

# USE OF IRON OXIDES TO ENHANCE METAL REMOVAL IN CROSSFLOW MICROFILTRATION

By Lloyd Emil Voges,<sup>1</sup> P.E., Mark M. Benjamin,<sup>2</sup> and Yujung Chang<sup>3</sup>

**ABSTRACT:** This research investigated whether iron oxyhydroxides used in conjunction with microfiltration could improve the removal of metals from a waste while maintaining adequate flux. Filtration of individual metals, a mixture of metals, and the mixture with two iron oxides were investigated. The research indicated that use of a coagulant (an iron-containing salt) might not be as important in microfiltration systems as in conventional gravity separation systems, because of the small pore size of microfilters. In some cases, filtration efficiency was relatively poor at the beginning of a treatment cycle, but in almost all cases it became excellent once a layer had built up on the membrane surface. The greatest benefit provided by iron oxides might be to reduce membrane fouling. A crystalline iron oxide such as goethite is more attractive than ferrihydrite. The flux improvement with goethite is greatest if a thin layer is deposited on the membrane surface before the contaminant metals are injected into the system, so that the goethite can trap the potentially foulant metal hydroxide particles away from the membrane surface.

## INTRODUCTION

Wastewater from metal finishing processes typically contains a number of metals whose release to the environment or to a municipal wastewater treatment facility is regulated. Conventional treatment for the metals involves chemical additions to insolubilize them (e.g., by precipitation or adsorption) followed by sedimentation and/or filtration. Often, the metal precipitates that form in such systems are coagulated and flocculated to ease their separation from solution. However, conventional coagulants (e.g., alum, ferric chloride) add significantly to the amount of sludge generated and can significantly increase the resistance to water flow through filters.

Microfiltration is being used increasingly to separate solids from solution in industrial waste treatment because of its efficiency and compactness (Broom et al. 1994). The major limitation to the use of this technology is that microfilters are more likely to clog than conventional filters, and the deposits that cause clogging can be very difficult to dislodge or dissolve. Coagulant addition might improve metal removal in microfilters as it does in conventional processing, but it would also increase the total solids loading on the filter and the mass of solids ultimately requiring disposal. While the increased filter loading can exacerbate membrane fouling, research investigating the removal of organics from water shows that, in some cases, addition of preconditioned coagulants can reduce fouling (Pirbazari et al. 1992; Chang and Benjamin 1996; Chang et al. 1998).

This research investigated the performance of a combined precipitation/coagulation/microfiltration process for treating various metal-bearing wastes. The coagulants used were iron oxyhydroxides prepared from simple Fe-containing salts. The specific objective of the research was to develop an understanding of the effects of the dose and type of iron oxide on metal removal and on permeate flux through the membrane, and to use that understanding to optimize the overall treatment process. The treatment system investigated in the research was designed to simulate a full-scale process at the Boeing Defense

and Space Group Facility in Kent, Wash., which treats a variety of waste streams from electroplating and other metal finishing operations.

## BACKGROUND

### Metal Treatment by Precipitation and Membrane Filtration

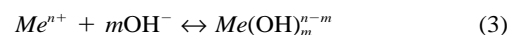
The precipitation of a metal hydroxide solid can be represented by the following reaction:



At equilibrium, the concentration of free metal ion ( $Me^{n+}$ ) in contact with the solid is controlled by the solubility product

$$K_{so} = \frac{(Me^{n+})(OH^{-})^n}{[Me(OH)_n(s)]} \quad (2)$$

where the activity of  $Me(OH)_n(s)$  equals 1.0 for the pure solid. Soluble metal hydroxide complexes can also form in such systems by reactions of the type



In the absence of complexing ligands other than hydroxide, the total concentration of soluble  $Me$  species in equilibrium with the solid is

$$[Me(aq)]_{tot} = (Me^{n+}) + \sum_{m=1}^N [Me(OH)_m^{n-m}] \quad (4)$$

$$[Me(aq)]_{tot} = (Me^{n+})[1 + \beta_m(OH^{-})^m] \quad (5)$$

where  $\beta_j$  = overall complexation constant for formation of  $Me(OH)_m^{n-m}$ . Because the formation of cationic metal species (species with  $m < n$ ) decreases with increasing pH while that of anionic species (with  $m > n$ ) increases, the total solubility of most metals passes through a minimum at some pH. The theoretical solubility (Schecker 1994) of the metals investigated in the current research are shown as a function of pH in Fig. 1.

Coprecipitation of a mixture of metals can generate a solid solution in which the activity of each individual metal hydroxide solid is less than unity. In such a case, the activity (solubility) of  $Me^{n+}$  ions must decrease to satisfy (2), reducing the total metal solubility below that given by (5). The solubility of a contaminant metal can also be lowered below that given by (5) if it adsorbs onto other precipitated metals, e.g., onto Fe oxide in systems where an Fe-based coagulant has been added. Thus, in mixed metal systems, conventional treat-

<sup>1</sup>Engr., Kennedy/Jenks Consultants, 530 South 336 St., Federal Way, WA 98003.

<sup>2</sup>Prof., Dept. of Civ. Engrg., Univ. of Washington, Seattle, WA 98195.

<sup>3</sup>Nat. Dir., Advanced Water Treatment, HDR Engineering, Inc.

Note. Associate Editor: Mark Wiesner. Discussion open until October 1, 2001. To extend the closing date one month, a written request must be filed with the ASCE Manager of Journals. The manuscript for this paper was submitted for review and possible publication on December 1, 1998; revised June 27, 2000. This paper is part of the *Journal of Environmental Engineering*, Vol. 127, No. 5, May, 2001. ©ASCE, ISSN 0733-9372/01/0005-0411-0419/\$8.00 + \$.50 per page. Paper No. 19733.

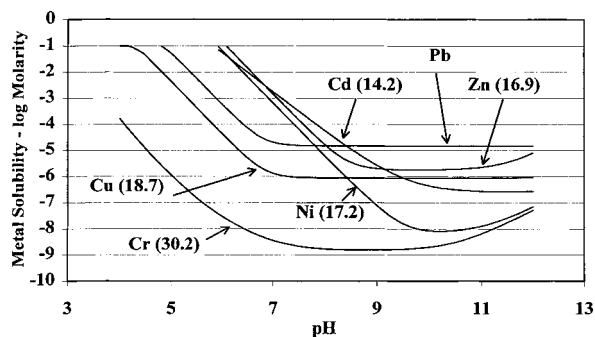


FIG. 1. Solubility of Metals Studied in This Research as a Function of Solution pH and as Modeled by Mineql<sup>+</sup>. [Solubility Products (pK<sub>sp</sub>) Are Shown in Parentheses, No K<sub>sp</sub> Is Given for Pb because of Many Different Insoluble Hydroxide Complexes It Can Form]

ment can sometimes remove metals from solution to concentrations lower than can be achieved in single-metal systems. For instance, Edwards and Benjamin (1988) demonstrated that the solubility of six common metals is less in a coprecipitated mixture than when each metal is present alone. When iron was present in the mixture [as ferrihydrite, Fe(OH)<sub>3</sub>], the solubility of other metals was greatly reduced over a wide pH range.

### Crossflow Microfiltration

Membrane filters with pore sizes ranging from 0.005 μm to >1 μm (ultrafiltration to microfiltration) have been used to filter colloidal or flocculated metal precipitates (Broom et al. 1994). In such filters, particles are removed by size exclusion (sieving), by impact on and binding to pore walls, and/or by being trapped in a cake layer of previously removed particles adjacent to the membrane surface.

Water flow through membrane filters is a function of the transmembrane pressure and the hydraulic resistance imparted by the membrane itself and by contaminants that accumulate on or in the membrane. The flow rate of permeate per unit area of filter surface is called the permeate flux, *J*, and can be represented as the ratio of the transmembrane pressure (Δ*P*) to the product of the viscosity (μ) and the hydraulic resistance (*R*)

$$J = \Delta P / \mu R \quad (6)$$

which is sometimes written as

$$J = j \Delta P \quad (7)$$

where  $j = 1/\mu R$  and is defined as the "specific flux."

The total resistance to flow through a membrane is sometimes divided into components attributed to the membrane itself (*R<sub>m</sub>*), material that enters into and partially blocks the pores (*R<sub>p</sub>*), and material that accumulates on the surface of the membrane as a cake (*R<sub>c</sub>*)

$$R = R_m + R_p + R_c \quad (8)$$

*R<sub>m</sub>* can be determined under conditions where clean water is filtered through a clean membrane. In treatment applications, *R<sub>m</sub>* is usually considerably smaller than one or both of the other contributors to the overall resistance. The resistance contributed by contaminants that have been removed from the water (*R<sub>p</sub>* + *R<sub>c</sub>*) is commonly referred to as membrane fouling.

The extent of fouling is controlled by complex interactions related to the solids concentration, particle morphology, membrane pore size, and surface chemistry. When particles first enter a microfiltration system, some are transported to the filter surface and into the pores, causing the sum of *R<sub>c</sub>* + *R<sub>p</sub>* to increase and the flux to decline. As more water is processed, the accumulation of particles at the surface continues, but usu-

ally at a decreasing rate due to the reduction in the flux. Often, the flux declines rapidly at the beginning of a run to levels significantly below that through the clean membrane. In practice, once hydraulic resistance caused by fouling increases to some predetermined value, the membrane is usually backwashed in an attempt to remove the accumulated material. If this approach is unsuccessful, more severe cleaning approaches (often involving addition of chemicals to dissolve the accumulated material) might be used.

One approach for minimizing fouling is to induce relatively rapid water flow along the filter surface. Such a flow, referred to as tangential flow or crossflow, is relatively easy to incorporate into the system if tubular filters are used. Crossflow imparts a sweeping action to the top of the cake layer, limiting particle buildup. Under crossflow conditions, a layer of particles deposited on the membrane is sometimes referred to as a dynamic membrane, because it can shrink or grow as a function of crossflow velocity, transmembrane pressure, and the concentration of solids in the influent. In some cases, dynamic membranes are intentionally deposited to improve particle removal, i.e., to act as a precoat filter. If the precoat layer contains adsorbent particles, it might further enhance permeate water quality by adsorbing dissolved contaminants as the water passes through it (Pirbazari et al. 1992; Chang and Benjamin 1996; Chang et al. 1998).

### Adsorption of Metals on Iron Oxides

This project investigated two types of iron oxides (ferrihydrite and goethite) as potential adsorbents and/or coagulants for the target metals. Ferrihydrite [Fe(OH)<sub>3</sub>] is the amorphous, gel-like iron oxide that precipitates in most systems when ferric chloride or ferric sulfate is used as a coagulant, whereas goethite (α-FeOOH) is a well-defined crystalline phase. Although both goethite and ferrihydrite are very insoluble, goethite is considerably less soluble than ferrihydrite, especially in acidic solutions. Both ferrihydrite and goethite are good adsorbents for metals (Benjamin and Leckie 1981; Benjamin 1983; Anderson and Benjamin 1985; Johnson 1990; Coughlin and Stone 1995). The research investigated whether use of these iron oxides in conjunction with microfiltration could improve the removal of metals from a waste while maintaining adequate flux through the membrane.

## MATERIALS AND METHODS

### Synthetic Waste Solutions

Tests were conducted using two simulated metal-finishing waste solutions containing six target metals. The compositions of these solutions, prepared using metal nitrate salts and deionized water, are summarized in Table 1. The ratios of the different metals were chosen based on analyses of sludges from the full-scale treatment system being simulated. The total metal concentration in the simulated wastes are larger than would typically be found in metal finishing wastewater. The intent was to precipitate the metals to simulate the concentrated suspension that builds up in a microfiltration system

TABLE 1. Metal Concentrations in Concentrated Synthetic Wastes Used in Research

Target metal	Synthetic waste No. 1	Synthetic waste No. 2
Cd	10	100
Cr	125	400
Cu	25	300
Ni	20	100
Pb	20	100
Zn	15	100

after a substantial amount of metals have been retained, rather than simulating the relatively dilute wastewater that is fed to such systems.

## Iron Oxides

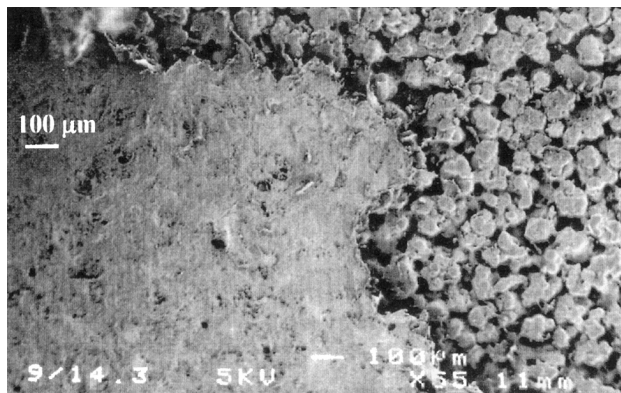
Ferrihydrite and goethite were both synthesized from a stock solution containing 1.0 M  $\text{Fe}(\text{NO}_3)_3$ . Ferrihydrite was precipitated immediately prior to each test by neutralizing an aliquot of stock solution using sodium hydroxide. Goethite was prepared in 1-L batches following the procedure of Schwertmann and Cornell (1991), which yields relatively pure crystals with an acicular shape. Next, 50 mL of 1 M  $\text{Fe}(\text{NO}_3)_3$ , 90 mL of 5 M KOH, and 860 mL deionized water were mixed in polyethylene bottles, yielding a suspension with  $\text{pH} > 13$ . The suspension was aged for 60 h at  $70^\circ\text{C}$ , producing approximately 4.5 g of goethite. Batches were rinsed, settled, and decanted twice, achieving more than a 100-fold dilution of the ions present in solution. Several batches were combined, and the suspension was diluted to 1% suspended solids and stored for future use.

## Sludge Sample from Full-Scale Facility

A sludge sample containing approximately 0.6% suspended solids (6,000 mg/L dry solids) was taken from the full-scale treatment system at Boeing and was used in some experiments. The sludge contained 2,800 mg/L Fe (467 g Fe/kg of dry solids). Assuming that the iron was present in the sludge as ferrihydrite, with chemical formula  $\text{Fe}(\text{OH})_3$ , this solid accounted for 90% of the total mass of solids in the sludge ferrihydrite (900 g ferrihydrite/kg solids). The source of this iron in the sludge was  $\text{FeSO}_4$  that had been added as a coagulant. The concentrations of regulated metals in the sludge, as a weight fraction of the total dry solids, were: 0.25 g/kg Cd; 22.8 g/kg Cr; 6.83 g/kg Cu; 2.83 g/kg Ni; 1.67 g/kg Pb; and 3.17 g/kg Zn. These regulated metals were present either as precipitates or adsorbed on the ferrihydrite solids.

## Microfiltration Filters

The filters used in the experiments were 2.86-cm inner-diameter tubular microfilters that were identical to those in use at the full-scale facility. The filters consisted of a thin polypropylene membrane attached to the inner surface of a 2-mm-thick polyethylene support tube. A scanning electron micrograph of the inner wall of a sample of filter (Fig. 2) reveals pores in the membrane in the size range from  $<1 \mu\text{m}$  to  $50 \mu\text{m}$ . For use in the experiments, the filters were sectioned into 30-cm lengths, each having  $0.0274 \text{ m}^2$  of surface.



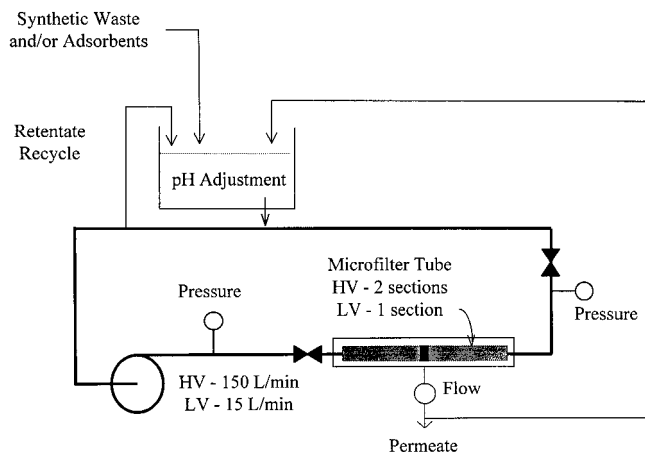
**FIG. 2.** SEM Photograph of Surface of Tubular Microfilter (Polypropylene Film Is Visible on Left Side of Photograph; This Layer Was Removed from Section on Right To Show Support Structure)

## Experimental Methods

Metal behavior was studied in both batch and continuous flow systems. The batch experiments were conducted as controls, providing a point of comparison for the efficiency with which metals could be removed by the microfiltration systems. In the batch experiments, the metal solution was prepared in 500-mL beakers and the pH was adjusted by a predetermined addition of NaOH. The solution was then mixed for 10 min before a sample was taken and passed through a  $0.45\text{-}\mu\text{m}$  filter for subsequent analysis. Another aliquot of NaOH was then added, and the procedure was repeated.

The microfiltration system used in the research is shown schematically in Fig. 3. Two types of experiments were conducted. In one, a suspension containing the solids of interest was pumped into the crossflow microfiltration system, and the system was pressurized to initiate permeate flow. The system was operated continuously, with both the permeate and retentate recycled back to the influent reservoir, where pH was maintained at the desired value by addition of NaOH or  $\text{HNO}_3$ . These tests are referred to below as semibatch tests, because they were batched with respect to the influent metals, even though the filtration system was operated continuously. In the other experiments, a stream containing a low (relative to the semibatch tests) concentration of soluble metals was continuously fed to the microfiltration system. The influent metals were precipitated in the feed reservoir by NaOH addition, and permeate was not recycled. These experiments are referred to as continuous-flow experiments. The permeate flux and the concentration of metals in the permeate solution were monitored over time in both types of experiments. When iron oxide particles were added to the treatment system, they were injected prior to feeding the simulated waste stream, in order to form a precoat layer of iron oxide particles on the membrane surface.

As indicated in Fig. 3, the microfilter was operated using two different flow rates in the circulation loop, i.e., two different crossflow velocities. Most tests were conducted using one filter section, a crossflow velocity of 0.3 m/s, and a feed pressure maintained steadily at 0.5 bar (7.5 psi). In these experiments, the vast majority of the solids in the circulation loop deposited on the filter surface, leaving a clear circulating fluid. A few tests used a higher crossflow velocity (3 m/s), two filter sections in series, and a feed pressure of 0.7 bar. Two filter sections were used in the system with a higher crossflow velocity in order to increase the volume of water in the circulation loop, and thereby prevent a significant temperature increase. In these latter tests, a substantial fraction of the solids



**FIG. 3.** Setup and Operating Parameters for Crossflow Filtration Systems Used In This Research (LV and HV Refer to Low and High Velocity Crossflow Experiments, Respectively; Retentate and Permeate Solutions Were Recycled to Feed Reservoir Only in Semibatch Experiments)

**TABLE 2.** Operating Characteristics of Systems in Which Layer of Solids Was Coated on Microfilter

Metal	Mass of metal ion (mg)	Suspension pH	Mass of Me(OH) <sub>3</sub> (s) applied (mg)	Specific flux, $j$ $\left(\frac{L}{m^2 \cdot h \cdot kPa}\right)$	Hydraulic resistance, $R$ $(10^{10} m^{-1})$
Cd	600	12	785	0.66	9.1
Cr	600	8.5	1188	0.36	16.7
Cu	600	12	921	0.10	60
Ni	600	12	947	0.15	40
Pb	600	12	698	0.50	12
Zn	600	12	912	0.20	30
Synthetic waste No. 2	600	10	1060	0.20	30
Ferrihydrite	525	10	1000	0.74	8.1
Plant sludge	~38	10	1000	0.096	62.5
Goethite	0	10	1000	0.144	41.7

remained in the circulating fluid at all times. Regardless of which crossflow velocity was used, the circulating flow caused the solids to be fairly evenly deposited along the filter surface. The reasons for using the different crossflow velocities are explained later.

### Analytical Methods

Metal samples were acidified with HNO<sub>3</sub> and then analyzed on an Ultrace inductively coupled argon plasma atomic emission spectrometer (ICP), model JY 138 (Jobin Yvon Emission). Permeate flow rate was measured using a Inline Flow Captor Type 4311.30 (Weber Sensors, Inc.).

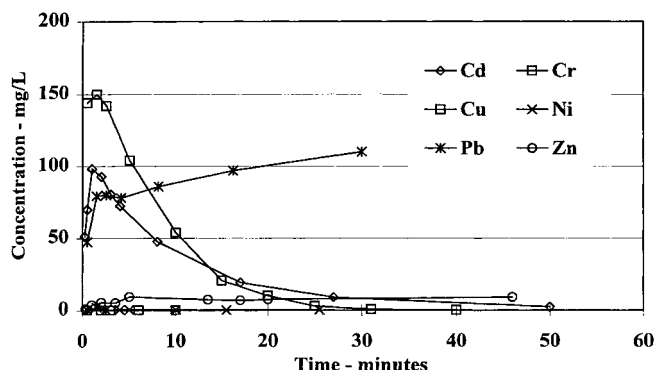
Solids in the cake layer that formed during operation of the low-velocity system were analyzed by scanning electron microscopy. To prepare these samples, approximately 300 mg of solids was filtered through a membrane section. A small sample of the membrane (with the associated solids) was then cut out, immobilized on a specimen mount, and air dried. The samples were coated with 2 nm of Au/Pd alloy using a Hummer II Sputter coater and were then viewed with a high-resolution field emission scanning electron microscope (SEM) model 6300F (JEOL JSM). SEM images of goethite and ferrihydrite were obtained in the same way, except that they were first collected on a Millipore filter rather than in the tubular microfilter.

## RESULTS AND DISCUSSION

### Particle Retention and Permeate Flux in Semibatch Experiments

Ten different types of solids were processed in the semibatch tests. Because equal masses of metal were used in these tests, and the metals investigated have different atomic weights and oxidation numbers, the mass of metal hydroxide solid varied from one experiment to the next. As indicated in Table 2, the mass of dry solids added in these tests is estimated to range from approximately 800 to 1200 mg, corresponding to 29–44 g of solids per m<sup>2</sup> of membrane surface. The solution volume in each case was 3 L. In six tests, the solids were freshly precipitated metal hydroxides, with one of the six target metals used in each test. In the other four tests, the solids were, respectively, freshly precipitated ferrihydrite alone, goethite alone, a metal hydroxide mixture precipitated from synthetic waste No. 1, and a sample of sludge from the full-scale treatment system. All samples were adjusted to a pH value (shown in Table 2) where the metals were expected to be mostly precipitated.

Each system was operated for several hours. In 7 of the 10 systems studied, the permeate was visually clear throughout the test. The exceptions were the systems treating Cr, Cd, and Pb, in which the permeate was very cloudy at the beginning of the run. However, in all three cases, the clarity of the per-



**FIG. 4.** Permeate Metal Concentration as a Function of Time for Filtration of 200 mg/L (600 mg in 3 L) of Each Metal Hydroxide, Individually, at pH 12 for Cd, Cu, Pb, Ni, and Zn and pH 8.5 for Cr

meate improved dramatically after 15–25 min. Thus, the clean filter was not efficient at retaining these metals, but removal improved as solids built up on the filter surface.

The metal concentrations in the permeate during the first portion of these tests are shown in Fig. 4. Within one minute of metal addition to the system, permeate concentrations of Cu, Ni, and Zn approached those expected based on the solubility of the corresponding metal hydroxide. Consistent with the observations of particulate breakthrough, Cd and Cr concentrations in the permeate were high initially, but they decreased quickly to values close to those expected for equilibrium systems. On the other hand, the Pb concentration in the permeate remained very high for at least 30 min, long after the visual evidence of breakthrough had ceased. The presence of <<100 mg/L Pb in the permeate in the absence of visual particulate matter indicates that most of the Pb passing through the membrane was soluble, even though the equilibrium solubility of Pb in the absence of complexing ligands at pH 12 is <<1 mg/L. Possible explanations for the observations include slow precipitation kinetics allowing maintenance of a highly supersaturated solution, an undetected error in the pH control system, or the presence of a complexing agent (e.g., CO<sub>3</sub><sup>2-</sup>) that was not considered in the analysis. The Pb concentration in the permeate did eventually decrease to <1 mg/L after 16 h of operation. Thus, overall, these results indicate that microfiltration can be an effective process for removing the target metals from waste streams if the metals are precipitated, even if no coagulant is added.

The permeate flux in these tests decreased substantially as soon as the solids were added, typically reaching steady-state values within 15–30 min. The steady-state flux varied widely among the different types of sludges (Fig. 5). Freshly precipitated ferrihydrite (lab Fe) and goethite had the lowest and highest specific flux (highest and lowest resistance), respectively, of all the solids studied. The specific flux for the metal mixture was intermediate among the specific fluxes of the six

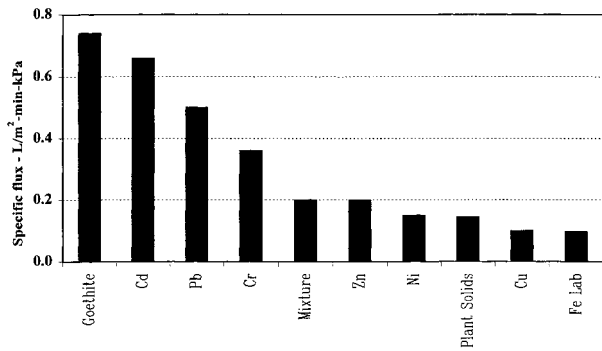


FIG. 5. Steady-State Specific Flux Values through Microfilter after Approximately 1 g (37 g/m<sup>2</sup>) of Various Solids Had Been Coated on Filter Surface

metals in the mixture. The specific flux in the system fed the sludge from the full-scale facility (plant solids) was slightly greater than that of the freshly precipitated ferrihydrite (lab Fe), consistent with the fact that ferrihydrite was the dominant solid in the sludge from the plant. The total hydraulic resistance in each system, calculated using (6) is shown in Table 2. An expected value of  $36 \times 10^{10} \text{ m}^{-1}$  can be computed for the resistance in the experiment with the metal mixture, based on a weighted average of the resistances in the single metal systems, with weighting factors proportional to the mass of the different metals comprising the mixture. This value is reasonably close to the experimental value of  $30 \times 10^{10} \text{ m}^{-1}$ .

Scanning electron micrographs of the solids that accumulated on the membrane surface [Figs. 6(a)–(f)] provide some insight into the causes for the observed particle breakthrough patterns and the relative resistance to flow of the different sol-

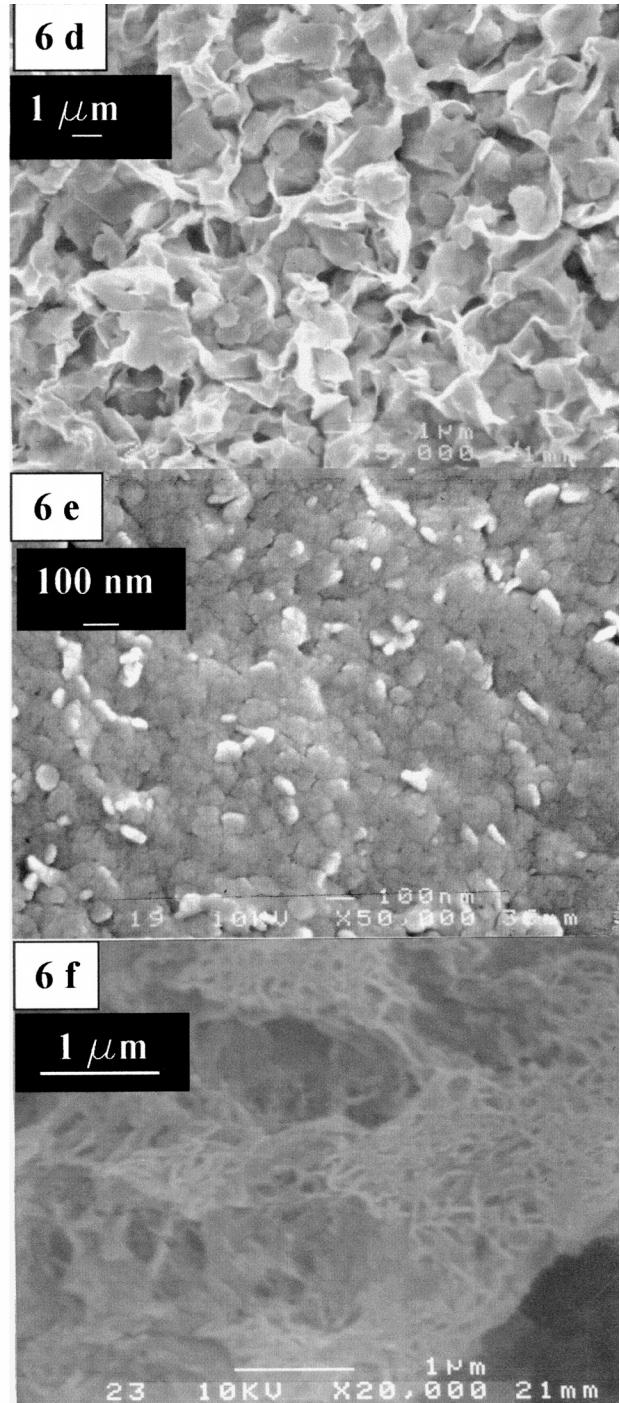
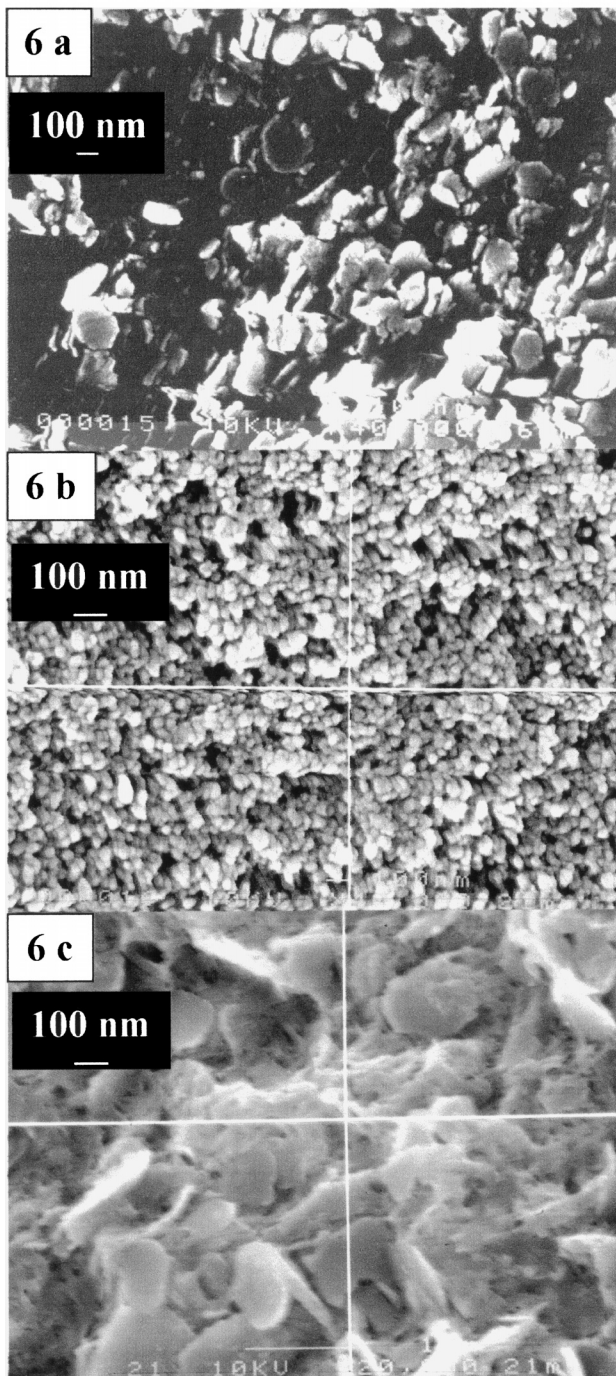


FIG. 6. SEM Photos of Waste Metal Hydroxides: (a) Cd; (b) Cr; (c) Cu; (d) Pb; (e) Ni; (f) Zn

ids. In the systems containing Cu, Ni, or Zn, virtually continuous layers of solids formed on the membrane surface, and the individual particles agglomerated to the point where it was difficult to distinguish among them. Thus, it appears that particles of these solids coagulated into larger flocs that were too large to pass through the membrane pores and that provided only small pores through which water could pass. By contrast, in the systems with Cd or Cr, individual particles were easily distinguishable in the cake layers, suggesting that these particles did not coagulate effectively. As a result, individual particles were able to pass through the membrane pores, and when a cake layer did build up, spaces between the particles provided relatively large flow paths for water. The morphology of the Pb solids on the membrane surface was roughly intermediate between that of the two groups previously described.

The extreme cases with respect to the flux resistance imparted by particles in these tests were goethite and ferrihydrite. The different morphologies of these particles are very evident in Fig. 7, which shows the cake layer that formed when a batch of ferrihydrite was filtered through a 0.45- $\mu\text{m}$  Millipore filter after a layer of goethite had been deposited on the membrane by a previous filtration step. The goethite consists of distinct, crystalline particles through which water could pass easily, whereas the ferrihydrite layer appears very tightly compacted.

The results presented suggest that the tendency of particles to foul the membrane, their tendency to be removed efficiently by microfiltration, and the structure of the cake layer that forms on the microfilter are all interrelated. In cases where the metals coagulate either in the circulating suspension or at the filter surface, compact layers with very small pores and low permeability can form, and the metals are separated from solution very effectively (lab Fe, plant solids, Cu, Ni, Zn). Coagulant addition is not needed in such systems to accomplish good solid/liquid separation, but fouling might be severe. In other cases, the metals do not coagulate well, and a cake with a relatively open pore structure and high permeability forms. Fouling is not severe in such systems, but some particle breakthrough might occur, especially at the beginning of a filtration cycle. It should be noted that other microfilters might have more uniform pore structures than the one used in this research, so that some of those membranes might reduce or eliminate breakthrough of particles early in the treatment cycle.

### Solubility of Regulated Metals in Batch Experiments

The next set of experiments investigated the solubility of the regulated metals in mixed-metal systems, both with and

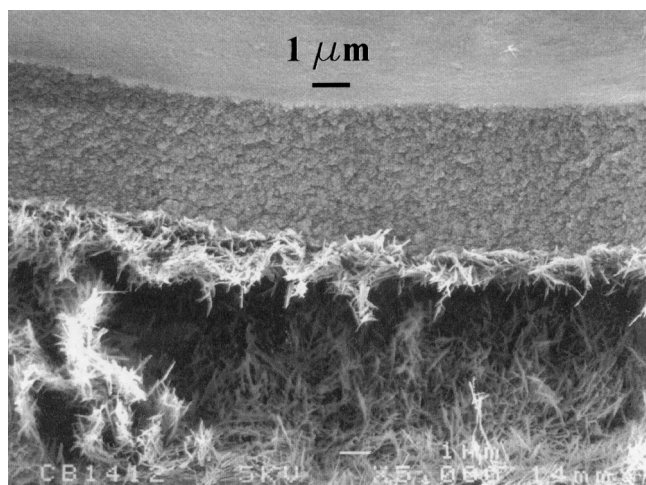


FIG. 7. SEM Photo of Layer of Ferrihydrite Deposited over Layer of Goethite

without iron oxides added. In these tests, synthetic waste No. 1 was adjusted to pH 5.0 and was then dosed with NaOH in steps. Samples were taken 10 min after each addition of NaOH and were filtered through a 0.22- $\mu\text{m}$  Millipore filter before analysis.

The solubility of all the regulated metals in these tests was near the instrumental detection limit over the pH range from 8.5 to 10, regardless of whether an iron oxide was added or not (Fig. 8). Furthermore, the solubility of each metal in the mixture was less than that in solution at the end of the single-metal experiments, suggesting that some metal removal was occurring by coprecipitation and/or adsorption of metals onto the surfaces of other solids, rather than entirely by precipitation of pure, single-metal solids. The presence of 1 g/L goethite in the suspension improved removal of Cr, Cu, Pb, and Zn, and the presence of 1 g/L ferrihydrite improved removal of all the target metals. Thus, good metal removal could be achieved in these systems without iron oxide addition, but the addition of iron oxides expanded the pH range over which good removal was achieved.

### Metal Removal Efficiencies in Continuous Flow Microfiltration System

The same mixed metal suspension was then used in a continuous flow treatment test without permeate recycle. The solution circulating in the retentate loop was maintained at pH 9.5–10.0. Removal of all the metals was poor initially, before improving sharply during the first hour of treatment (Fig. 9). The fact that all the metals passed through the membrane at early times in the test and that the concentrations of all the metals declined relatively uniformly thereafter suggests that the metals were at least intimately comingled in mixed solids, if not actually forming thermodynamically stable solid solutions. Permeate Cd and Ni concentrations increased from  $t \approx$

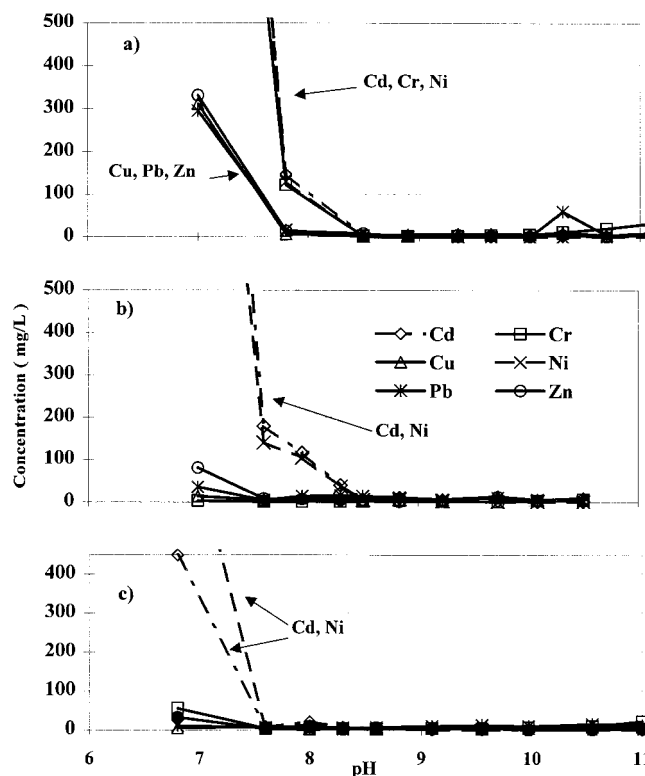
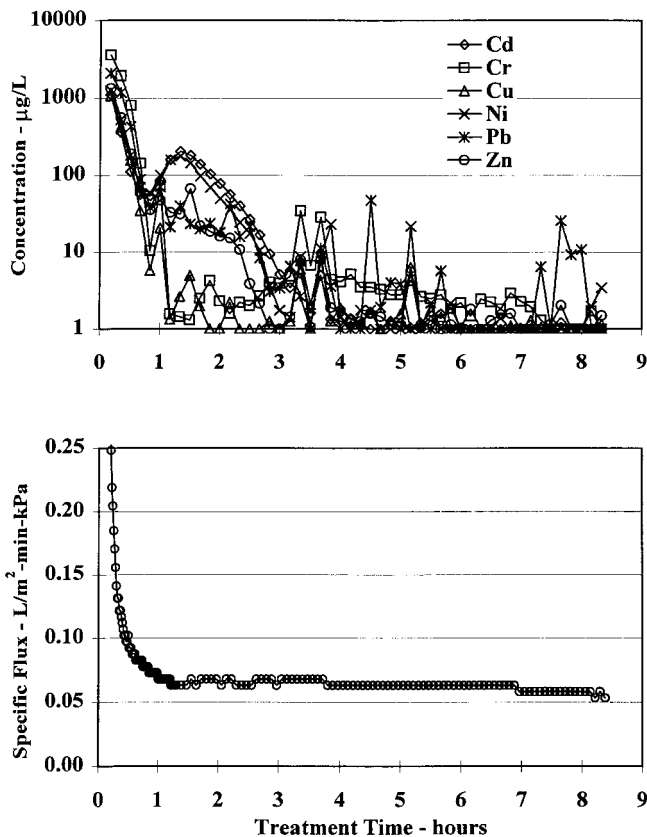


FIG. 8. Metal Concentrations as Function of pH in Synthetic Waste No. 1, in Presence and Absence of Iron Oxides, Total Metal Concentration (Excluding Fe) Was 200 mg/L in Each Case: (a) No Iron Oxide Added; (b) 1 g/L of Goethite Added; (c) 1 g/L of Ferrihydrite Added





**FIG. 9.** Permeate Metal Concentrations and Specific Flux during Treatment of Mixed Metal Solution at pH 9.5–10.0 (Influent Contained 67 mg/L Total Metals and Was Injected at Average Flow Rate of 80 mL/min)

0.8 to 1.5 h, after which they declined. The reason for this behavior is not clear. However, the fact that these two metals are the most soluble of the six metals tested suggests that the pH control might have been somewhat erratic during this period. In any case, permeate concentrations were near the instrumental detection limits for all metals from  $t = 3$  h until the end of the test, except for occasional spikes of up to a few tens of  $\mu\text{g/L}$  of Pb and Cr. The permeate concentrations achieved later in the test are similar to the soluble concentrations achieved in the batch precipitation tests when no adsorbent was present [Fig. 7(a)], providing additional evidence that coprecipitation of this metal mixture can significantly reduce metal solubility compared to precipitation of the metals individually.

The specific flux through the membrane dropped dramatically during the first hour of treatment in this test, after which it stabilized at approximately 1% of the flux through the clean membrane (Fig. 9). The vast majority of this decline ( $\approx 99\%$ ) occurred during the first 20 min of treatment, during which time  $<250$  mg ( $9 \text{ g/m}^2$ ) of metal hydroxide solids entered the system. By contrast, subsequent addition of  $>5,000$  mg more solids ( $195 \text{ g/m}^2$ ) produced only a modest additional decline in flux. This pattern of flux decline, which is commonly observed in membrane studies, might be caused by blockage of many small pores by particles present in the fluid that first enters the system. Particles entering the system subsequently might build up a cake that gradually reduces flux further, but the majority of the resistance is imparted by pore blockage early in the treatment cycle.

The results shown in Figs. 4 and 9 suggest that batch precipitation of metals followed by crossflow microfiltration might be problematic with respect to achieving good water quality at the beginning of a treatment cycle. If treatment is

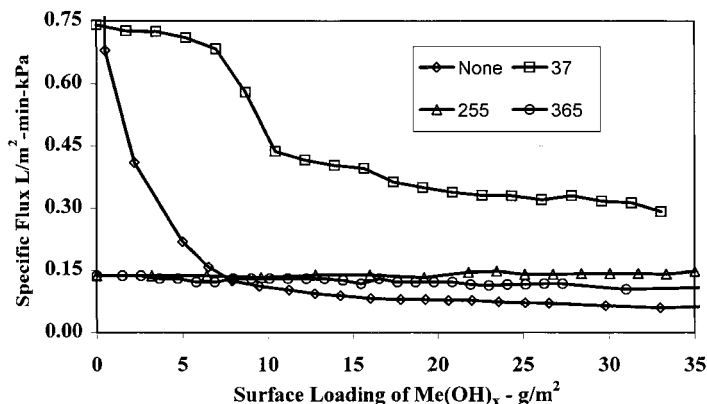
continued until a cake layer builds on the membrane surface, good metal treatment efficiency can be achieved for long periods of time, but probably at the cost of severe fouling. The results also indicate that addition of iron oxides to the waste might expand the pH range of good treatability. However, if one is concerned primarily with achieving good metal removal, the value of adding iron oxides is questionable, since the treatment goal can probably be met at moderately alkaline pH values without iron addition.

### Fouling Reduction by Addition of Adsorbent Particles

While the data presented do not appear to justify iron oxide addition as a means of improving effluent quality, such additions might be attractive if they also increase the flux through the membrane. Of the two iron oxides studied, the results shown in Fig. 5 suggest that, for the conditions investigated, only goethite has the potential to be useful in this regard. To assess this possibility, tests were conducted in which layers containing various amounts of goethite were deposited on the microfilter surface prior to injection of mixed-metal wastes. Virtually all of the added goethite was immobilized in the cake layer before waste metal feed was initiated.

Addition of goethite to achieve a  $37 \text{ g/m}^2$  surface coating (estimated to be  $200 \mu\text{m}$  thick) led to a dramatic increase in flux (about fivefold) over that in a system with no goethite added, for an equivalent loading of metal hydroxides (Fig. 10). Precoating with thicker goethite layers ( $255$  or  $365 \text{ g/m}^2$ ) also increased the flux during the first several hours of metal treatment, but the improvement was much less dramatic than when less goethite was used (Fig. 10).

Permeate metal concentrations during the tests with  $37$  and  $365 \text{ g/m}^2$  precoated goethite layers are shown in Fig. 11. The absence of significant breakthrough at the beginning of this test, in contrast to the results when no precoat layer was present, suggests that the precoat layer effectively filtered out colloidal particles that broke through the membrane at the beginning of the experiment characterized in Fig. 9. In both the low- and high-dose goethite experiments, the Cr concentration was much higher than that of the other metals. The concentrations of metals other than Cr were  $<10 \mu\text{g/L}$  in the permeate over most of each run, although spikes of a few tens of  $\mu\text{g/L}$  of Pb in one test and of Zn in the other are apparent. The concentration of Cd increased slowly but steadily toward the end of the run with the lower goethite addition, suggesting that the goethite might have been adsorbing Cd effectively early in the run, but that the goethite was losing the ability to sorb Cd later, perhaps because the sorption capacity of the goethite for Cd was nearing exhaustion. No comparable breakthrough of any of the metals was observed in the system with



**FIG. 10.** Specific Flux for Filtration of Metal Mixture after Deposition of Goethite Precoat Layer in Low-Velocity Crossflow System (Numbers Are Amount of Goethite Deposited per Square Meter of Filter Surface)

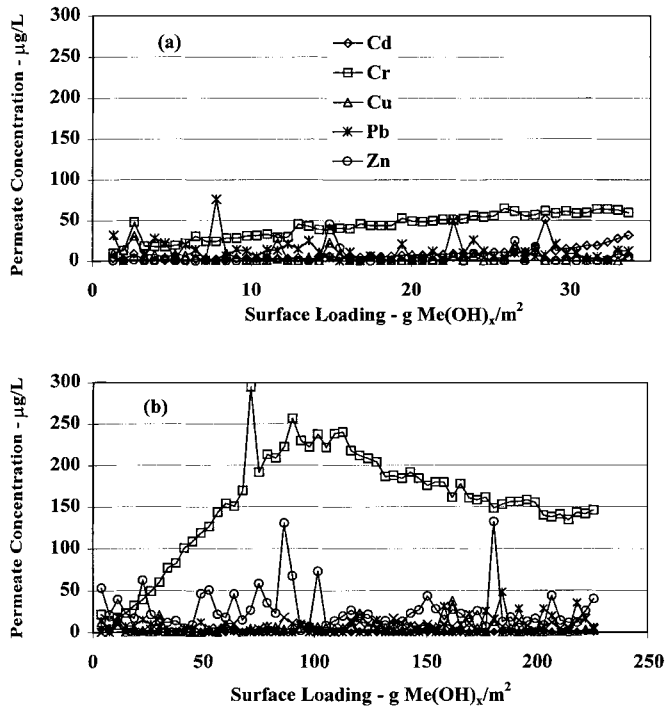


FIG. 11. Permeate (Effluent) Metal Concentrations for Treatment Tests Using Low-Velocity System with Goethite Coated on Filter Surface Prior to Treatment: (a) 37 g/m<sup>2</sup> Goethite; (b) 365 g/m<sup>2</sup> Goethite

the higher goethite dose even after a much larger volume of synthetic waste had been treated.

### Metal Removal and Permeate Flux in Systems with High Crossflow Velocity

The results from the tests previously described indicate that deposition of a thin precoat layer of goethite dramatically improved flux through the membrane, and they at least suggest that the greater the mass of goethite in the system, the larger the amount of waste solution that could be treated before substantial amounts of metals appear in the permeate. Therefore, an attempt was made to test a system that contained a large amount of goethite in the circulating fluid but only a thin layer of goethite on the membrane surface. To accomplish this, goethite was injected into the system at a dose equivalent to 547 g/m<sup>2</sup>, but the crossflow velocity was increased by a factor of ten compared to the previous tests. Under these conditions, only about 20% of the goethite became immobilized in the cake layer, forming a cake layer containing  $\approx 110$  g/m<sup>2</sup> on the surface. Because it was thought that use of a high crossflow velocity might reduce the effects of fouling by ferrihydrite as well, a system with high crossflow velocity and a high ferrihydrite dose was also tested.

The permeate water quality from the high-velocity systems dosed with goethite and ferrihydrite are shown in Fig. 12. The specific fluxes in the systems with precoated layers of goethite and ferrihydrite were approximately 0.23 and 0.07 L/m<sup>2</sup>-min-kPa, respectively. In both cases, consistent and excellent removal was achieved for all metals, although, as in the tests with the lower crossflow velocity, the removal efficiency for Cr was substantially less than that for any of the other metals.

Following each of the goethite precoat treatment tests, sections of the cake layers were removed from the membrane surface and inspected visually. In each case, the portion of the cake nearest the membrane maintained the golden-yellow color characteristic of goethite, while the portion in contact with the circulating suspension was greenish due to penetration of the metal hydroxides. When viewed from the edges,

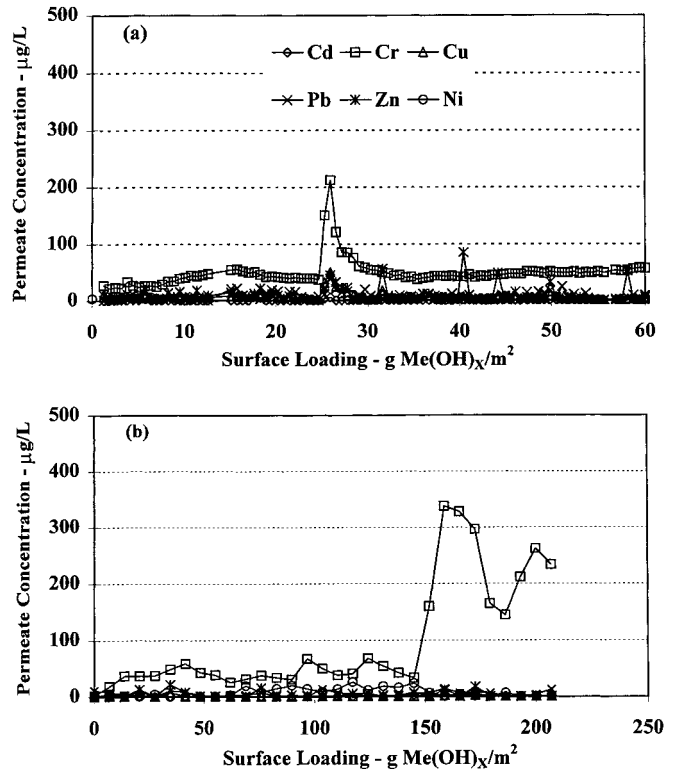


FIG. 12. Permeate Metal Concentration for Microfiltration of Mixed Metals in System with High Crossflow Velocity and Precoat Layer of: (a) Ferrihydrite; (b) Goethite

distinct layering was visible in the cakes, indicating that the metal hydroxide solids were retained at the surface of the goethite layer. Thus it appears that only soluble metals were in the water exiting the cake layer and contacting the membrane.

Based on the mass and thickness of the precoat layers, the concentration of goethite and ferrihydrite in these layers can be estimated to be  $>10,000$  mg/L. For the given fluxes, the time of contact of solution with these layers ranged from less than one second to a few seconds. In light of these estimates, and given the tendency of metals at trace concentrations to sorb to ferrihydrite and goethite, the metals concentrations exiting the cake layer and passing through the membrane were expected to be extremely small. Cd, Cu, and Ni were indeed consistently removed by the treatment systems to near the analytical detection limits. Pb and Zn were also generally removed well, although spikes of these metals were occasionally detected in the effluent. The most plausible explanation for these spikes is that colloidal particles containing Pb and Zn occasionally passed through or broke away from the cake layers and permeated the membrane.

Cr removal varied from one test to another, but in only a few tests was Cr removal as good as that in the batch tests or the test with no adsorbent added. The Cr might have passed through the filter in either particulate or soluble form. The hypothesis that much of the Cr in the permeate was particulate is supported by the facts that Cr removal tended to be better in systems with higher fouling (corresponding to tighter packing in the cake layer) and that the SEM images showed that Cr(OH)<sub>3</sub>(s) particles were the smallest and least likely to lose their distinctness of all the particles studied.

Other evidence, though, suggests that much of the Cr in the permeate might have been soluble. The experimental system was operated at pH 10, while the pH of minimum Cr solubility for a solution in equilibrium with Cr(OH)<sub>3</sub>(s) is near 9. As pH increases above 9, the formation of Cr(OH)<sub>4</sub><sup>-</sup> can increase solubility, and Cr(OH)<sub>4</sub><sup>-</sup> is unlikely to adsorb to goethite at pH



10 or above because the surface has a negative electrostatic potential ( $PZC \approx 8.0$ ). Additional research is needed to identify the form of the Cr passing through the membrane and the reason for the unusually high breakthrough of Cr compared to other metals. As noted above, if the Cr permeating the membrane is particulate, use of a different membrane with more uniform pores might overcome the problem.

## SUMMARY AND CONCLUSIONS

Adjusting pH to precipitate metals as hydroxide solids, followed by crossflow microfiltration, is an efficient means of achieving consistently low metal concentrations during treatment of a mixed metal waste stream. Some metals coagulate readily into particles large enough that they are removed efficiently by filtration from the beginning of the filter cycle. Other metals appear not to coagulate as readily, in which case some particles may pass through the filter early in the run. Over time, a cake layer builds up on the membrane surface and even the poorly coagulated particles are removed very efficiently. Good coagulation and immediate removal tend to be correlated with more severe membrane fouling. Although other membranes with different pore structures might behave differently with respect to the quantity of metals removed initially and the time before removal stabilizes, the qualitative trends observed in this research are probably fairly universal.

Treatment of a mixture of metals might decrease the solubility of the individual metals, and it might also affect the solids' tendency to coagulate. In the current work, all the metals were less soluble when they were treated in a mixture, but they also all passed through the microfilter at the beginning of a filter cycle, whereas only a few of them did so when present in single-metal systems.

Addition of iron oxides to these systems can be either beneficial or adverse, depending on the specific treatment goals. Both of the iron oxides tested (ferrihydrite and goethite) tend to improve metal removal, but the treatability of the solutions tested was so good without iron oxide addition that the addition of the iron oxides to improve water quality would probably not be justified. Whether such additions might prove valuable for removing metals from other wastes remains an open question.

Addition of goethite to the system to form a thin precoat layer on the filter surface improved flux through the membrane substantially, apparently by trapping metal hydroxide particles before they reached the membrane surface. These benefits could be obtained either by adding a small amount of goethite to the system before the contaminant metals were added, or by adding a larger amount of goethite and using a high crossflow velocity. In the latter case, for the particular conditions studied in this research, only a portion of the goethite deposited in the cake layer, while the rest remained in the suspension circulating rapidly through the retentate side of the system. The potential advantage of the latter approach is that it provides a large amount of goethite to serve as a metal adsorbent, at the cost of higher energy input (for the higher crossflow velocity) and higher goethite consumption. The cost associated with the use of goethite in either system might be reduced substantially by recovery of the goethite after use (Voges 1996).

Overall, this work shows that crossflow filtration is an attractive solid/liquid separation technology for metal-bearing wastes, and that the need for and role of coagulants in the process can be quite different from those in conventional deep bed filtration processes.

## ACKNOWLEDGMENTS

This project was, in part, by the Idaho National Engineering and Environmental Laboratories (INEEL) University Research Consortium. The INEEL is managed by Lockheed Martin Idaho Technologies Company for the U.S. Department of Energy, Idaho Operations Office, under Contract No. DE-AC07-941D13223. Technical support was provided by the Safety, Health, and Environmental Affairs Department of the Boeing Defense and Space Group located in Kent, Wash. The support of Andro Wipplinger, David Sizemore, Keith Badgley, and Ronald Wu was especially valuable.

## REFERENCES

- Anderson, P. A., and Benjamin, M. M. (1985). "Effects of silicon on the crystallization and adsorption properties of ferric oxides." *Envir. Sci. and Technol.*, 19, 1048–1053.
- Benjamin, M. M. (1983). "Adsorption and surface precipitation of metals on amorphous iron oxyhydroxide." *Envir. Sci. and Technol.*, 17, 686–692.
- Benjamin, M. M., and Leckie, J. O. (1981). "Competitive adsorption of Cd, Cu, Zn, and Pb, on amorphous iron oxyhydroxide." *J. Colloid Interface Sci.*, 83, 420–419.
- Broom, G. P., Squires, R. C., Simpson, M. P. J., and Martin, I. (1994). "The treatment of heavy metal effluents by crossflow microfiltration." *J. Membrane Sci.*, 87, 219–230.
- Chang, Y.-J., and Benjamin, M. M. (1996). "A combined iron oxide adsorption and ultrafiltration process for natural organic matter removal and fouling control." *J. Am. Water Works Assn.*, 88(12), 74–88.
- Chang, Y.-J., Choo, K.-H., Benjamin, M. M., and Reiber, S. (1998). "Combined adsorption-UF process increases TOC removal." *J. Am. Water Works Assn.*, 90(5), 57–71.
- Coughlin, B. R., and Stone, A. T. (1995). "Nonreversible adsorption of divalent metal ions (Mn(II), Co(II), Ni(II), Cu(II), and Pb(II)) onto goethite: Effects of acidification, Fe(II) addition, and picolinic acid addition." *Envir. Sci. and Technol.*, 29, 2445–2454.
- Edwards, M. (1988). "Application of ferrihydrite adsorbents in treatment of metal bearing wastes." Masters thesis, Department of Civil Engineering, University of Washington, Seattle.
- Johnson, B. B. (1990). "Effect of pH, temperature, and concentration on the adsorption of cadmium on goethite." *Envir. Sci. and Technol.*, 24, 112–118.
- Pirbazari, M., Bradrihya, B. N., and Ravindran, V. (1992). "MF-PAC for treating waters contaminated with natural and synthetic organics." *J. Am. Water Works Assn.*, 84(12), 95.
- Schecker, W. (1994). *Mineql+, Chemical Equilibrium Management System*, Version 3.01a.
- Schwertmann, U., and Cornell, R. M. (1991). *Iron oxides in the laboratory: Preparation and characterization*, VCH, New York.
- Voges, L. E. (1996). "The use of iron oxides to enhance metal removal in crossflow microfiltration." Masters thesis, Department of Civil Engineering, University of Washington, Seattle.

## NOTATION

The following symbols are used in this paper:

- $aq$  = aqueous;  
 $K_{so}$  = solubility constant;  
 $J$  = flux;  
 $j$  = specific flux ( $J/\Delta P$ );  
 $Me$  = metal;  
 $R$  = hydraulic resistance;  
 $(s)$  = solid;  
 $\beta$  = complexation constant;  
 $\Delta P$  = differential pressure;  
 $\mu$  = viscosity; and  
 $\Sigma$  = summation.

## Subscripts

- $c$  = cake layer;  
 $m$  = membrane;  
 $p$  = pore fouling; and  
 $tot$  = total.