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Regeneration and reuse of iron hydroxide adsorbents in treatment of metal-bearing wastes

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ABSTRACT: Sludge from a treatment process using iron was exposed to a mildly acidic solution to investigate iron hydroxide's capacity to collect metals from waste. Batches of iron hydroxide were regenerated and reused 50 times to treat both synthetic and real plating waste. Treatment efficiency was very high and steady, and there was no indication of deterioration in any aspect of process performance. Over time, the treated metals were concentrated in the regenerant solution and may be recoverable. The acid and base requirements were comparable to those for conventional coagulation. Overall, the process appears promising for metal treatment, sludge minimization, and possibly metal recovery. *J. Water Pollut. Control Fed.*, **61**, 481 (1989).

KEYWORDS: metals, removal, (ferric hydroxide) iron regeneration, reuse, adsorption, (recovery).

The search for efficient, cost effective options for treating metal-bearing wastes has intensified in recent years in light of increasingly stringent discharge limits. Simultaneously, the high economic and environmental costs associated with land disposal are forcing generators to reduce sludge volumes.

Conventional treatment in the metal finishing industry involves the addition of base to precipitate metals as hydroxides.[1] In conjunction with hydroxide precipitation, coagulants such as iron salts are often added to improve solid/liquid separation.[2] Further benefits of iron addition may be attributed to contaminant adsorption onto ferrihydrate (iron hydroxide). Among these are enhanced treatment efficiency, stable effluent qualities over a wide pH range, and removal of at least some soluble metal-ligand complexes. Unfortunately, because the adsorptive ability of ferrihydrite is rarely considered, let alone optimized in the design of such systems, the potential for enhanced metal removal through adsorption is often not fully realized.

Conventionally, ferrihydrite coagulants/adsorbents are used only once to treat metal-bearing waste and are then disposed of along with the hazardous metals; hence, ferrihydrite often dominates the bulk of the sludge produced and the cost of sludge disposal. For instance, sludge samples from a local electroplating shop and a printed circuit board manufacturer contained over 50 and 70% iron hydroxide, respectively. This leads to a dilemma because the beneficial properties of ferrihydrite adsorbents are directly related to their concentration: the more ferrihydrite is used, the better the metal treatment efficiency can be and the higher the costs of sludge treatment and disposal become. The cost increase associated with purchasing the iron salts as well as the base required for its neutralization may also be significant.

The work reported here represents an effort to overcome these problems through regeneration and reuse of ferrihydrite. Regeneration consists of exposing the sludge to a small volume of mild acid solution to release adsorbed metals, before reusing the iron to treat subsequent batches of influent waste.[3]

In this paper we describe the effectiveness of regenerated ferrihydrite for treating both real and synthetic metal finishing wastes. In addition, we compare ferrihydrite-based systems to conventional hydroxide precipitation with respect to metal removal as a function of pH, solids settleability, and acid or base requirements.

Materials and Methods

Preparation of adsorbent and waste solutions. The adsorbent applied in these experiments was an amorphous iron oxyhydroxide solid commonly called ferrihydrite. It was prepared by transferring 0.1 M $Fe(NO_3)_3$ solution to a centrifuge tube and diluting with deionized water to an iron concentration of 10^{-2} M. Concentrated sodium hydroxide was added dropwise until the solution reached pH 11.0 (± 0.3), precipitating the ferrihydrite in the process. Five minutes of centrifugation separated the solids from the supernatant solution, which was decanted. The solids were then used in adsorption experiments without further processing.

Two synthetic waste solutions were prepared from metal nitrate salts and acidified to pH 1.5 (± 0.1). Solution 1 contained 3×10^{-3} M each of copper (Cu), nickel (Ni), and zinc (Zn), 2.6×10^{-3} M each of chromium III (Cr(III)) and chromium VI (Cr(VI)), and 1.5×10^{-3} M cadmium (Cd). Solution 2 contained Cu, Ni, Zn, and Cr(III) at 6×10^{-3} M each and Cd and lead (Pb) at 3×10^{-3} M. After dilution in each experiment, ionic strength was adjusted to 10^{-2} M with $NaNO_3$.

Samples of a mixed-metal wastewater were collected daily from a metal plating job shop for one week before treatment. These samples were used unaltered in experiments within 3 days of collection.

Metal removal as a function of pH. The aim of these experiments was to investigate soluble metal removal as a function of pH in systems with and without ferrihydrites present. Initially, a 1:50 dilution of Solution 2 was added to a suspension of fresh ferrihydrite (0.5×10^{-2} M Fe_T) in 1-L beakers. Sequential additions of base raised the pH in increments. After each pH adjustment, the solution was stirred for 10 minutes and a sample was then taken, filtered using a 0.45-μm millipore filter, acidified, and saved for analysis. An identical experiment without ferrihydrite addition characterized soluble metal removals attainable through precipitation.

Settleability. Settling experiments were conducted to evaluate the ease with which solids generated by the various metal removal processes could be separated from solution. In these experiments, 500 mL of a 1:200 dilution of Solution 2 was added to a graduated cylinder (4.9 cm diameter × 35 cm tall), and solution pH was adjusted to 10.0 with NaOH. In some cases, coagulant was added at this point. The coagulants investigated were pre-formed ferrihydrite solids (0.5×10^{-2} M Fe_T) or 5 ppm of an anionic polymer with sulfonic acid functional groups. The suspension was stirred for 10 minutes, then samples were taken at various times from a point 4.0 cm below the solution surface at the center of the cylinder.

Adsorption with regeneration of the solids. In these experiments, one complete process cycle was defined as adsorption, solids separation, desorption and regeneration of the solids, and a second solids separation (Figure 1). The adsorption step involved addition of 50 mL plating waste to a suspension of ferrihydrite, increasing the pH with NaOH, and allowing 10 minutes or more for metal adsorption to occur. Then, solids were separated by 3 minutes of centrifugation, and the supernatant "treated" plating waste was decanted, acidified, and saved for analysis. The solids, consisting of ferrihydrite plus associated metals, were then added to 50 mL of an acidic regeneration solution. Ten to thirty minutes reaction time was allowed before solids were separated by centrifugation, the regeneration solutions was decanted, and a sample was taken. Another 50 mL dose of plating waste was then added to the regenerated ferrihydrite to initiate another cycle. The same 50 mL of regenerant solution was used for 50 cycles, with small additions (1 to 2 mL per cycle) of deionized water and acid to replace the sample volumes removed.

Solution pH was monitored with a pH meter throughout the adsorption reaction. The desired regeneration pH was maintained with a pH stat to within ± 0.15 pH unit. The volume of acid and base used in each cycle was recorded. The reaction vessels used in these experiments were 85-mL polycarbonate centrifuge tubes, with a magnetic stir bar inserted during the adsorption and regeneration steps to maintain a visually homogeneous suspension.

Analyses. All samples were acidified with a few drops of 1 M HNO_3 preceding atomic absorption (AA) analysis. Cr(VI) was analyzed by following method 312 B of "Standard Methods"[4] with diphenylcarbazide as an indicator. Cr(III) was determined by subtraction of Cr(VI) from total Cr as determined by AA.

Results and Discussion

Metal removal as a function of pH. Soluble metal concentrations as a function of pH for six metals in systems both with and without ferrihydrite are presented in Figure 2. Throughout the pH range investigated ($3 < pH < 13.5$), removal in the system with ferrihydrite was as good as or better than that in the iron-free system for all six metals.

The pH range 8 to 12.5 is of particular interest (Figure 3). Over this wide range there was essentially complete removal (>98%) of all metals in the presence of ferrihydrite. In contrast, the system relying on precipitation for

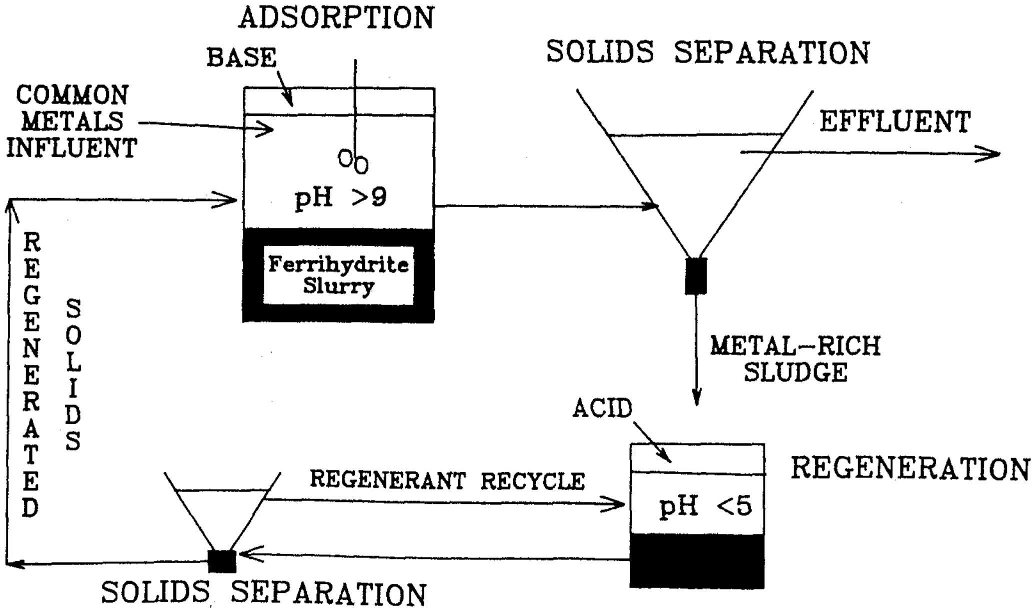

Figure 1—A process schematic for applying ferrihydrite adsorbents in metals treatment with regeneration.

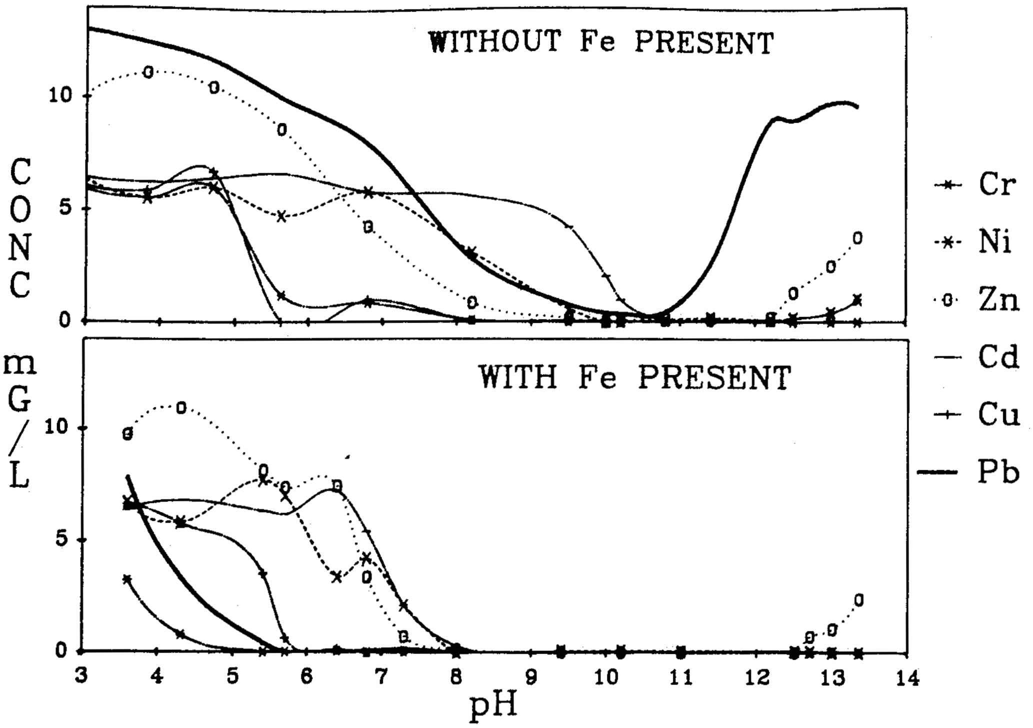

Figure 2—Soluble metal concentrations as a function of pH in systems with and without ferrihydrite present. Soluble metals determined after filtration.

metal removal had no range in which all metals could be removed simultaneously. Although Ni, Zn, Cu, and Cr were removed at pH 10, Cd was not effectively removed at pH < 11. However, as Cd approached complete removal, Pb reentered solution. At still higher pH values, resolubilization became more prevalent. It is for these

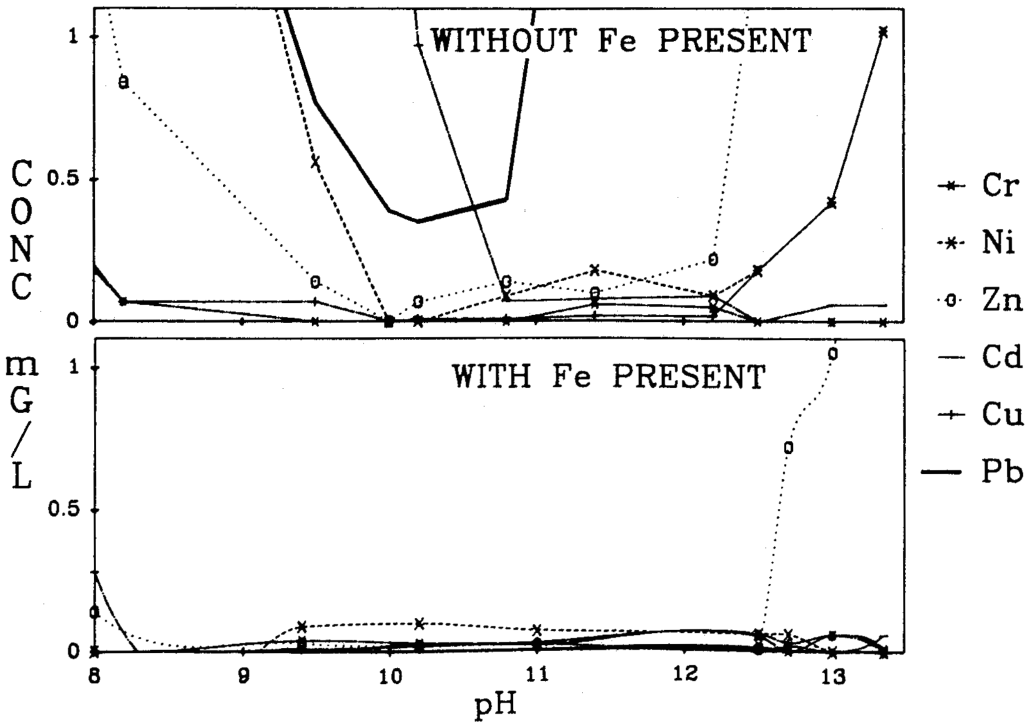

Figure 3—Soluble metal concentrations as a function of pH in systems with and without ferrihydrite present (expanded axis).

reasons that selecting a pH for precipitating multi-contaminant waste streams is so problematic.

Another significant difference between the two systems is the absolute minimum concentration of each metal that may be achieved. Figure 3 demonstrates that the minimum soluble Pb concentration attainable through precipitation was 0.4 mg/L, while the system with ferrihydrite was able to reduce soluble Pb concentration to <0.05 mg/L.

Even in the pH range where precipitation removed most metals quite effectively, metal treatment was better in the system containing ferrihydrite. It is also important to recognize that further reduction of metal concentrations could be accomplished in an adsorption-based system simply by adding more adsorbent. In a precipitation-based system, the minimum concentrations attainable are fixed by the solubility product of the solid being precipitated, and this lower limit cannot be passed.

Thus, metal removal experiments indicate several advantages of adding ferrihydrites during treatment of metal-bearing wastes, beyond the benefits conventionally attributed to its coagulant properties. Ferrihydrites allow more efficient removals over a wide pH range, encompassing both lower and higher pH regions than those where precipitation alone is effective. Because of this, systems applying ferrihydrites are much more capable of treating multi-contaminant waste streams.

Settling tests. In practice, solids produced during the treatment process are likely to be removed by some form of solids settling. The next set of tests compared the settling properties of solids generated by hydroxide precipitation with and without polymer addition, and those generated in an adsorption process. Initial Cd, Pb, Cu, Ni, Zn, and Cr(III) concentrations were 1.5 to 3.0 mg/L. Results of these tests are presented in Figure 4.

Not surprisingly, the solids settling properties in systems with coagulant (ferrihydrite or polymer) were clearly superior to those in the coagulant-free system. In the system without coagulants, removal through settling was quite poor; as much as 45% of the solids remained suspended after 50 minutes. By contrast, in the system with ferrihydrites, 90% of the suspended metals settled within 3 minutes, and only 4% remained suspended after 50 minutes. When polymer was added to coagulate the solids produced by hydroxide precipitation, they settled approximately as well as in the system with ferrihydrite.

Compounding the poorer settling in the precipitation-based systems were the soluble concentrations of metals remaining in the treated water after settling for 30 minutes (Table 1). The soluble residual in the precipitation-based systems may be high enough to violate discharge limits, even assuming complete solids removal. Therefore, although polymer may improve solids settleability, the effect on metal solubility (through coagulation of colloids filterable through a 0.45-millipore filter) is not significant.

Regeneration and reuse of the ferrihydrite. In the next series of experiments, a single batch of ferrihydrite was regenerated with acid and reused in treating 50 batches of a 1:67 dilution of Solution 1. In particular, we wished to assess whether repeated regeneration and reuse of the ferrihydrite would alter its ability to adsorb the metals. Two sets of experiments were conducted to test the feasibility of the regeneration scheme outlined in Figure 1, with solids being regenerated at pH 3.5 in one and 4.5 in

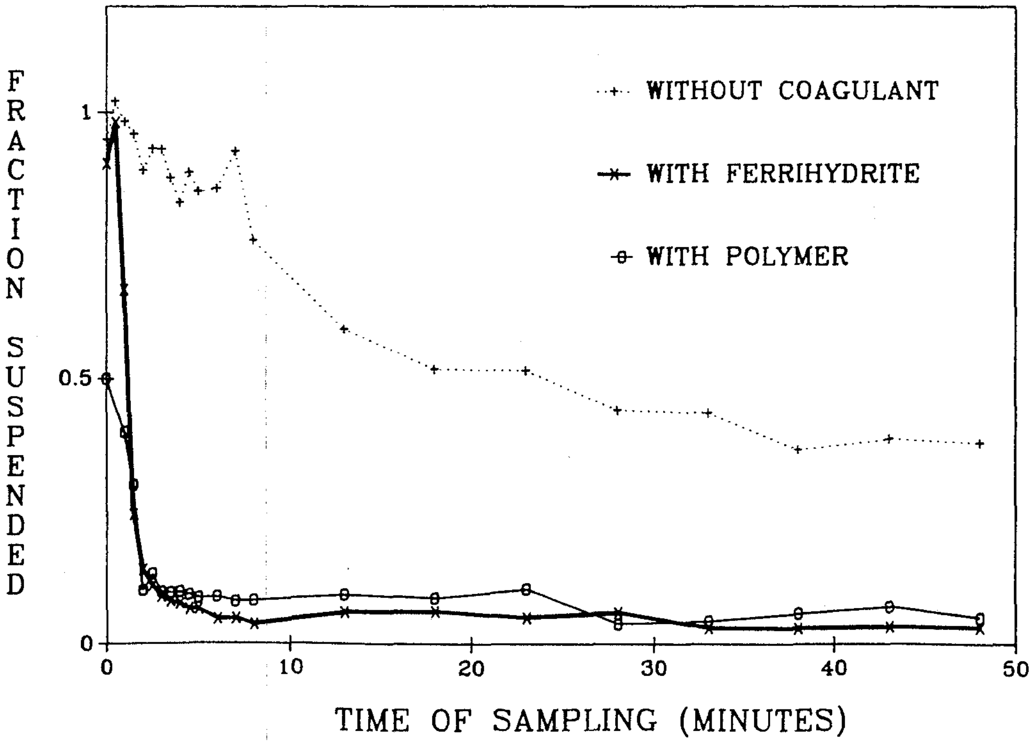

Figure 4—Settling of metals from solution in systems with and without ferrihydrites present.

Table 1—Filterable metals after 30-minute settling.

System	Metal	
	Cd	Pb
Hydroxide precipitation	0.13	0.43
Precipitation with polymer addition	0.11	0.28
Ferrihydrite adsorbent/coagulant	<0.02	<0.05

the other (both ± 0.15 pH unit). The pH of the adsorption steps ranged from 8.9 to 10.6 in both sets.

Effluent concentrations of all metals after each metal-removal step in treating 50 successive batches of synthetic waste are presented in Figure 5a (regeneration pH 4.5). Influent metals concentrations are indicated with the labeled horizontal lines between 2.1 and 3.0 mg/L, while effluent concentrations are compressed along the x-axis. Several of the small spikes observed in the effluent were likely caused by solids carryover during supernatant decanting. Cr(VI), denoted by the data set near influent levels, was not appreciably adsorbed in any of the runs. This was expected, as Cr(VI), an anion, is sorbed by ferrihydrites only at much lower pH's.[5,6]

Small spikes of Cr(III) appear consistently, but these are artifactual. Cr(III) was quantified by subtracting the measured Cr(VI) concentration from the measured total Cr concentration. Small errors in measuring either of these two larger values could easily account for a calculated concentration of a few tenths of a mg/L Cr(III) in the sample.

The effluent metal concentrations that were attained are more apparent in Figure 5b, which presents data for 10 cycles from Figure 5a with an expanded concentration axis. The horizontal line in the graph indicates the maximum allowable effluent Cd concentration for compliance with the EPA's New Source Pretreatment Standard (NSPS) Maximum Monthly Average, the most stringent EPA discharge guideline.[7] Over the course of treating 50 batches of synthetic waste, Cd was removed to below this level with only one exception (not appearing in Figure 5b). NSPS compliance levels for the other metals in the waste were at least 20 times higher than that of Cd and were attained quite easily. Equally satisfactory results were obtained in the run using pH 3.5 regeneration. No loss in metal removal efficiency was observed over 50 cycles for any metal when synthetic waste with either a pH 3.5 or 4.5 adsorbent regeneration step was used.

Metal recovery in acid regenerant solution. Figure 6 presents data describing the release of Cu and Cr(III) from the ferrihydrite to the pH 3.5 and 4.5 regenerant solutions. Also presented for comparison are the concentrations that would be found if all of the metals previously removed were released. Because all cations in the system were essentially completely removed from the influent in all cycles, and because the volumes of the influent and regenerant batches were the same, the potential metal concentration in the regenerant solution at any time equals (Influent Concentration) × (Cycle Number).

Nearly all of the Cu removed from the waste stream was released to the regenerant solution after each cycle during the pH 3.5 regeneration, while ferrihydrite regenerated at pH 4.5 retained a small portion of the collected Cu.

Metal retention on the ferrihydrite was more significant for Cr(III) than for Cu. Initially, adsorbed Cr(III) remained firmly bound to the ferrihydrite, even at pH 3.5. As the experiment progressed, the concentration in the regeneration solution eventually became measurable and thereafter increased steadily. The same pattern was observed in both experiments, but Cr(III) appeared first and in greater concentrations in the pH 3.5 compared to the pH 4.5 solution.

Cd, Zn, and Ni were nearly completely recovered in the regenerant solution regardless of regeneration pH.

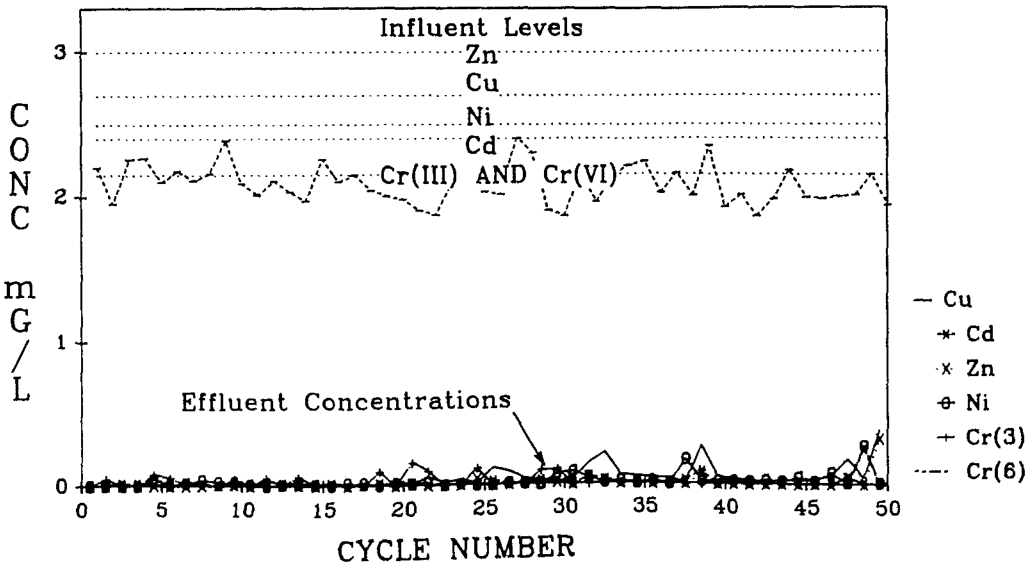

Figure 5a—Effluent metals concentrations. Influent concentrations are horizontal lines between 2.1 and 3.0 mg/L.

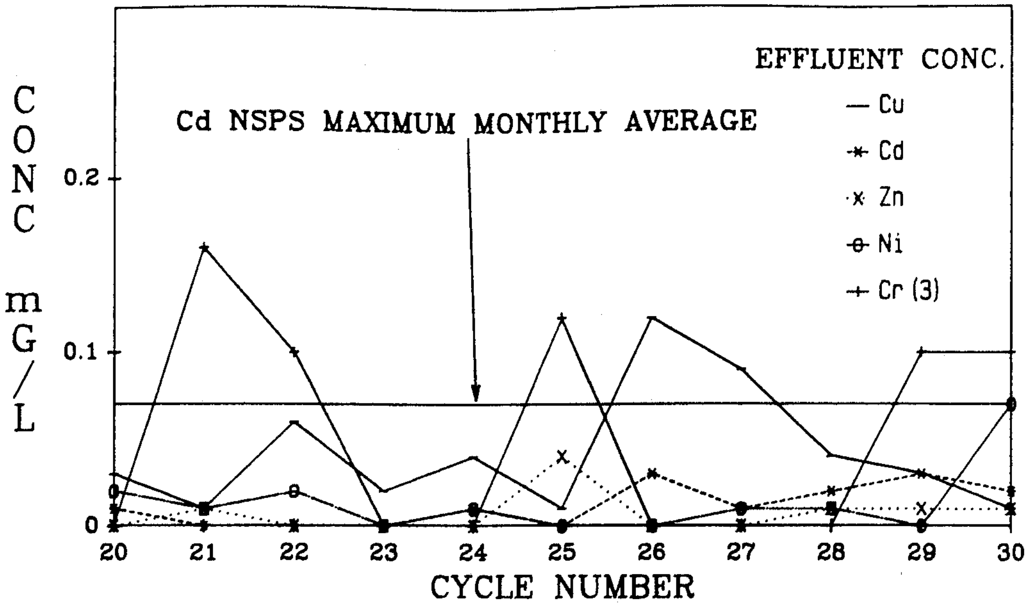

Figure 5b—Effluent metals concentrations over 10 of the 50 batch metal-removal cycles described in Figure 5a.

Cr(VI) did not appear in the regenerant, as it was not significantly removed during the metal removal step.

Characterization and treatment of real-waste influent. After success in treating synthetic wastes, the process was applied to treat real waste from a plating job shop. The metal concentrations in the 7 samples of real waste collected are presented in Table 2. The pH of the samples ranged from 6.0 to 9.7. As would be expected at these pH's, most of the metals were present in particulate form.

The range and average of concentrations observed are fairly typical of mixed-metal plating waste streams, with most metals averaging between 1 and 3 mg/L. The average Cd concentration of 5.7 mg/L is nearly an order of magnitude higher than the reported industry average of 0.613 mg/L.[2] Another difference between this waste and a typical plating waste stream is the presence of Cr(VI), as most shops reduce Cr(VI) to Cr(III) before treatment.

The results obtained using a single batch of ferrihydrite

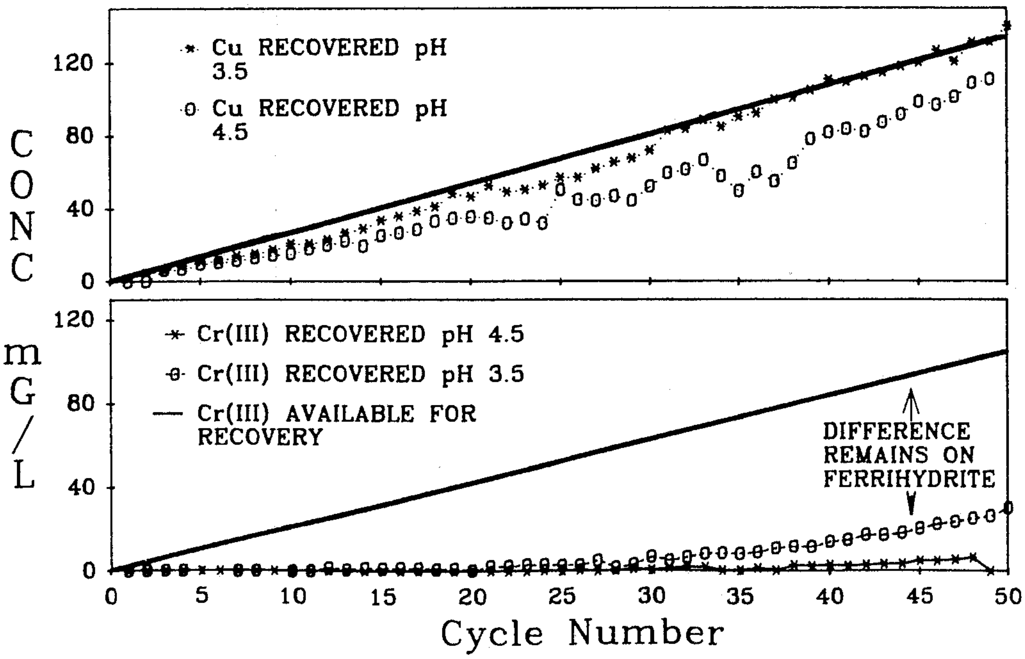

Figure 6—Cu and Cr(III) buildup in the ferrihydrite regenerant solution as a function of regeneration cycle number.

Table 2—Range and average of metal contaminant concentrations in real-waste samples.

Metal	Cr(VI)	Cr(III)	Ni	Zn	Cd	Cu
Average soluble, mg/L	3.0	0.4	0.2	0.2	0.8	0.1
Average particulate, mg/L	0.0	1.1	1.8	1.2	4.9	1.0
Range, mg/L*	0.9–6.1	0–2.6	1.2–4.2	0.7–3.3	1.9–12.5	0.2–2.0

* Range given for total concentrations.

to treat 50 batches of real-waste influent were similar to those observed earlier in the synthetic waste (Table 3). Removals were essentially complete for all wastestream cations, while Cr(VI) was not appreciably removed in the adsorption step. No detectable loss in metal removal efficiency was observed over the 50 cycles.

The pH values in the regeneration step for real waste varied from 2.9 to 6.9. At the high end of this pH range, metals other than Cd and Ni are nearly completely retained on the ferrihydrite. No loss in metal removal efficiency was observed in effluents following these unintentional "process upsets."

Process efficiency. Average effluent concentrations attained over 50 metal-removal cycles for all the experiments are summarized and compared in Table 3, along with applicable standards.[7] For the experiments using synthetic waste influents, cation removals were >98% and approached experimental detection limits. Cd concentrations in the treated effluent are on the order of primary drinking water standards (<0.01 mg/L). Treatment was about equally effective regardless of whether regeneration was accomplished at pH 3.5 or 4.5. There were no dramatic differences in treating synthetic and real wastes, and the small differences observed may be attributed to higher particulate and initial metal concentrations in the real-waste influents.

Because the majority of the influent and effluent metals from the experiment with real waste were in the particulate fraction, another experiment was conducted to evaluate removal of soluble metals by using filtered real waste as the influent. The average results from 50 treatment cycles using this influent are also presented in Table 3 and indicate that even at very low initial metal concentrations, adsorption is a very effective treatment process.

Effluent Cu, Zn, Ni, and Cr(III) concentrations met standard limits[7] without exception for both real and synthetic wastes. Effluent Cd limits were exceeded by 0.02 mg/L when treating the real waste, in spite of greater than 98% removals (average influent 5.7 mg/L). A substantial portion of the total Cd escaped removal in just a few of the 50 samples, suggesting solids carryover into the decanted effluent during those cycles. Elimination of three of these spikes would have decreased average effluent values to 0.04 mg/L. As similar spikes were seen for all metals in the system, it would appear that solids separation is a limiting factor in minimizing effluent concentrations. This problem can be overcome by immobilizing the ferrihydrite on a filter media such as sand.[8]

Mass balances for the metal cycling experiments. A mass balance was completed on all of the metals used in the study to determine their ultimate destinations in the proposed treatment process. The results for Cu in the synthetic waste system with pH 4.5 regeneration are shown schematically in Figure 7, and the results for all the systems studied are summarized in Figure 8. At the end of the 50 cycles, the majority (78%) of the influent Cu had been concentrated in the regenerant solution, while about 2% had escaped in the process effluent. The remaining 20% was attached to and cycling with the ferrihydrite, but was not interfering in any measurable way with the adsorption process. As noted earlier, this Cu could be released to the regenerant solution by regenerating at a lower pH. The mass balances closed reasonably well for all of the other metals in the system.

Acid and base requirements. The approximate acid/base requirements of treatment through precipitation versus adsorption plus regeneration are given in Table 4 (in which the values for $FeCl_3$ are calculated assuming all the Fe

Table 3—Average effluent concentrations attained over 50 metal removal/regeneration cycles.

	Synthetic waste		Real waste			
	Regeneration		Regeneration at pH 3.5			
Metal	pH 3.5	pH 4.5	Filtered	Unfiltered	EPA NSPS** monthly average	EPA NSPS daily maximum
Cu	<0.03	0.04	<0.03	0.09	2.07	3.38
Cd	0.01	0.01	0.01	0.09	0.07	0.11
Zn	0.04	0.01	0.01	0.07	1.48	2.61
Ni	0.03	0.03	<0.02	0.07	2.38	3.98
Cr (3)	<0.05	<0.05	<0.10*	<0.10*	Total chrome	Total chrome
Cr (6)	2.01	2.00	3.36*	3.51*	1.71	2.77

* = Calculated for 32 cycles.
** = EPA NSPS standards given for comparisons.

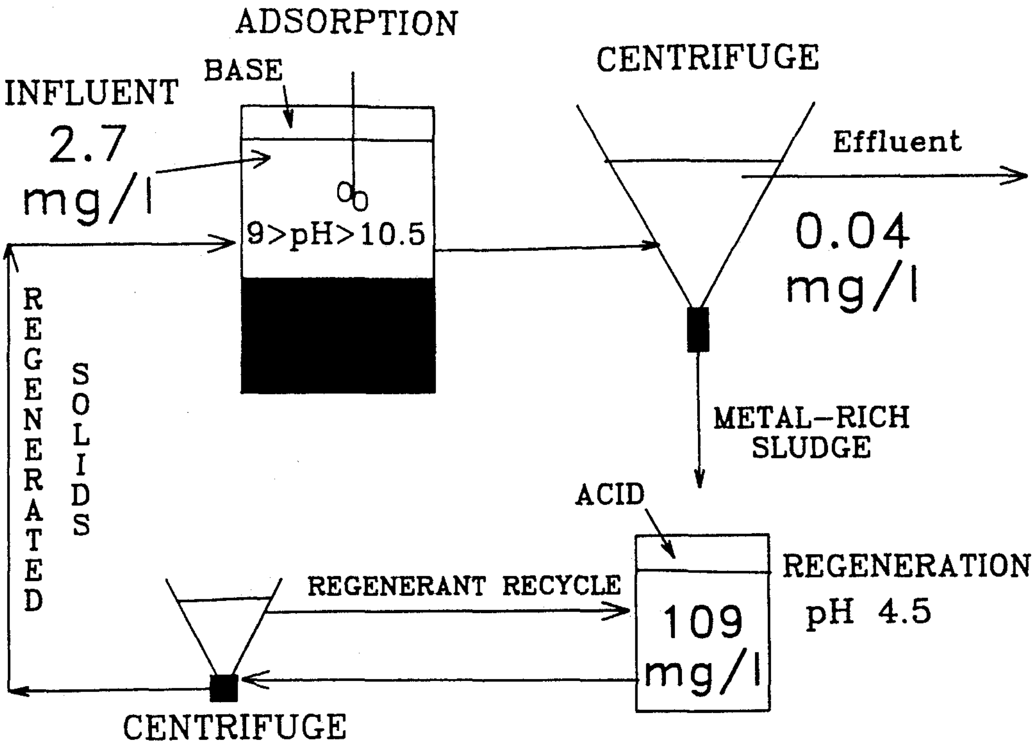

Figure 7—Schematic mass balance showing the disposition of Cu after 50 treatment cycles.

precipitates as $Fe(OH)_3$). Reagent requirements depend primarily on the quantity and type of adsorbent or coagulant used in each process. A process using 10^{-2} M ferrihydrite regenerated at pH 3.5 would require nearly 5 times the acid or base of conventional treatment with a non-acidic coagulant. However, a conventional precipitation process using 10^{-3} M $FeCl_3$ as coagulant requires nearly the same amount of reagent as a regeneration scheme cycling 10^{-2} M ferrihydrite.

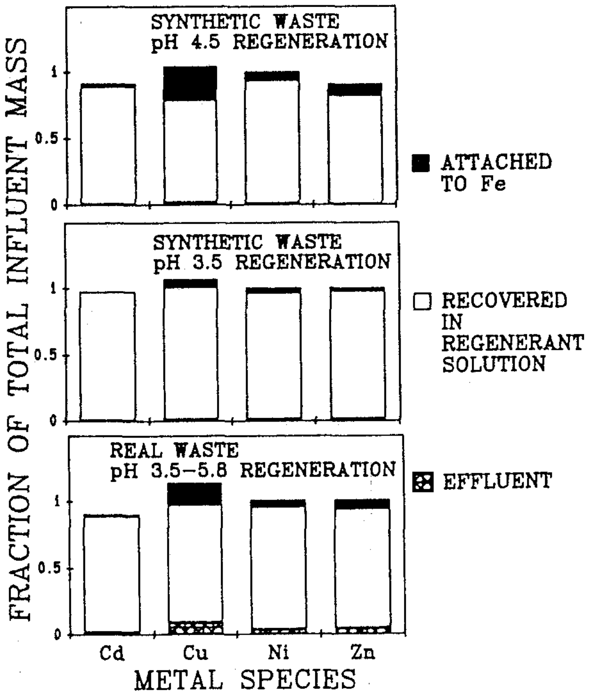

Figure 8—Mass balance showing the final disposition of the metals in all systems studied.

Additional savings may be realized through optimization of the regeneration process. For instance, because most of the acid or base used for regeneration simply overcomes ferrihydrite buffering capacity, reducing the frequency of regeneration could lead to considerable chemical savings. For example, if two batches of waste were treated before each regeneration step, the chemicals required would be reduced by about 40%.

A complete economic comparison of adsorption versus precipitation would have to consider tankage, sludge treatment and disposal costs, the effluent limits that must be attained, and the costs of the coagulants themselves. However, the overall indication is that differences in chemical costs between the two processes are not very significant.

Potential separation of metals using ferrihydrite. One experiment was conducted to evaluate the ability of the ferrihydrite to release metals at different pH values as a means of selective metal recovery. In this experiment, base (NaOH) was added to a suspension containing the ferrihydrite adsorbent and acid regenerant solution from 50 treatment cycles with real waste until a pH of 10 was achieved. The suspension was then acidified from pH 10 to 3 in increments, with a 10-minute equilibration period at each pH. At the end of each period, the entire solution volume was decanted and replaced with a fresh solution. The concentrations of metals recovered in the sequential batches are given in Table 5.

Table 4—Comparison between pH requirements of adsorption and precipitation for metal removal.

Process	Metal removal	Coagulant neutralization	Regeneration	Total
Adsorption (0.01 Fe(III))				
pH 3.5 regeneration	3.3	0.0	2.4	5.7
pH 4.5 regeneration	3.3	0.0	2.1	5.4
Precipitation				
No coagulant	1.2	0.0	0.0	1.2
0.001 M $FeCl_3$	1.2	3.0	0.0	4.2

Table 5—Metal recovered at the pH indicated from the process end-products (ferrihydrite plus regenerant solution) after 50 cycles.

	pH								
Metal	**3.0**	**3.8**	**4.2**	**5.4**	**6.0**	**7.7**	**8.5**	**8.5**	**9.0**
Cr(VI), mg/L	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
Cr(III), mg/L	0.7	1.5	0.5	0.0	0.0	0.0	0.0	0.0	0.0
Ni, mg/L	0.0	5.5	8.1	5.5	4.0	5.0	2.6	0.3	0.3
Zn, mg/L	0.8	4.5	11.5	9.5	6.3	3.0	0.5	0.0	0.0
Cd, mg/L	0.5	5.0	17.3	19.8	20.8	27.8	18.8	1.7	1.2
Cu, mg/L	10.0	10.8	17.5	1.5	0.3	0.1	0.0	0.0	0.0

Most of the Cd and Ni desorbed over a range of 4 pH units, from about pH 8 to 4, while the Cu and Cr desorbed over a more acid pH range. Although there was some preferential dissolution of Cd at high pH, separation of cations was generally not impressive. Potentially, greater selectivity could be achieved using longer regeneration times and smaller pH increments.

Summary and Conclusions

These experiments compared several aspects of two treatment processes for metal-bearing wastes: hydroxide precipitation and adsorption to ferrihydrite. In general, ferrihydrites removed an equal or greater percentage of soluble Cu, Cd, Zn, Cr(III), Ni, and Pb from a synthetic-waste solution at all pH's. Ferrihydrites allowed highly efficient removals of metals from solution over the pH range 8 to 12.5, while precipitation was not similarly successful at any pH. Cr(VI) was not removed efficiently by either process.

Settling tests with a synthetic waste indicated that particulate metals settle out of solution about as well in a system containing ferrihydrite as in a conventional precipitation system to which an anionic polymer has been added. However, the ferrihydrite system would be preferred based on lower soluble metal residuals.

Ferrihydrite can be regenerated and reused to adsorb metals with no measurable loss in metal removal efficiency. For the conditions tested, the regeneration process could be repeated at least 50 times using both real and synthetic wastes. In light of the short reaction times applied in these experiments (10 minutes), the process is rapid enough for most industrial applications.

In our experiments, metal concentrations in the regenerant solution gradually increased to a few hundred mg/L, and there is every indication that much greater concentrations could be achieved. Ultimately, these metals could be collected (for example, by precipitation or electrolytic recovery) and sold or possibly returned to the process lines.

Differences in chemical costs between adsorption with regeneration and precipitation are not very significant. As regeneration effectively separates ferrihydrite from any sludge that may be produced, it now appears possible to attain the advantages of adsorption without significant economic cost.

Acknowledgments

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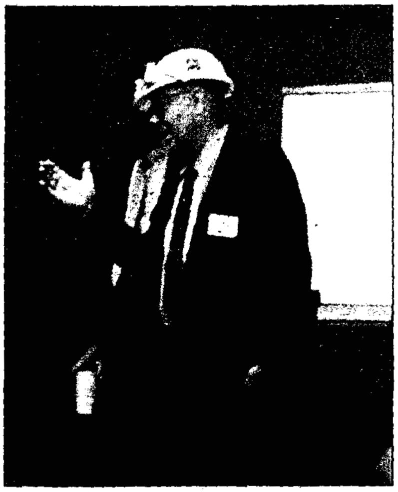

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Cover: Optimization is the task of activated sludge treatment professionals in the U.S. and United Kingdom, as reported by the Canham scholar on p.446. The photo shows the ceramic fine bubble aeration system in Albuquerque, New Mexico.

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