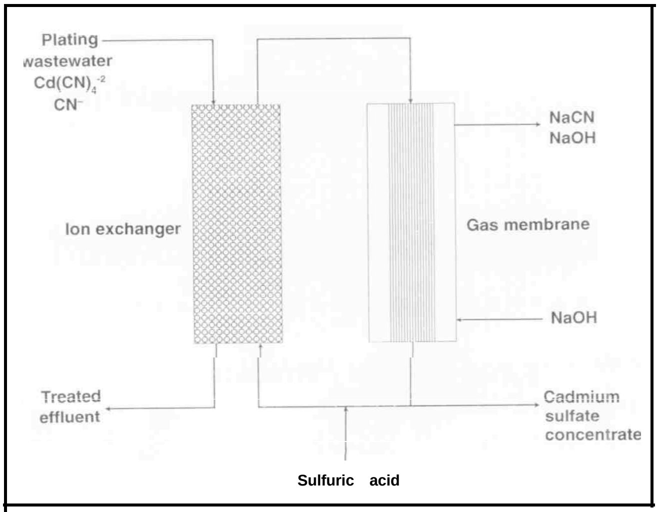
By Christopher T. Riley and Michael J. Semmens

A combination of ion exchange and membrane extraction successfully recovered cadmium and cyanide from simulated cadmium-cyanide rinsewaters. The ion exchange loading was most effective at cyanide-to-cadmium molar ratios of 4:1 or less; when the molar ratio exceeded 4:1, cadmium-cyanide complexes caused a chromatographic displacement of free cyanide from the resin. Cyanide-to-cadmium molar ratios in excess of 4:1 could be reduced to 4:1 or less by pumping the solution through a sand filter loaded with cadmium oxide. Regeneration of the anionic resin with sulfuric acid restored the full resin capacity and recovered the cadmium and cyanide in separate solutions.

Cadmium plating is, and will continue to be, specified primarily by defense-related industries.’ Concern about the toxic and carcinogenic effects of this metal requires very tight effluent controls. This study was an investigation of the effectiveness of the process in recovering cadmium and cyanide from electroplating rinsewaters. The loading characteristics of complexed cadmium-cyanide and free cyanide on strong-base anion resins, the effectiveness of resin regeneration with sulfuric acid (H_2S0_4), and free-cyanide control, using a sand filter loaded with cadmium oxide (CdO), were all investigated.

The Recovery Process

The process’ comprises two steps[2] studied previously in the recovery and separation of metals and cyanides from simulated and actual electroplating rinsewaters.[34] The first step in this process removes metal-cyanide complexes and free cyanide by loading onto a strong-base anionic exchange resin. The second step regenerates the exhausted resin with strong acid, removing the volatile hydrogen cyanide (HCN) in a module containing hollow-fiber, gas-permeable membranes. The HCN is neutralized in a stream of concentrated sodium hydroxide (NaOH) solution. The process results in separate solutions of NaOH/NaCN and acid/metal. The process is shown in Fig. 1.



g. 1—The recovery process.

Cadmium Cyanide Ion Exchange Column Studies

Computer equilibrium calculations have shown that at the pH of typical cadmium cyanide plating baths, the predominant cadmium cyanide complex form is $Cd(CN)_4^{-2}$.[5] The ion exchange column studies were conducted to characterize the free- and complexed-cyanide exchange behavior on anionic exchange resin by evaluating the influence of cyanide-to-cadmium molar ratio and the influence of feed cyanide concentrations on removal performance. The effectiveness of regeneration with 10-percent H_2S0_4 was also measured by evaluating the resin performance over two ion exchange cycles for each test condition (Runs A and B). The resin used for the B-run was regenerated resin from the A-run.

Method

Sample wastewaters were prepared by dissolving known masses of NaCN and CdO in tap water. The pH of the solution then was adjusted to 11.5 with NaOH. The wastewaters were pumped from 60-liter plastic feed tanks to the top of glass ion exchange columns measuring approximately 1 in. in diameter. The columns were loaded with 150 to 200 mL of strong-base anion resin ($S0_4^{-2}$ form). The resin was backwashes with distilled water to free air bubbles and settle the bed prior to use.

The effluent from the columns flowed to an Erlenmeyer flask, then overflowed to the drain. An automatic sampler collected 200 mL of the effluent from the flask once every hour. At least four samples of the influent wastewater were collected and analyzed during each run.

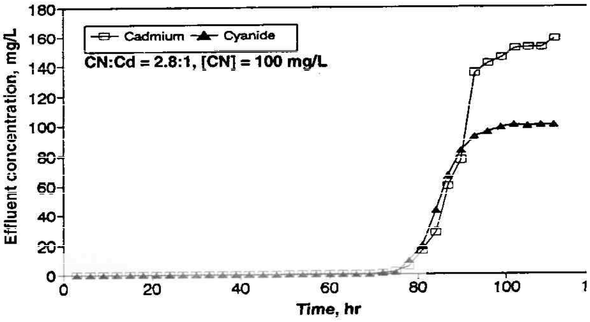


Fig. 2- Cadmium cyanide loading, CN:Cd = 2.8:1, [CN] = 100 mg/L.

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[a] Michael J. Semmens, GM-IX, U.S. patent

Table 1
Ion Exchange Conditions Tested

Run #	Bed Vol (ml)	$[Cd]_{in}$ (mg/L)	$[CN]_{in}$ (mg/L)	CN:Cd (molar)	Capacity (meg/L) Cd	Capacity (meg/L) CN
1A	150	116	94	3.5	1.39	2.16
1B	150	153	96	2.7		
2A	200	199	189	4.1	0.91	1.83
2B	200	202	183	3.9		
3A	200	213	273	5.5	1.06	1.96
3B	200	208	280	5.8		
4A	150	25	27	4.7	0.65	1.23
4B	150	27	25	4.0		
5A	150	105	96	4.0	0.93	1.84
5B	150	106	98	4.0		
6A	150	432	402	4.0	1.06	2.13
6B	150	433	401	4.0		

Loading Rate = 6 BC/hr Inlet pH = 11.5

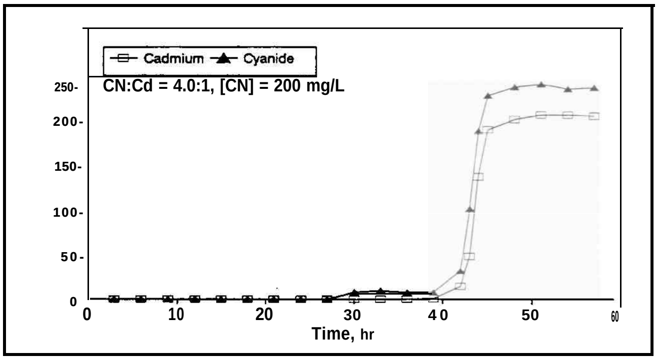

Fig. 3-Cadmium cyanide loading, CN:Cd = 4.0:1, [CN] = 200 mg/L.

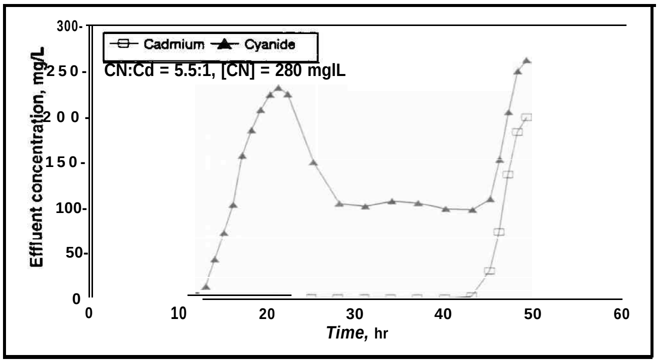

Fig. *4-Cadmium cyanide loading, CN:Cd = 5.5:1, [CN] = 280 mg/L.*

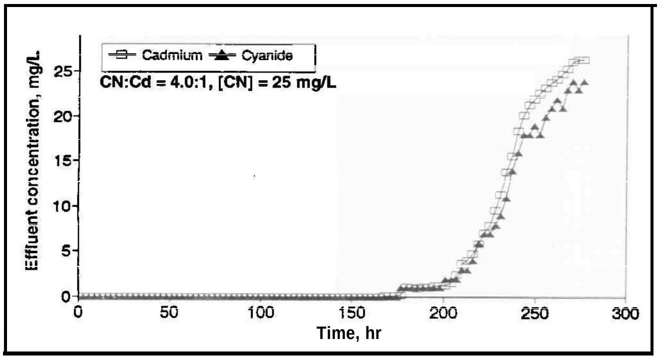

Fig. 5-Cadmium cyanide loading, CN:Cd = 4.0:1, [CN] = 25 mg/L.

Influence of cadmium-to-cyanide ratio

Runs 1,2, and 3 tested solutions with approximate cyanide-to-cadmium (CN:Cd) molar ratios of 3:1,4:1, and 6:1, respectively. The operating conditions tested are presented in Table 1. Figures 2,3, and 4 show typical breakthrough curves obtained at these approximate ratios.

Where the experimental conditions resulted in a CN:Cd molar ratio less than or equal to 4:1, as in Figs. 2 and 3, the breakthrough curves show that the cadmium and cyanide break through at essentially the same time. This is a result of complexation of all the cyanide present with the cadmium. When the CN:Cd molar ratio exceeds 4:1, as in Fig. 4, there is free cyanide (CN^-) present in the solution, and an early breakthrough of free cyanide is noted. The free cyanide leakage results from a chromatographic displacement of the previously adsorbed free cyanide by the cadmium-cyanide complex. Strong base anion resins do show an unusually high selectivity for negatively-charged metal complexes,[6] and this selectivity is apparently high enough to cause displacement of the monovalent CN^- ion.

In a cadmium electroplating bath, CN:Cd molar ratios will typically be 10:1 or higher. The implication of these results is that when ion exchange is used to treat cadmium-cyanide rinsewaters, free cyanide will leak from the column before the capacity of the resin has been fully utilized.

Influence of concentration

Runs 4, 5, and 6 tested solutions with approximate cyanide concentrations of 25, 100 and 400 mg/L, respectively. The CN:Cd molar ratio was constant at 4:1. Table 1 shows the actual operating conditions tested. Figures 5, 6, and 7 show typical breakthrough curves obtained at these concentrations.

Run 4A (figure not shown) used a feed CN:Cd molar ratio greater than 4:1. As a result, free cyanide leaked through the column. All other runs maintained a CN:Cd molar ratio of 4:1, and no free cyanide leakage was observed.

Table 2 shows the time to 50-percent breakthrough for runs 2,4,5, and 6; also the loadings of cadmium and cyanide on the resin. The time for 50-percent breakthrough showed an inverse relationship to the initial concentration. Typically, doubling the influent concentration resulted in halving the time to 50-percent breakthrough. The capacity of the resin was essentially insensitive to the influent concentration.

Run 4, which used a concentration of 25 mg/L cyanide, had a shorter time to breakthrough than would be expected, given the data from the other runs. At this low concentration, competition from other anions, such as nitrate, carbonate, chloride, or hydroxide, may have retarded adsorption of cadmium and cyanide. A precipitate was observed also in the bed during this run. Calcium in the rinsewater probably combined with the sulfate liberated from the resin to form insoluble calcium sulfate. This precipitate may have resulted in channeling of the bed and premature breakthrough.

Findings

Cadmium and cyanide were removed very effectively, using a strong base anion exchange resin when the cadmium-to-cyanide molar ratio was 4:1 or less. Cyanide-to-cadmium molar ratios greater than 4:1 resulted in preferential adsorption of the cadmium-cyanide complex, with resultant displacement of free cyanide. The capacity of the resin was essentially insensitive

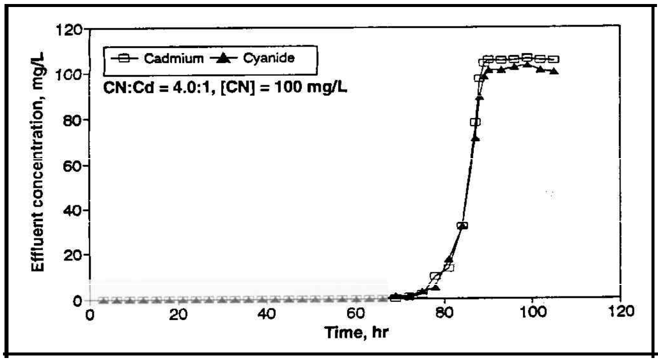

Fig. 6-Cadmium cyanide loading, CN:Cd = 4.0:1, [CN] = 100 mg/L.

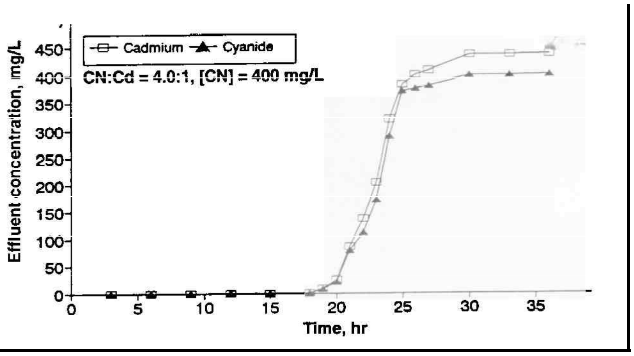

Fig. 7-Cadmium cyanide loading, CN:Cd = 4.0:1, [CN] = 400 mg/L.

to feed concentration, and the resin service time was inversely related to the feed concentration at the same hydraulic loading rate.

Ion Exchange Regeneration Studies

Regeneration studies were performed to evaluate the influence of regenerant volume and concentration on cadmium and cyanide recovery and the subsequent ion exchange performance of the regenerated resin. Loading runs 1 through 6 each included two loading cycles with one regeneration cycle between. These regenerations were performed using three bed-volumes of 10-percent H_2SO_4.

To optimize the regeneration procedure, a further assessment was made of the rate of cyanide recovery under different operating conditions. Keeping the regenerant volume as small as possible would certainly decrease equipment sizes and chemical handling concerns. Keeping the regenerant as concentrated as possible should improve the rate of cyanide recovery. The effectiveness of regeneration with 2.2 bed-volumes of 15 percent H_2SO_4 acid was also studied, with regeneration times of 2, 4, and 6 hr.

In addition to the effectiveness of the regeneration, the subsequent loading cycle behavior was also analyzed by monitoring the column effluent for cadmium and cyanide during the subsequent loading cycle.

Method

A column of exhausted resin was transferred to a fume hood and coupled with a membrane module (made at the University of Minnesota). The membrane module measured approximately 0.5 m in length and about 1 cm in diameter. Contained in the module were 200 hollow fibers, each having a diameter of about 400 µm. H_2SO_4 was pumped at 200 mL/min through the resin and cycled through the inside of the membranes. To neutralize the HCN liberated during the regeneration 500 mL of 5M NaOH solution were recirculated at 200 mL/min through the membrane module and over the outside of the hollow fiber membranes.

Table 2
Influence of Feed Concentration On Ion Exchange Performance

Run #	$[CN]_{in}$ (mg/L)	Time to 50% Breakthrough (hr)	Cadmium Capacity (lb/ft^3)	Cyanide (lb/ft^3)
4	25	230-260	2.24	2.01
5	100	85	3.24	2.99
2	200	44	3.19	2.97
6	400	22	3.72	3.45

The regenerated columns were rinsed and evaluated in subsequent loading tests. In the case of the 10-percent H_2SO_4 regenerations, loading performance was evaluated in the B-runs. In the case of the 15-percent H_2SO_4 regenerations, evaluations were made in a 24-hour loading performance test. The regenerated columns were all loaded at six bed-volumes per hour, and cadmium and cyanide leakage levels were monitored.

Results and Discussion

The use of three bed-volumes of 10-percent H_2SO_4, recycled through the membrane module, over a six-hr regeneration time proved very effective. The regenerated resins (B-runs) showed no leakage of cyanide or cadmium and no loss of capacity.

The effectiveness of the regeneration may also be assessed by comparing the mass balances on the amounts of cadmium and cyanide removed by the resin and released in the subsequent regeneration. The masses of cadmium and cyanide removed by the resin during the loading cycle and the masses released in the regenerations are compared in Table 3. The data show that within experimental error, all of the cadmium and cyanide captured by the resins during the ion exchange loading cycle is recovered by the regeneration procedure.

Fast cyanide recovery rate curves were obtained during regeneration with either 10- or 15-percent H_2SO_4. A comparison of cyanide recovery rates for these acid solutions is shown in Fig. 8. This figure indicates complete regeneration within one to two hr with either strength of acid. The ion exchange loading performance tests following the 15-percent H_2SO_4. regenerations revealed potential problems, however. Cadmium leakage

Table 3
Ion Exchange Loading and Regeneration Test Results

Run #	Ion Exchange Mass Cd Removed (mg)	Mass CN Removed (mg)	Regeneration Mass Cd Released (mg)	Mass CN Released (mg)
1A	11,712	8,428	11,900	7,500
2A	10,231	9,512	10,900	10,000
3A	11,895	10,209	11,100	9,250
4A	5,452	4,790	5,600	4,000
5A	7,790	7,187	7,300	7,000
6A	8,935	8,295	8,400	7,875

Acid Volume = 3 Bed-Volumes
Acid Strength = 10% H_2SO_4
Base Volume = 500 mL
Base Strength = 5M NaOH
Acid and Base Flow-rates = 200 mL/min

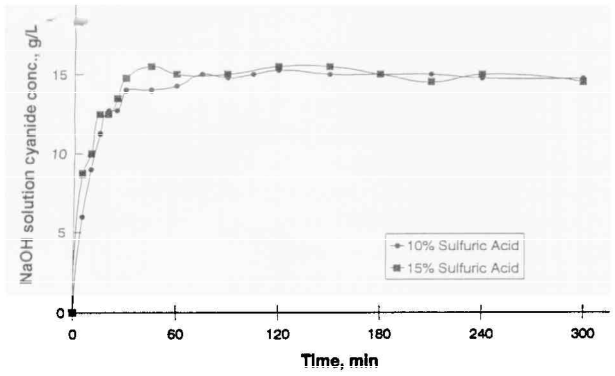

Fig. 8—Cyanide recovery rate curve (sulfuric acid regenerant).

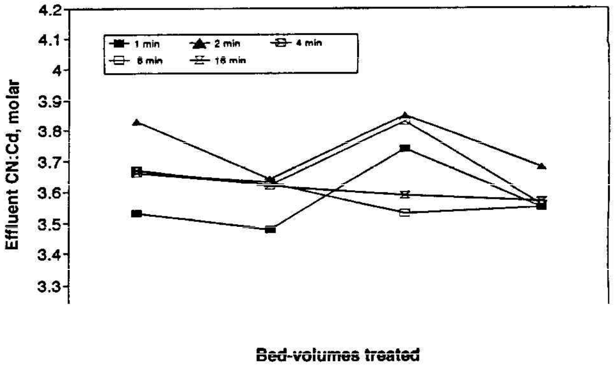

Fig. 9-Cadmium oxide pretreatment, contact times at pH 10.

during subsequent loading was detected from each column regenerated with 15-percent H_2SO_4. No cyanide leakage was detected from any of the columns. By comparison, none of the ion exchange loading cycles following regeneration with 10-percent H_2SO_4 showed any cadmium or cyanide leakage. The leakage following regeneration with 15-percent H_2SO_4 is likely attributable to resin shrinkage during the regeneration process. The resin beads contract in the presence of a strong regenerant and the kinetics of cadmium release may be impaired. As a result, cadmium and acid were left in the resin phase even after the normal rinsing step.

Findings

With the membrane-assisted regeneration, excellent recoveries of cadmium and cyanide were obtained, while the full capacity of the resin was restored. Cadmium and cyanide recovery in the regeneration using three bed-volumes of 10-percent H_2SO_4 was slightly slower than that using 2.2 bed-volumes of 15-percent H_2SO_4. Subsequent column loading studies revealed, however, that the more concentrated regenerant resulted in cadmium leakage at the beginning of each loading cycle. Regeneration with 10-percent H_2SO_4 is therefore recommended.

Cadmium Oxide Pretreatment Studies

The presence of free cyanide in cadmium-cyanide wastewaters results in early leakage of the free cyanide from the resin column. To improve the removal of free cyanide by strong-base anion resin, a wastewater containing free cyanide was contacted with cadmium oxide in a pretreatment step. In the presence of free cyanide, CdO dissolves to convert free cyanide into cadmium-cyanide complexes that are strongly adsorbed onto ion exchange resin. Tests were conducted to evaluate the kinetics of CdO dissolution and the pretreatment requirements for complete cadmium-cyanide complex formation.

Method

A sand filter was made by loading approximately 450 mL of silica sand into a column approximately 2 in. in diameter. The sand was supported by gravel. Ten grams of powdered CdO were mixed into the top of the sand bed, A wastewater containing excess free cyanide was made up with a sodium cyanide-to-cadmium ratio of 4:1 by weight (approximately 10:1 on a molar basis) and pumped through the sand filter. Residence times of 1,2,4,8, and 16 min were tested at pH values of 10, 11, and 12. The effluent from the sand filter was analyzed for cyanide and cadmium after at least two bed-volumes were pumped through the filter.

Results and Discussion

Figure 9 shows the effluent CN:Cd molar ratio plotted as a function of the hydraulic residence time (empty bed contact time) for a solution of pH 10. Similar figures for solution pH values of 11 and 12 are shown in Figs. 10 and 11.

Figure 9 shows that at pH 10, the pretreatment is extremely effective in reducing free cyanide. The CN:Cd molar ratio of the solution entering the column was 10:1; when the solution exited the column, the ratio was between 3.5:1 and 3.8:1 for all contact times tested. The earlier ion exchange performance studies

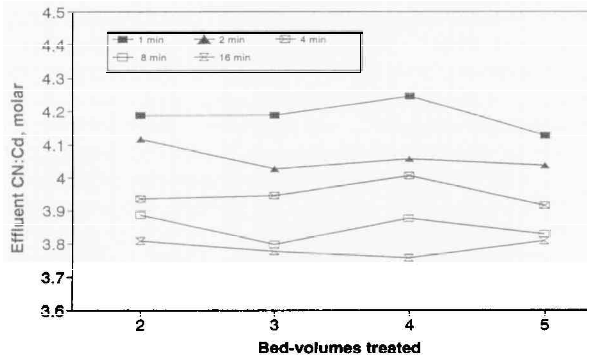

Fig. 10-Cadmium oxide pretreatment, contact times at pH 11.

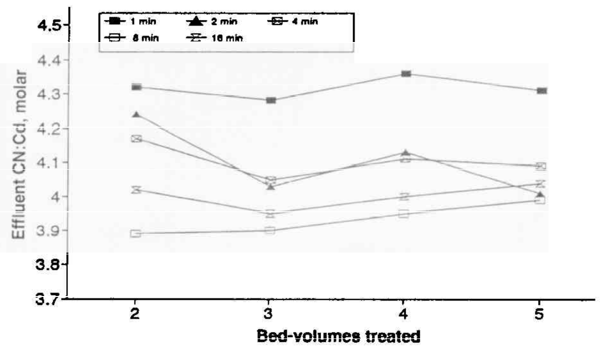

Fig. 11—Cadmium oxide pretreatment, contact times at pH 12

showed that at a molar ratio less than 4:1, cadmium-cyanide removal by strong-base anion resin is excellent, with no cyanide leakage.

The rate of dissolution of CdO at pH 10 was very rapid, and there was very little difference in the effluent quality with changing contact times. As the pH of the solution was increased, the kinetics of dissolution slowed and a longer contact time was required to ensure that all the cyanide was complexed. From Fig. 10, it can be seen that at a solution pH of 11, a contact time of at least four min was required to obtain the desired ratio of less than 4:1. Figure 11 shows that at pH 12, a contact time in excess of eight min would be required.

Findings

Free cyanide can be complexed by dissolution of cadmium oxide in the wastewater. Adequate contact time for this was achieved in a sand filter loaded with cadmium oxide. An optimum solution pH of 10 minimized the necessary contact time.

Summary

The process performed very well in recovering cadmium and cyanide from simulated cadmium-cyanide wastewaters. The effectiveness of the ion exchange loading step was sensitive to the cyanide-to-cadmium molar ratio, with the removal being most effective at CN:Cd molar ratios of 4:1 or less. Molar ratios greater than 4:1 caused free cyanide leakage from the resin.

The regeneration step with strong acid and membrane extraction of the HCN was fast, and restored the full capacity of the resin. The regeneration resulted in a solution of cadmium sulfate and a solution of sodium hydroxide/sodium cyanide. The cadmium could be recovered by electrowinning or precipitation, while the cyanide solution could be reused in a plating solution.

The CN:Cd molar ratio of a free-cyanide-containg wastewater was reduced by pumping the water through a sand filter loaded with excess cadmium oxide. A hydraulic residence time of one min was effective in reducing the CN:Cd molar ratio from 10:1 to less than 4:1 at an influent pH of 10. At higher pH values, longer contact times are required.

Ion exchange is an effective means of removing cadmium-cyanide complexes from electroplating wastewaters. The pH of the solution determines the speciation of the cadmium-cyanide complex, while the molar ratio of cyanide to cadmium controls the amount of free cyanide present. Both of these factors are important in optimizing the effectiveness of this process. Strong acid regeneration with membrane extraction, under controlled circumstances, has also proven effective in recovering both the cadmium and cyanide from the ion exchange resin.

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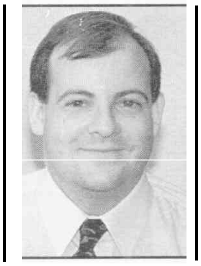

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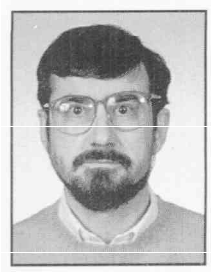

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