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Heavy Metal Removal by Chemical Reduction with Sodium Borohydride. A Pilot-Plant Study

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Abstract

A 1000 L/h continuous pilot-plant study dealing with Cu^{2+} and Co^{2+} removal from simulated industrial wastewater by means of chemical reduction with sodium borohydride is presented. Initial metal concentrations in the 25 to 40 mg/L range have been tested. Residual concentrations lower than 0.1 mg/L have been achieved when operating under optimal conditions. Prior addition of sodium dithionite was required to avoid reoxidation problems arising from dissolved oxygen. Flocculation–sedimentation and sand filtration have been studied for sludge separation.

INTRODUCTION

Removal of heavy metals from industrial wastewaters using conventional alkaline precipitation has some technical limitations, one of the most important being related to the nature and handling of the sludge obtained, which is mainly a mixture of oxihydroxides showing poor settling characteristics and giving rise to disposal problems derived from leaching. Of course, these technical limitations are reflected in the overall cost, which may be substantially increased as a result of sludge separation, treatment, and disposal. Other available technologies, such as ion exchange, reverse osmosis, adsorption, and solvent extraction, allow for higher quality effluents but produce concentrated streams that, if not recycled, should be treated before discharge.

Chemical reduction may substantially improve sludge handling if the heavy metal ions can be precipitated in the metallic state or in some intermediate form that shows improved settling and dewatering character-

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istics. In some cases the corresponding metal could be recovered or the sludge reclassified as nonhazardous if leaching tests prove that there is a reasonable margin of safety.

Sodium borohydride ($NaBH_4$) is a mild but highly effective reducing agent. The half reaction (Eq. 1) shows that eight electrons are released, so the equivalent weight is rather small.

$$BH_4^- + 3H_2O \rightarrow H_3BO_3 + 7H^+ + 8e^- \tag{1}$$

The general redox reaction for a divalent metal ion can be written as

$$BH_4^- + 4Me^{2+} + 3H_2O \rightarrow H_3BO_3 + 4Me^0 + 7H^+ \tag{2}$$

Table 1 gives the theoretical removal weight ratios that can be achieved for different cations of environmental interest.

Nevertheless, when other oxidant species are present, some other reactions may take place that will increase the amount of reagent needed. The most common oxidants in water systems, including dissolved oxygen, may be removed by prior treatment with less expensive reducing agents (i.e., dithionite), but water reduction will always occur when $NaBH_4$ is added to a water solution, giving rise to hydrogen release. This reaction (Eq. 3) has been reported (*1–3*) to be first order with respect to H^+ when

TABLE 1
Theoretical Weight Ratios of Reduced Metal Obtainable from Ionic Species

Oxidation state	Weight ratio[a]
Cd^{2+}	12
Co^{2+}	6
Cu^{2+}	7
Ag^{+}	23
Pb^{2+}	22
Hg^{2+}	21
Hg^{+}	42
Ni^{2+}	6

[a] Weight ratio = maximum grams of metal reduced/gram of $NaBH_4$.

the pH is below 9, following Expression (4) where the preexponential factor is given in L·mol^{-1}·s^{-1}.

$$BH_4^- + 3H_2O + H^+ \rightarrow H_3BO_3 + 4H_2 \quad (3)$$

$$-\frac{d[BH_4^-]}{dt} = 6.62 \times 10^{12} e^{-4680/T}[H^+][BH_4^-] \quad (4)$$

Work has been reported, including industrial examples, on the use of sodium borohydride for the removal and recovery of precious metals, lead, mercury, copper, nickel, and cadmium (*4–12*).

The most common commercial form of sodium borohydride is as a caustic water solution (40% NaOH, 12% $NaBH_4$). Commercial quantities of sodium borohydride powder sell for ~\$48/kg and stabilized water solutions (SWS) sell for ~\$40/kg of contained $NaBH_4$ (*13*). Use of the latter form not only has economic advantages but also facilitates chemical addition and improves mixing.

EXPERIMENTAL

Copper(II) and cobalt(II) removal from water was investigated at a pilot-plant scale in a 1000 L/h continuous installation whose scheme is shown in Fig. 1. Simulated wastewater is pumped from two 500-L polyethylene storage tanks. Addition of 0.5 *N* NaOH and 0.5 *N* H_2SO_4 for pH adjustment

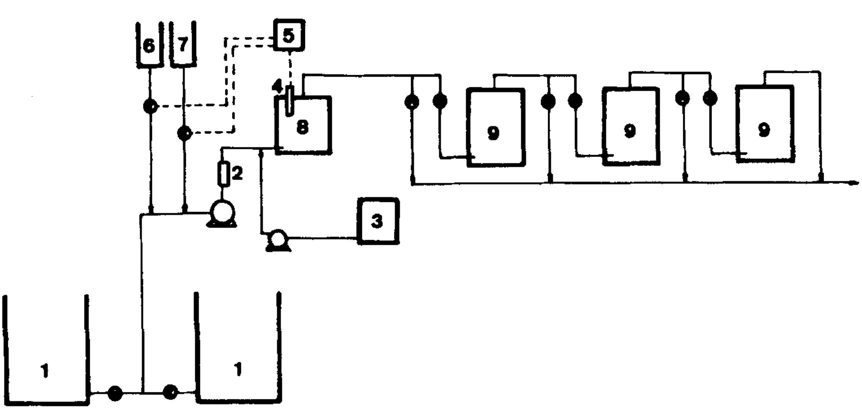

FIG. 1. Pilot-plant scheme: (1) 500 L storage tanks, (2) flowmeter, (3) borohydride solution deposit, (4) pH probe, (5) pH controller, (6) NaOH solution deposit, (7) H_2SO_4 solution deposit, (8) mixing reaction chamber, (9) reaction chambers (38 L each).

takes place upstream of the main pump, flowing by gravity through a solenoid valve into the influent line. The solenoid valve is operated by a pH controller (Bowater DPM 23X) connected to a pH probe placed in the first mixing-reaction chamber (19 L). After the waste stream has passed through the main pump, the stabilized water solution of sodium borohydride is fed into the stream by means of a peristaltic pump placed just before the first reaction chamber, which is followed by a series of three other reaction chambers (38 L each). All the reaction chambers are made of Lucite, and samples can be collected at the exit of each one. Effluent pH and redox potential were continuously measured using glass electrodes placed at the pipe exit line and connected to two Cryson MicropH 2002 model pH meters. All redox potential values given in this paper are referred to an Ag/AgCl, KCl (3 *M*), reference electrode. Oxygen concentration was measured by means of HI 8543 Dissolved Oxygen meter.

Simulated wastewaters were prepared by dissolving the desired amounts of $CuCl_2{\cdot}H_2O$ and $CoCl_2{\cdot}6H_2O$ in tap water to achieve the desired initial ion concentration. Values in the range of 25–40 mg/L were tested. Sodium borohydride (Merck, for synthesis) was prepared as 0.25–0.50 *M* aqueous solution stabilized with 0.5 *N* NaOH. This solution was maintained at temperatures below 10°C, and its reducing capacity was determined by the Lyttle method (*14*).

Effluent samples were collected, filtered through a Millipore membrane (pore size = 0.22 μm), and analyzed for copper or cobalt by atomic absorption (AA) using a Varian AA-475 spechtrophotometer with IL lamps. The copper precipitate was analyzed by x-ray diffraction by means of a Siemens D-501 apparatus. The cobalt precipitate was dissolved in HNO_3 (60%) and analyzed for cobalt and boron by AA and the curcumine method (*15*), respectively.

When sodium bisulfite was used to remove dissolved oxygen, it was added as sodium dithionite ($Na_2S_2O_5$) in the 500-L storage tanks 5 min before the start of the corresponding experiment.

RESULTS AND DISCUSSION

Copper Removal

When one studies redox systems, Pourbaix diagrams are useful to define the pH/potential regions of existence of chemical species. Figure 2 shows the corresponding diagram for copper(II) at 10 and 40 mg/L. As can be seen, when working close to neutral pH, copper(II) can easily be reduced to Cu_2O. To reach the metallic state, a more reducing environment is needed. The diagram also presents the line describing the H^+/H_2 equilib-

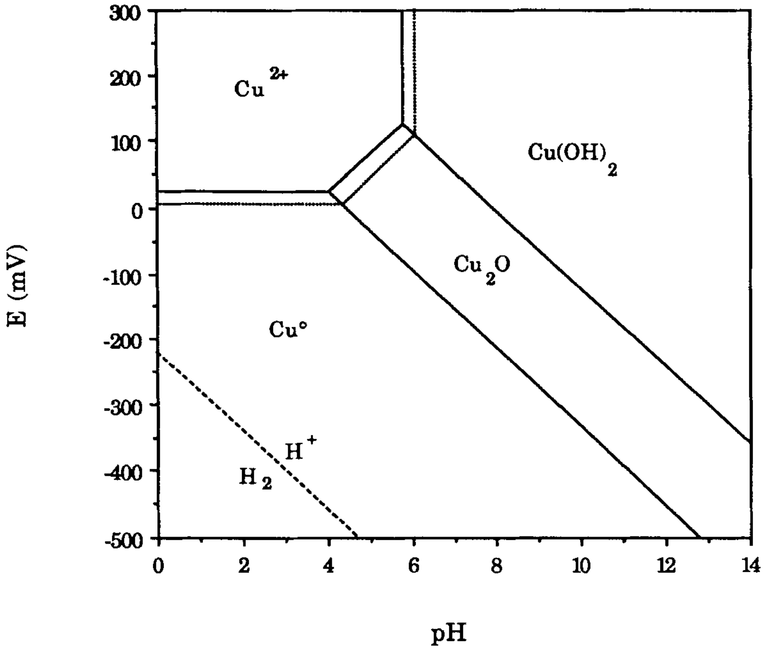

FIG. 2. Pourbaix diagram for copper: Copper(II) concentrations of 40 (——) and 10 (···) mg/L. Oxidation potentials referred to Ag/AgCl, KCl 3 *M*.

rium, which falls substantially below that corresponding to equilibrium between Cu^0 and other oxidized copper species. Thus, there is no pH value at which water can reoxidize the metallic form. Nevertheless, reoxidation may be promoted by dissolved oxygen.

Therefore, when $NaBH_4$ is fed to a water solution containing copper(II), the following reactions may take place in addition to Reaction (1):

$$BH_4^- + 8Cu^{2+} + 7H_2O \rightarrow 4Cu_2O + H_3BO_3 + 15H^+ \quad (5)$$

$$BH_4^- + 4Cu^{2+} + 3H_2O \rightarrow 4Cu^0 + H_3BO_3 + 7H^+ \quad (6)$$

$$BH_4^- + 2O_2 + H^+ \rightarrow H_3BO_3 + H_2O \quad (7)$$

$$Cu_2O + \tfrac{1}{2}O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O \quad (8)$$

$$Cu^0 + \tfrac{1}{2}O_2 + 2H^+ \rightarrow Cu^{2+} + H_2O \quad (9)$$

Batch experiments on a laboratory scale (*16*, *17*) demonstrated that for pH values close to 7, copper undergoes reduction at a higher rate than does water. But as Cu^{2+} reduction takes place, the pH value of the solution decreases, and the water reduction rate increases following Eq. (4) until H^+ production and consumption rates are equal. If the pH value is not controlled, the overall stoichiometry of Cu^{2+} reduction tends to follow Eqs. (10) and (11), giving rise to a borohydride consumption 8 or 16 times higher than that resulting from the Cu^{2+} reduction reactions (Eq. 5 or 6, respectively).

$$2BH_4^- + Cu^{2+} + 6H_2O \rightarrow 2H_3BO_3 + 7H_2 + Cu^0 \qquad (10)$$

$$2BH_4^- + Cu^{2+} + 6H_2O \rightarrow 2H_3BO_3 + \tfrac{15}{2}H_2 + \tfrac{1}{2}Cu_2O \qquad (11)$$

Table 2 shows the results obtained on copper removal in the pilot plant at different operating conditions. Initial ion concentration, pH set value at the controller, effluent pH, borohydride/copper(II) mole ratio, amount of sodium bisulfite added to the 500 L feeding tanks, dissolved oxygen concentration, effluent Cu^{2+}, and the nature of the precipitate as analyzed by x-ray diffraction are reported for each experiment.

As can be seen, very low levels of residual Cu^{2+} in the effluent are achievable. It is important to notice the substantial borohydride savings which result from prior removal of dissolved oxygen with sodium bisulfite. For instance, Experiment 7 shows a very low effluent Cu^{2+} concentration together with a sludge consisting of metallic copper, using a BH_4^-/Cu^{2+} molar ratio of 1.2, whereas a ratio of 2.7 is not sufficient to obtain the same sludge quality when oxygen is not removed. Some other experiments were performed using larger amounts of bisulfite but they resulted, upon borohydride addition, in sulfide formation leading to copper(II) precipitation as the highly stable sulfide, which does not undergo further reduction. Although some results (*8*, *9*) have been reported in the sense that the use of excess bisulfite leads to stabilization of the metallic precipitate obtained, it seems more likely that the nature of the precipitate corresponds to sulfide, thermodynamically a highly stable form. Lab scale experiments carried out in similar conditions to those described for the pilot plant runs showed that the highest concentration of bisulfite not causing sulfide formation corresponds to 575 μmol/L, namely about 2% excess with respect to the stoichiometric amount for complete oxygen reduction in the solution.

Tap water bears some other oxidant species (with redox potential values in the range 485–865 mV) incorporated from chlorination in the municipal treatment facilities. These species may remain in solution after sodium bisulfite addition since this is practically exhausted by dissolved oxygen.

TABLE 2
Pilot Plant Results for Copper at Different Operating Conditions

Exp.	$[Cu^{2+}]_0$ (mg/L)	pH (controller)	pH (effluent)	$[BH_4^-]/[Cu^{2+}]_0$	$[NaHSO_3]$ (μM/L)	$[O_2]$ (mg/L)	$[Cu^{2+}]_{eff.}$ (mg/L)	Nature
1	25	6.8–7.2	6.5	1.55	—	9.0	1.50	Cu_2O
2	25	6.8–7.2	7.2	4.20	—	9.0	0.03	$Cu_2O + Cu^0$
3	25	8.4–8.6	8.3	4.20	—	9.0	<0.01	Cu^0
4	25	8.4–8.6	8.3	2.70	—	9.0	<0.01	$Cu^0 + Cu_2O$
5	25	8.4–8.6	8.2	1.30	—	9.0	0.10	$Cu^0 + Cu_2O$
6	25	8.4–8.6	8.6	1.40	575	0.3	0.03	Cu^0
7	25	8.4–8.6	8.2	1.20	575	0.4	0.06	Cu^0
8	25	8.4–8.6	8.6	1.00	575	0.3	0.10	$Cu^0 + Cu_2O$
9	25	9.0–9.2	8.8	1.00	575	0.3	0.03	$Cu^0 + Cu_2O$
10	37	8.4–8.6	7.0	1.15	575	0.4	0.03	Cu^0
11	37	8.4–8.6	8.1	1.00	575	0.4	0.10	$Cu^0 + Cu_2O$
12	43	8.4–8.6	8.3	0.80	575	0.3	0.15	$Cu^0 + Cu_2O$

Lab experiments carried out with oxygen-free (N_2 stripped) tap water and distilled water showed that 30–35% larger amounts of borohydride are needed with stripped tap water to obtain results similar to those obtained with distilled water (*16*).

The importance of pH control can be deduced from Experiments 1 and 5. As can be seen, when the pH value in the controller is set within a more alkaline range, improved removal efficiency and sludge quality are possible at lower BH_4^-/Cu^{2+} molar ratios. No further significant improvements can be observed at pH values above 8.5 (Experiments 8 and 9).

Regarding borohydride addition, it is important to avoid working above the optimum dose, not only for economical but also for technical reasons, because the increase of hydrogen evolution resulting from excess borohydride leads to massive stabilization of the precipitate particles, the settling of which is hindered.

Cobalt Removal

Reaction between cobalt(II) and borohydride does not follow the general equation for reduction of ionic metals (Eq. 2). The formation of a boride with a mixed stoichiometry, which is generally expressed as Co_2B, has been reported in the literature (*18*, *19*). Analysis of the precipitate obtained from lab and pilot plant experiments are in good agreement with this formula. Thus, the reaction can be written as

$$BH_4^- + 2Co^{2+} \rightarrow Co_2B + \tfrac{1}{2}H_2 + 3H^+ \qquad (12)$$

Since no thermodynamic data have been reported for cobalt boride, we cannot include this species in the Pourbaix diagram, although conclusions that may be obtained from the diagram assuming that the precipitate corresponds to the metallic element agree reasonably with the experimental results. This could be explained in two ways: either the redox potential of Co^{2+}/Co_2B is close to that corresponding to Co^{2+}/Co^0, or the sludge is not really a cobalt boride but a mixture of cobalt and boron. The latter is supported by the results presented by Kim and Brock (*20*), where they report that boron is placed at the surface of small particles of cobalt and thus explains the different stoichiometric values for the Co/B ratio that appear in the literature. The ferromagnetic properties of the precipitate would also support this point of view.

Figure 3 shows the Pourbaix diagram for cobalt(II) at 40 and 10 mg/L. As can be seen, the line describing water decomposition with H_2 evolution intercepts that corresponding to Co^{2+}/Co^0 equilibrium. Thus, precipitate reoxidation may take place not only by the action of dissolved oxygen but also by water at pH values lower than 6. Reduction of Co^{2+} to cobalt

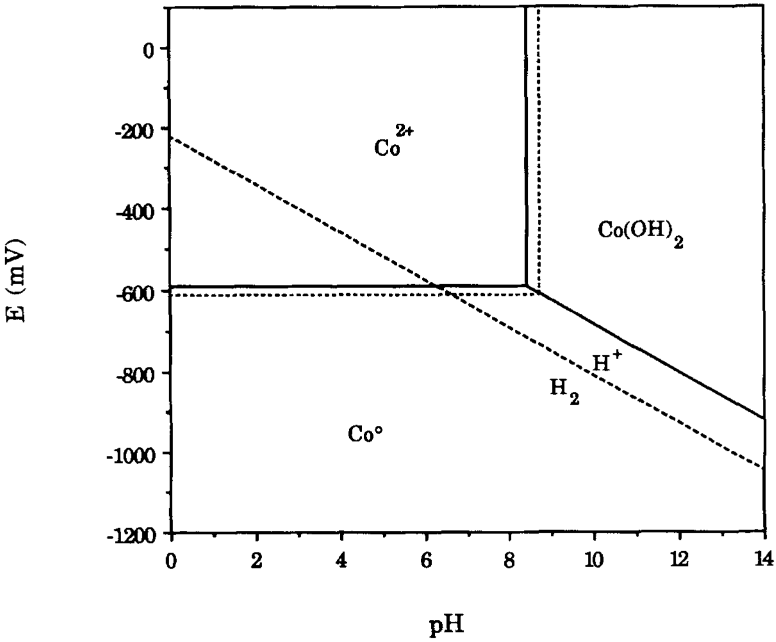

FIG. 3. Pourbaix diagram for cobalt: Cobalt(II) concentrations of 40 (——) and 10 (···) mg/L. Oxidation potentials referred to Ag/AgCl, KCl 3 *M*.

boride releases H^+, leading to a pH decrease. If the pH is not controlled, the rate of water reduction will be increased until the rate of H^+ production and consumption are equal. The overall stoichiometry is given by

$$2BH_4^- + Co^{2+} + \tfrac{9}{2}H_2O \rightarrow \tfrac{3}{2}H_3BO_3 + \tfrac{25}{4}H_2 + \tfrac{1}{2}Co_2B \qquad (13)$$

It has been reported in the literature (*21*) that cobalt boride has a catalytic effect on the borohydride/water reaction. Our previous laboratory results allow us to consider as well an autocatalytic effect on Co^{2+} reduction itself. This behavior would explain the induction period which appears with operation in an unstoppered reactor where the presence of oxygen leads to a rapid reoxidation of the Co_2B initially formed. Once the dissolved oxygen is exhausted, the $NaBH_4/Co^{2+}$ reaction proceeds almost instantaneously.

All the experiments performed at a pilot-plant scale without previous dissolved oxygen removal led to cobalt hydroxide, and no formation of the reduced species was observed, even at $NaBH_4/Co^{2+}$ molar ratios ten times higher than that corresponding to Eq. (12). Thus, all the experiments presented in Table 3 have been carried out using sodium dithionite for

TABLE 3
Pilot Plant Results for Cobalt at Different Operating Conditions

Exp.	$[Cu^{2+}]_0$ (mg/L)	pH (controller)	pH (effluent)	$[BH_4^-]/[Co^{2+}]_0$	$[NaHSO_3]$ (μM/L)	$[O_2]$ (mg/L)	$[Cu^{2+}]_{eft.}$ (mg/L)
1	25	6.8–7.2	6.8	3.25	575	0.5	2.05
2	25	8.4–8.6	8.6	3.95	575	0.3	<0.10
3	25	8.4–8.6	8.2	2.55	575	0.3	7.05
4	25	8.4–8.6	8.3	3.00	575	0.5	0.10
5	25	9.0–9.2	8.9	2.75	575	0.4	0.35
6	25	8.4–8.6	8.4	2.75	575	0.5	0.40
7	40	8.4–8.6	8.2	2.75	575	0.6	<0.10
8	40	8.4–8.6	8.1	2.05	575	0.6	0.15
9	40	8.4–8.6	8.1	2.20	575	0.5	0.10

oxygen removal. Again, the maximum possible dose of bisulfite is limited by the formation of sulfide upon borohydride addition. As in the copper experiments, other oxidants that are not reduced by bisulfite may be present in water, and laboratory runs performed to compare the behavior of distilled and tap water solutions showed a 33% increase of borohydride consumption in the tap water run.

As can be seen, in order to obtain low Co^{2+} levels in the effluent, one needs a borohydride/metal molar ratio substantially higher than that required for copper.

The effect of pH is similar to that observed for copper, as can be deduced from Experiments 1 and 4, in which an increase in the pH control set point from 7 to 8.5 allows a lower residual Co^{2+} concentration in the effluent even with a smaller addition of borohydride. As observed for copper, a further increase of the pH control set point above 8.5 does not result in major borohydride savings, as can be seen from Experiments 5 and 6. Lower $NaBH_4/Co^{2+}$ ratios may be needed at an increasing influent Co^{2+} concentration.

Copper/Cobalt Mixtures

Experiments for binary mixtures of Cu^{2+} and Co^{2+} have been carried out. The results obtained showed that complete Cu^{2+} removal can be achieved and that the presence of this ion does not further increase the borohydride consumption needed to reach a low Co^{2+} concentration in the effluent. Sludge settleability was substantially improved.

Sludge Separation Experiments

Flocculation-sedimentation and filtration have been studied as sludge separation techniques.

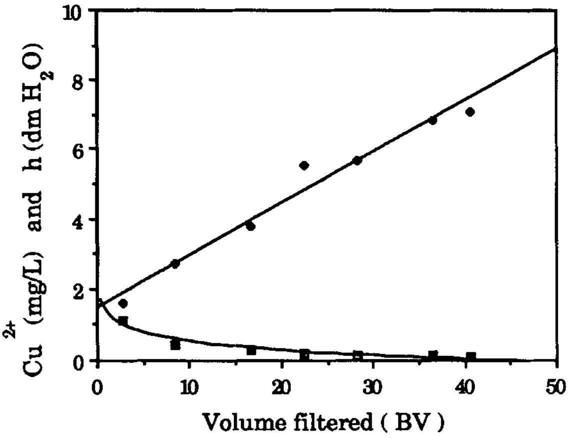

FIG. 4. Copper concentration (□) and head loss, *h* (●), versus volume of effluent filtered.

Flocculation jar tests were accomplished by making use of the anionic polyelectrolyte Nalcolyte. Optimum conditions were established as 120 rpm stirring velocity, 0.5 mg/L flocculant dose, and 20 min stirring time. The cobalt precipitate showed somewhat faster flocculation than the copper precipitate, although in both cases the flocs exhibited fairly good settleability.

Filtration runs were carried out in a gravity sand filter of 30 cm depth and 2.5 cm^2 cross-section. The effective size of bed material was 0.5 mm with a 1.5 uniformity coefficient. A 14 $m^3/m^2 \cdot h$ loading rate was always used. Figures 4 and 5 show the results obtained for suspended solids fil-

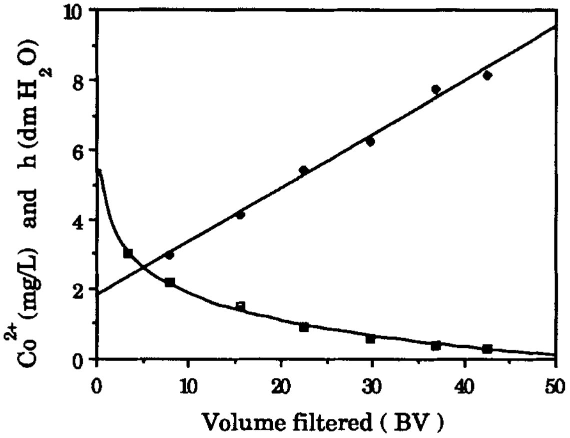

FIG. 5. Cobalt concentration (□) and head loss, *h* (●), versus volume of effluent filtered.

TABLE 4
Chemical Costs

	Copper	Cobalt
$NaBH_4$ (\$40/kg) (SWS)	17.8 g/m^3, 71.3 ¢/m^3	48.1 g/m^3, 192.4 ¢/m^3
NaOH (\$0.20/kg)	50 g/m^3, 1.0 ¢/m^3	
H_2SO_4 (\$0.10/kg)		155 g/m^3, 1.5 ¢/m^3
$Na_2S_2O_5$ (\$0.40/kg)	54.5 g/m^3, 2.2 ¢/m^3	54.5 g/m^3, 2.2 ¢/m^3
TOTAL	74.5 ¢/m^3	196.1 ¢/m^3

tration. Filtration efficiencies comparable to that of 0.22 μm Millipore membranes were achievable. Backwashing required about three bed volumes, so the effective filtration rate for an available headloss of 1 m is close to 95%.

According to these results, a good configuration for solid–liquid separation would be a combination of a first step of flocculation-sedimentation followed by sand filtration of the preclarified liquid. The backwash of the sand filter can be recycled to the settling tank.

ECONOMIC STUDY

Economic data for pilot plant operation are presented in Table 4.

The pilot plant used in this study was built in 1989 for a cost of \$10,000. Therefore, a total capital cost amortized at 15% rate over ten-year period would be \$3985/year. For a 300 d/year operation at 24 m^3/d this cost amounts of 27 ¢/m^3.

As can be seen in Table 4, borohydride cost is over 90% the chemical cost, so even major variations in price of the other chemicals used would not produce important changes in the chemical cost estimation. Obviously, a larger capacity industrial plant would have a much lower capital cost (\$/m^3) compared to the borohydride cost. The borohydride plant would be simple to implement and operate, and in some cases would allow the

TABLE 5
Cost Summary

	Copper	Cobalt
Capital	27 ¢/m^3	27 ¢/m^3
Chemical	74.5 ¢/m^3	196.1 ¢/m^3
Total	101.5 ¢/m^3	233 ¢/m^3

reclamation of the metallic values of the precipitate. Also, the costs of sludge handling and disposal would be substantially lower as compared with conventional alkaline precipitation (7). Nevertheless, the chemical cost for cobalt removal seems to be fairly high even if important savings in other aspects of the treatment are achieved. On the other hand, copper removal by chemical reduction with sodium borohydride could be economically favorable in those cases where land costs are high. A final polishing treatment to remove residual boron from the effluent would be necessary in most cases, and the corresponding additional cost must be considered.

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