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CROSS-CURRENT FLOTATION FOR METAL
REMOVAL FROM PLATING WASTES

by

S.M. Barnett, F.J. DeLuise, E. Nir

Dept. of Chemical Engineering/Dept. of Mechanical Engineering

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16. Abstract <p>While countercurrent flotation pilot plants have been shown to be effective and economical in removing metals such as cobalt, copper, lead, zinc and iron by means of various precipitate flotation techniques, many plating facilities have troughs or other horizontal conduits which would make flotation more economically attractive if these existing channels could be adapted for such use. The purpose of this study was to investigate the feasibility of crosscurrent precipitate flotation for these troughs. The metals investigated were copper, nickel and lead. The most important trend found in the results is that the shorter trough more effectively removes metals by precipitate flotation for a given pH and given flow rates than the longer trough. Thus, the horizontal flotation process should be done over a minimum length to avoid undersized enrichment of the water due to foam breakage.</p>				
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CROSS-CURRENT FLOTATION FOR METAL REMOVAL FROM PLATING WASTES

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S.M. Barnett, F.J. DeLuise, E. Nir

In October, 1982, new federal regulations went into effect which set new limits on the level of heavy metals in the process water discharged by industrial users (1). Among those most significantly affected by the new regulations are the approximately 10,000 plating firms in the U.S. A significant number of these firms will be subject to less stringent contamination levels because they discharge less than 10,000 gal/day, but even for such firms, the flotation process as described below holds considerable promise as a treatment system.

Flotation is an operation in which a solute is removed from solution by being adsorbed at a gas-liquid interface. This interface is usually provided by rising gas bubbles or foams. Surface active agents are often used, since they serve not only to stabilize a foam by increasing surface tension and thus retard bubble coalescence, but, if the surfactant is ionic, the polar (charged) portion of the surfactant molecule can be utilized to attract charged solute particles, be they ions or polar molecules. Several thorough reviews of the types of flotation along with their operation principles can be found in the literature (2-4).

In the early 1970's, a particularly stable foam called a microgas dispersion (MGD) was developed by Felix Sebba (5). The MGD gains its stability because of its double interface. It provides the advantage of a high surface area/volume ratio found with small bubbles, along with the rapid rise velocities of larger ones, since the bubble network rises with the effective diameter of a larger bubble (6). Here at the University of

Rhode Island, countercurrent flotation has been used to remove organic dyes (6), manganese (7), and a mixture of metal ions in both simulated and real wastewater (8). While countercurrent flotation pilot plants have been shown to be effective and economical in removing metals such as cobalt, copper, lead, zinc and iron by means of various precipitate flotation techniques (9-11), many plating facilities already have troughs or other horizontal conduits. It would make flotation more economically attractive if these existing channels could be adapted for such use, and save the cost of a column. Such a method would be cross-current rather than countercurrent. The purpose of this study was to begin to investigate the feasibility of crosscurrent precipitate flotation using MGD. The metals investigated were copper, nickel and lead.

Apparatus

Two troughs were constructed, one six feet long, the other twelve feet in length, made out of two-six foot sections. Both troughs were made of 1/4" thick plexiglas and lined on the inside with 3-mil thick polyethylene. The bottom and side panels were bound together with acrylic glue, and by being bolted to strips of Dexion.TM Sections were sealed on the outside with silicone caulk. The polyethylene lining served to separate the solution from both the caulk and the bolts binding the plexiglasTM to the Dexcon,TM both of which would otherwise have been sources of contamination. In the case of the twelve-foot trough, the two sections were joined by reinforcing them with two one-foot long strips of plexiglas, one on each side of the bottom panels. The side panels were caulked on the outside to prevent leakage, even though the polyethylene already served this purpose. To facilitate flow, the troughs were tilted 1/2" from horizontal for each six feet of length. At

the effluent end of each trough was a sampling tube, located about 2" above the bottom of the end plate.

The contaminant solution was held in a 110-gallon tank, with flow controlled by a valve. When opened, the valve allowed solution to flow down an 18 ft. tall, 1-ft ID vertical column, which served as a conduit from the tank to the trough. Flow through the column could be regulated by a PVC valve at the bottom. Because the tank was located approximately 20 feet above the trough, no pump was used to move the solution; flow was entirely the result of gravity.

The surfactant used was ethylhexadecyldimethylammonium bromide (EHDA), which was added to distilled water to produce a 300ppm solution. Nitrogen, rather than air, was used as the gas in the dispersion. A pail of cold water was used as a crude heat exchanger, and the foam reservoir was a 2-inch ID, 14 ft. tall column adjacent to the larger column. A venturi-type generator was used, in which the surfactant solution moves from a region of high pressure and low velocity to a point of high velocity and low pressure. Nitrogen enters through a sidearm, and passes through a narrow gap between the male and female parts of a 7/12 ground joint. The dispersion was thus formed, and was recirculated through the generator so that coalescing bubbles would again be broken up. The pump used was a Sears #563.26461) driven by a Sears #113.19706, 1/3 hp motor. Surfactant solution was stored in a 20-liter propylene tank situated above the foam reservoir, and was able to flow from the foam tank into the reservoir solely by gravity.

Analytical Instruments

To determine metal ion concentration, a Perkin-Elmer 5000 Atomic Absorption spectrophotometer was used with background correction. The pH

meter used was an Orion model 601A Digital IONALYZER.

Procedure

Stock solutions of each of the metals was made by weighing out the proper amount of the nitrate salt of each of the three metals - Pb $(NO_3)_2$, Cu $(NO_3)_2 \cdot 3H_2O$ and Ni $(NO_3)_2 \cdot 6H_2O$ - to form one liter of a 2,000ppm solution, using distilled water. For each run, 60-gallons of a dilute contaminated solution to be treated were made by appropriate dilution of the stock solution with tapwater. For most of the runs, the pH of the contaminated solution was adjusted to the range of 9.0 - 10.0, which according to Ciriello, is the optimum pH range for removal of the metals under investigation. The pH was adjusted with 0.6M NaOH solution.

To start each run, surfactant solution was introduced into the foam reservoir, the N_2 gas was opened up, and the pump to circulate foam through the reservoir was turned on. Foam was allowed to circulate for ten minutes, so that the quality would exceed 50%. (Quality is the percent air entrained in the foam.) While foam quality was building up, the valves leading from the tank and at the bottom of the column were opened up, and contaminant solution filled up the trough. Once the trough was filled and began to overflow, the foam was introduced into the trough by opening a clamp that held the foam lines leading to the trough shut. There were two foam lines, both secured to the bottom panel. One line introduced foam about six inches from the influent end, the other entering at the midway point. Every five or seven minutes (it varied from run to run), samples were taken of both the influent and effluent, to be analyzed later. Samples of foam were also taken to ensure that it was of sufficient quality. The runs continued until the tank emptied. After

each run, tank and trough were cleaned, first with dilute (.01M) HNO_3 , and then with tapwater.

Percent removal was calculated by the following formula:

$$\% \text{ Removal} = \frac{\text{Initial conc.} - (\text{Final conc./dilution factor})}{\text{Initial concentration}} \times 100$$

Dilution factor would be defined here as inflow divided by outflow, or the contaminant solution flow rate divided by the sum of the contaminant and surfactant solution flow rates. This figure varied markedly over the course of a run for two reasons - 1) adjustments to surfactant solution flow rate had to be made by hand, which offered fair but not strict control, and may have caused the flow rate to vary from the desired 0.3 pm flow rate. 2) The rate of flow of aqueous solution, of course, varied, depending on the height of liquid in the tank. Table 1 relates time, liquid level in the tank, and flow from the tank.

Results and Discussion

A chart of flow rate vs. time is shown in table 1. These rates of drainage are well below what would be predicted for drain-rate from a tank through an orifice 1" in diameter at the bottom of the tank. Obviously, in this drainage, the limiting diameter was not the orifice at the bottom of the tank, but rather the diameter of the open valve, which was considerably less, but not measured, and which was situated 18 cm beneath the bottom of the tank.

The removal of metal ions using the twelve foot trough are shown in table 2. Three runs were done using nickel, one at an unadjusted pH of 5.9, the other at pH basic enough so that precipitate flotation of the hydroxide could be the primary mechanism of removal. While it was considered unlikely that the findings of this investigation would

contradict those of Ciriello (8), who found good rates of removal of pH greater than 8, and poor removal at pH less than 7 when using EHDA as a surfactant, it nevertheless merited a second look, because of the effluent could be effectively treated without altering its pH, we save on the cost of a pH control process. For nickel, however, not only was the untreated solution not effectively cleaned, neither was the pH adjusted one. This was probably caused by two factors - 1) the coalescence of most of the foam while the water being treated was still in the trough, 2) some of the precipitate adhered to the lining, and would recontaminate the solution at a later point in time.

Three runs were also made to investigate the removal of copper, one at an unaltered pH, the second and third conducted using a basic solution. Again, the untreated water proved ineffective, indicating that in crosscurrent as well as countercurrent methods, ion flotation using MGDs is not a useful mechanism. One run done at a higher pH produced noticeable removal rates early on, but effectiveness dropped with time, most likely the result of backcontamination.

Table 3 shows the results of flotation using the shorter, six-foot trough. For this series of runs, all contaminant solutions were pH adjusted so as to induce precipitate flotation of the hydroxides. Further, lead was also investigated this time. Removal rates for nickel varied from a low of 20.0% to a high of 55.4%, with an average removal rate of 40.6%. For copper, the average percentage removed was 60.7%, and for lead it was 49.0%. The improved removal rates in the shorter trough are probably due to the shorter residence time of the solution in the trough, which means less time for the foam to drain and coalesce, and less recontamination of solution.

Conclusion:

The most important trend found in the results is that the shorter trough more effectively removes metals by precipitate flotation for a given pH and given flow rates than the longer trough. This can be explained by the fact that for a given flow rates of both contaminant and surfactant solutions, the residence time for both foam and bulk liquid will be about twice as great in the longer trough. This means that the foam used to effect removal has more time to coalesce, resulting in return to the bulk solution of the same metal ions removed earlier. Thus, if any horizontal flotation process should be done over a minimum length to avoid undesired enrichment of the water due to foam breakage. One other mechanism, not investigated here, is the need to separate quickly the foam from the bulk liquid, a process which can largely, but not completely, be done by mechanically skimming foam off the top.

There are numerous other variables which need to be investigated. With removal rates under the conditions used in this investigation averaging about 60% for a short trough, it seems fair to say that these removal rates can probably be improved by experimenting with the following use of chelating agents, increasing the dilution factor, using a different surfactant, or use of an adsorbing colloid such as FeCl_3 or alum, Ciriello (8), for example, found greatly improved removal, in some cases reaching 100% by using chitosan as a chelating agent. The desired minimum removal rate is 90%-95%, and this should be possible with further investigation into conditions.

The horizontal process also seems capable of handling greater loads than a vertical process. The trough had a cross-sectional area of 27.5 sq. in., (0.191 ft^2), so at its peak of 1.8 gpm, its volumetric velocity was $9.4 \text{ gal/ft}^2\text{-min}$, about three times the typical load per

unit cross-sectional area as any vertical flotation setup.

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Table I

Sol'n height, contaminant solution flow rate, and dilution factor as a function of time.

<u>Time after opening valve (min.)</u>	<u>Height of sol'n in tank (cm)</u>	<u>Sol'n flow rate (previous minute)</u>	<u>Dilution factor(*)</u>
1	52.4	1.93 gpm	.960
2	50.8	1.93	.960
3	49.2	1.93	.960
4	47.6	1.93	.960
5	46.0	1.93	.960
6	44.45	1.87	.959
7	42.9	1.87	.959
8	41.35	1.87	.959
9	39.8	1.87	.959
10	38.3	1.81	.958
11		1.81	.958
12	35.3	1.81	.958
13		1.75	.956
14	32.4	1.75	.956
15		1.75	.956
16	29.5	1.75	.956
17		1.69	.955
18	26.7	1.69	.955
19		1.63	.953
20	24.0	1.63	.953
21		1.63	.953
22	21.3	1.63	.953
23		1.57	.951
24	18.7	1.57	.951
25		1.57	.951
26	16.1	1.57	.951
27		1.51	.950
28	13.6	1.51	.950
29		1.45	.948
30	11.2	1.45	.948

(*)Assumes surfactant flow of 0.3 lpm.

Table 2
Metal removal by flotation in twelve-foot trough.

<u>Run #</u>	<u>Metal</u>	<u>pH</u>	<u>Time of sampling</u>	<u>influent</u>	<u>effluent</u>	<u>% Removal</u>
1	Ni	5.9	7	3.978	3.907	1.8
			15	4.011	3.787	5.6
			20	4.108		
2	Cu	5.9	7	4.227	3.815	9.8
			15	3.917	4.823	
			20	3.714	4.811	
3	Cu	8.9	5	2.976	0.907	62.8
			10	3.870	2.327	39.9
			15	3.540	3.082	13.0
4	Ni	9.7	5	3.653	3.801	
			10	3.534	3.452	2.3
			15	3.550	3.334	6.1
5	Cu	9.4	7	3.046	3.169	
			15	3.423	3.438	
			20	sample lost		
6	Ni	9.2	7	3.562	3.140	11.8
			15	3.884	3.626	7.1
			20	3.019	3.130	

Table 3
Metal removal by flotation in six-foot trough

<u>Run #</u>	<u>Metal</u>	<u>pH</u>	<u>Time of Sample</u>	<u>Influent</u>	<u>Effluent</u>	<u>% Removal</u>
1	Ni	8.78	5	2.223	1.760	20.8
			10	2.690	2.153	20.0
			15	2.944	1.524	48.2
			20	2.868	1.447	49.6
2	Cu	8.80	10	2.600	1.085	58.3
			15	3.051	1038	66.0
			20	3.942	0.432	89.0
			25	3.371	0.803	76.2
3	Pb	8.97	10	3.18	1.91	39.9
			15	2.92	2.29	21.6
			20	3.55	2.09	41.1
			25	3.61	1.85	48.8
4	Ni	9.10	10	2.297	1.025	55.4
			20	2.295	1.227	46.5
			30	2.365	1.330	43.8
5	Pb	9.03	10	2.87	0.76	73.5
			20	3.37	1.31	61.1
			30	3.46	1.54	56.4
6	Cu	8.95	10	3.727	2.250	39.6
			20	4.045	1.843	54.4
			30	4.438	2.612	41.1