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# Hexavalent Chromium Removal in a Foam Flotation Pilot Plant

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## Abstract

Hexavalent chromium was removed from dilute simulated wastewater in a continuous flow pilot scale foam flotation plant. Cr(VI) was reduced to Cr(III) with ferrous sulfate, and the floc resulting on pH adjustment was then removed by precipitate flotation. Sodium lauryl sulfate was used as the carrier surfactant. Effluent Cr concentrations below 0.5 mg/L are easily achieved over the pH range 4.5 to 7.0. The effects of varying the hydraulic loading rate and the ferrous sulfate dose were studied.

## INTRODUCTION

Chromium is widely used as a scratch- and corrosion-resistant decorative finish for metals, onto which it is electroplated. Chromium in industrial wastes often occurs in the hexavalent form as chromate ($CrO_4^{2-}$) and dichromate ($Cr_2O_7^{2-}$). Industrial sources of chromium-containing wastes include: (a) metal cleaning and treatment; (b) electroplating operations; (c) the manufacture of corrosion control additives, inks, pigments, and dyes; (d) chrome tanning; and (e) aluminum anodizing (*1, 2*). The most commonly used method of hexavalent chromium disposal is reduction of the hexavalent chromium to the trivalent state with a chemical reducing agent such as sulfur

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dioxide, sodium bisulfite, or ferrous sulfate. The trivalent chromium is then removed by precipitation, usually with lime (*1, 3*).

Chromium is a moderately toxic element. Trivalent chromium significantly impairs the reproduction of ***Daphnia magna*** at levels of 0.3 to 0.5 ppm. Hexavalent chromium retards the growth of Chinook Salmon at 0.2 ppb (*4*). Hexavalent chromium is also corrosive, a potent human skin sensitizer, and a carcinogen (5).

For direct discharges, the 30-day averaged standard for "Best Practicable Control Technology Currently Available" (BPT)-equivalent control technology is 1.0 ppm for chromium (*6*). The Best Available Technology Economically Achievable (BAT) provides a more stringent standard; the BAT-equivalent effluent level achievable on a 30-day averaged basis for chromium is 0.50 ppm (*6*).

Foam separations of hexavalent chromium have been developed by a number of investigators (*7–19*). A number of variations of these techniques have been used, including foam fractionation, ion flotation, precipitate flotation, and adsorbing colloid flotation; these have been reviewed by Grieves (*9*) and by Huang et al. (*15*). Ion flotation has an advantage over foam fractionation in that for ion flotation the precipitation reaction between the surfactant and the metal ion colligend generally requires a surfactant concentration only slightly above stoichiometric, while foam fractionation requires surfactant concentrations well in excess of stoichiometric. Surfactant utilization may be reduced even further by first precipitating the colligend and then floating the precipitate. An example of this is a three-stage process for hexavalent chromium removal. Cr(VI) is reduced with $NaHSO_3$ at a pH of 2.5–3.0, and the resulting Cr(III) is then precipitated with NaOH at a pH above 6.0. The chromic hydroxide is then removed by batch flotation with an anionic surfactant (sodium lauryl sulfate) at a pH of 7.0–8.8. Chromium removals of 97% were obtained from solutions initially containing 48.3 mg/L of chromium (*10*).

Hexavalent chromium was also removed by reducing it to Cr(III) with $FeSO_4$ in the pH range 4.5–7.0; the resulting precipitate [(of $Fe(OH)_3$, $Cr(OH)_3$, and possibly some coprecipitated Cr(VI)] was then removed by batch flotation at pH 4.5–7.0 with sodium lauryl sulfate as the collector. This gave over 99% removal of Cr from solutions initially containing 50 mg/L of Cr. This technique provides several advantages over other techniques, as follows:

(a) Residual chromium levels are less than 0.5 mg/L
(b) Removal is rapid

(c) The separation is effective at relatively high ionic strengths (0.1 *M* NaCl)
(d) High separation efficiencies (residual Cr < 0.5 mg/L) are achieved even at higher initial Cr levels (90 mg/L)

Adsorbing colloid flotation of hexavalent chromium with either $Fe(OH)_3$ or $Al(OH)_3$ was also found to be effective (*15*).

Precipitate and adsorbing colloid flotation techniques appear to possess some advantages when applied to dilute waste streams. Operation is rapid, low residual metal concentrations can be achieved, space requirements are relatively small, the flexibility of the technique permits its application to a variety of metals on a wide range of scale, and sludge volumes are relatively small. Recent estimates of costs indicate that it should be competitive with lime precipitation and settling in many instances (*17, 19, 20*).

We report here on the removal of Cr(VI) by adsorbing colloid flotation in a continuous-flow pilot plant. Hexavalent chromium is reduced to Cr(III) with $FeSO_4$, and the resulting mixed precipitate is removed by flotation with sodium lauryl sulfate. Effluent Cr concentrations below 0.3 mg/L were routinely obtained by this technique.

## EXPERIMENTAL

The continuous flow foam flotation pilot plant used in this work has been described in detail in earlier papers (*17, 19*). Figure 1 shows a schematic diagram of the plant.

Simulated wastewater is pumped to the apparatus from a 1040-L (275 gal) storage tank. The addition of $FeSO_4$ (for reduction of Cr(VI) and coprecipitation of $Fe(OH)_3$) and of NaOH (for precipitation of the hydroxides) occurs upstream from the main pump, which provides a rapid mix. $FeSO_4$ solution is fed at the required rate by a Masterflex variable feed pump. The NaOH solution flows by gravity through a solenoid valve which is controlled by a Horizon 5650 pH controller set to produce the desired pH range in the first mixing chamber, in which the Cr(VI) is reduced and in which the mixed hydroxides begin to flocculate. The electrode of the pH controller is mounted in this chamber.

After the wastewater passes through the main pump, it moves through a series of three mixing-reaction chambers of total volume 43.9 L (11.6 gal) in which the redox reaction and subsequent flocculation of the hydroxide precipitates go essentially to completion. Sodium dodecyl sulfate is metered into the waste stream as it leaves these chambers; the waste then passes

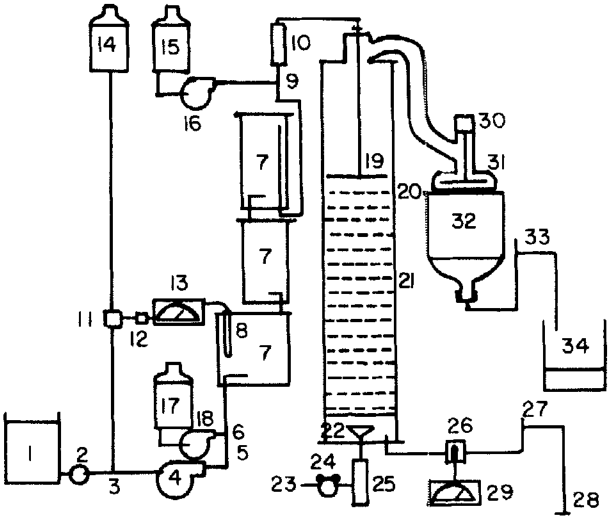

FIG. 1. Schematic diagram of 30-cm pilot plant.

1. Waste tank
2. Waste tank valve
3. NaOH injection tee
4. Main pump
5. Flow control valve
6. $FeCl_3$ injection tee
7. Mixing chamber
8. Control pH electrode
9. NLS injection tee
10. Waste flow rotometer
11. NaOH solenoid valve
12. Electrical junction box
13. Control pH meter
14. NaOH tank
15. NLS tank
16. NLS feed pump
17. $FeCl_3$ tank
18. $FeCl_3$ feed pump
19. Flow dispersion head
20. Column
21. Baffles
22. Air diffuser
23. Air supply line
24. Air pressure regulator
25. Air flow rotometer
26. Monitoring pH electrode
27. Column liquid level control
28. Effluent line
29. Monitoring pH meter
30. Foam breaker motor
31. Foam breaker
32. Clarifier
33. Clarifier liquid level control
34. Broken foam container

through a flowmeter and goes to the flotation column. It is discharged into the column through a spider-shaped dispersion head with eight radial arms and located 76 cm (2.5 ft) below the top of the column.

The column itself consists of two 122 cm (4 ft) sections of Lucite pipe, 29.2 cm i.d. by 30.5 cm o.d. (11.5 × 12 in.), flanged together and sealed with an O-ring. The column contains an assembly of 19 baffles spaced 7 cm (2.75 in.) apart at the top and 9.5 cm (3.75 in.) apart at the bottom. The baffles impede axial dispersion from channeling and overturning in the foam. House air is filtered before passing through a 12.7 cm (5 in.) diameter "fine" porosity fritted glass disk in the bottom of the column. The treated effluent leaves the column from the bottom, and foam is piped from the top of the column to a rotating disk foam breaker. The collapsed foamate is collected in a 49.2-L (13 gal) plastic clarifier mounted under the foam breaker. The effluent pH is monitored continuously.

Simulated Cr(VI)-bearing wastewater was prepared by dissolving potassium dichromate in tap water to reach an initial Cr(VI) concentration of 20 mg/L. Ferrous sulfate was used as the reducing agent—the reaction product $Fe(OH)_3$ then acts as the coprecipitating agent. The pH was adjusted with 0.1 *M* NaOH, and Fisher laboratory grade sodium dodecyl sulfate (SDS) was the surfactant used. All the solutions except NaOH were prepared daily. All runs were made at room temperature. The concentration of SDS used was 40 mg/L for all runs. The airflow rate was 21.5 $N \cdot m^3/m^2$ (50 SCFH) unless otherwise specified.

Analyses for effluent chromium and ion concentrations were done by atomic absorption on a Perkin-Elmer 305B atomic absorption spectrophotometer.

## RESULTS AND DISCUSSION

The variables having an influence on the efficiency of the system which were studied are pH, Fe(II) nominal concentration, and wastewater hydraulic loading rate.

Table 1 shows the influence of pH on chromium removal. It was found that when steady-state operation was reached, the effluent pH was always 0.5 to 1.5 units lower than the pH in the first mixing chamber, in contrast to the earlier findings on the flotation of copper (*17*) and lead (*18*) in this pilot plant. This discrepancy is readily accounted for by the finite rates of the following two reactions:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 17H_2O \rightarrow 2Cr(OH)_3 + 6Fe(OH)_3 + 10H^+$$

TABLE 1
Influence of pH on Chromium Removal[a]

| pH controller lower set point | pH in first mixing chamber | Steady-state effluent pH | Residual chromium in effluent (mg/L) |
|---|---|---|---|
| 5.9 | 6.0 | 4.5 | 0.50 |
| 6.0 | 6.0–6.5 | 5.2 | 0.25 |
| 6.5 | 6.4–7.0 | 6.0 | 0.17 |
| 7.0 | 7.0–7.4 | 6.1 | 0.30 |

[a] Operating conditions: initial Cr(VI) = 20, NLS = 40, Fe(II) = 70 mg/L, hydraulic loading (H.L.) = 0.45 $m^3/h$ (2 gal/min), hydraulic loading rate (H.L.R.) = 6.8 $m^3/m^2 \cdot h$ (2.8 gal/min·$ft^2$), air flow rate = 21.5 $N \cdot m^3/m^2$ (50 SCFH).

and

$$O_2 + 4Fe^{2+} + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$$

both of which may very well not be complete when the influent leaves the first mixing chamber. When the lower set point on the pH controller was 5.9 or less, the pH of the solution in the first mixing chamber stabilized at about 6.0 and no NaOH was consumed (the NaOH solenoid valve was never activated). The initial pH of the simulated wastewater was 6.8. The effluent pH gradually approached a steady-state value of 4.5. When the lower set point on the pH controller was in the 6.0–7.0 range, the pH of the solution in the first mixing chamber oscillated over a range of about 0.5 pH unit. There is a range of over one pH unit in which residual chromium levels of less than 0.5 mg/L are obtained; the optimum effluent pH is about 6.0. The effluent pH decreased gradually from an initial value of about 7.0, taking 40 to 50 min to reach steady state. However, as shown in Table 2, residual chromium concentrations well below 0.5 mg/L are obtained within 15–20 min after start-up; initial high and variable values decrease and become relatively steady as soon as foam is established throughout the length of the column.

The influence of the Fe(II) dose rate on chromium removal is shown in Table 3. The total iron levels in the effluent are also given. The effluent chromium concentration changes little with decreasing Fe(II) dose until this is somewhat less than that required by stoichiometry (64 mg/L of Fe(II)). The total residual iron concentration increases with increasing Fe(II) dose. We note that divalent iron is rather difficult to remove as $Fe(OH)_2$ because of the relatively high solubility of $Fe(OH)_2$ (solubility product = $1.8 \times 10^{-15}$ $m^3/L^3$). This dictates that excessive dose rates of $FeSO_4$ should be avoided. It is interesting to note that when the dose rate of Fe(II) was 57.6 mg/L, 10%

TABLE 2
Variation in Effluent pH and Chromium with Time[a]

| Time (min) | Effluent pH | Chromium in effluent (mg/L) |
|---|---|---|
| 20 | 6.5 | 0.29 |
| 30 | 6.0 | 0.29 |
| 40 | 5.9 | 0.25 |
| 50 | 5.9 | 0.22 |
| 60 | 5.9 | 0.23 |

[a] Operating conditions: initial Cr(VI) = 20, Fe(II) = 64, NLS = 40 mg/L, H. L. = 0.45 $m^3$/h (2 gal/min), H.L.R. = 6.8 $m^3/m^2 \cdot h$ (2.8 gal/min·$ft^2$), air flow rate = 21.5 N·$m^3/m^2$ (50 SCFH).

TABLE 3
Influence of Fe(II) Dose and pH on Chromium and Iron Removal[a]

| pH controller lower set point | Steady-state effluent pH | Fe(II) dose (mg/L) | Effluent Cr (mg/L) | Effluent Fe (mg/L) |
|---|---|---|---|---|
| 6.0 | 5.2 | 70 | 0.25 | 12 |
| 6.0 | 5.2 | 64 | 0.26 | 7 |
| 6.5 | 6.0 | 70 | 0.17 | 14 |
| 6.5 | 5.9 | 64 | 0.22 | 3 |
| 6.5 | 6.0 | 60.5 | 0.25 | 2 |
| 6.5 | 6.0 | 57.6 | 0.25 | 2 |
| 6.5 | 6.1 | 51.2 | 1.10 | 1 |

[a] Operating conditions: initial Cr(VI) = 20, NLS = 40 mg/L, H.L. = 0.45 $m^3$/h (2 gal/min), H.L.R. = 6.8 $m^3/m^2 \cdot h$ (2.8 gal/min·$ft^2$), air flow rate = 21.5 N·$m^3/m^2$ (50 SCFH).

TABLE 4
Effect of Hydraulic Loading on Chromium and Iron Removal[a]

| pH controller lower set point | Effluent pH | Airflow (SCFH) | Hydraulic loading (gal/min) | Effluent Cr (mg/L) | Effluent Fe (mg/L) |
|---|---|---|---|---|---|
| 6.5 | 6.0 | 50 | 2.0 | 0.25 | 2 |
| 6.5 | 6.2 | 70 | 1.5 | 0.20 | 1 |

[a] Operating conditions: initial Cr(VI) = 20, Fe(II) = 57.6, NLS = 40 mg/L.

TABLE 5
Optimum Operating Parameters for 30-cm Pilot Plant[a]

| Parameter | Value |
|---|---|
| pH controller lower set point | 6.5 |
| Effluent pH | 6.0 |
| Fe(II) (mg/L) | 57.6–60.5 |
| Hydraulic loading rate ($m^3/m^2 \cdot h$) | 6.8 (2.8 gal/min·$ft^2$) |

[a] Other parameters: initial Cr(VI) = 20, NLS = 40 mg/L, air flow rate = 21.5 N·$m^3/m^2$ (50 SCFH).

less than that required by the stoichiometry of the reaction, 99% of the chromium was removed and the residual chromium concentration was as low as 0.25 mg/L. This was also observed in our earlier batch studies on the separation of Cr(VI) by reduction and flotation with $FeSO_4$ and sodium lauryl sulfate (*15*). Presumably the excess hexavalent chromium, present in anionic form, is adsorbed on or coprecipitated with the positively charged $Fe(OH)_3$ floc. The total iron concentrations in the effluents obtained in the present study are higher than those obtained in the earlier batch runs in which residual total iron concentrations in the effluent were less than 0.5 mg/L. This is probably due to failure of the redox reaction between Cr(VI) and Fe(II) to go to completion in the time interval during which the wastewater is moving through the pilot plant. One might be able to reduce the effluent total iron concentration by increasing the total volume of the mixing chambers or decreasing the hydraulic loading rate, either of which would increase the detention time of the waste in the mixing chambers. The effect of hydraulic loading rate on chromium and iron removal is shown in Table 4. Both residual chromium and residual iron decrease with decreasing hydraulic loading rate. We note, however, that at the lower hydraulic loading rate (1.5 gal/min), it takes a much longer time (about 40 min) to establish a stable foam in the column even at an increased airflow rate. We therefore regard 2.0 gal/min as a more desirable hydraulic loading rate.

Table 5 lists the optimal operating parameters for this separation as run in our 30-cm continuous flow pilot plant column. Residual chromium concentrations of 0.25 mg/L and residual iron concentrations of 2 mg/L can be achieved routinely under these conditions.

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