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The Removal of Metallo-Cyanide Complexes by Foam Flotation

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Abstract

Precipitate and adsorbing colloid flotation techniques are used to remove simple and complexed cyanides from aqueous solutions. Adsorbing colloid flotation using ferric hydroxide and sodium lauryl sulfate at pH's of around 5 seems to be effective for removing complexed cyanides; free cyanide is removed by formation of ferric ferrocyanide followed by adsorbing colloid flotation. Zinc is not as well removed in these procedures as are copper, chromium, nickel, and cobalt.

INTRODUCTION

The term "cyanides" refers to inorganic and organic compounds containing the functional group CN (*1*). The inorganic cyanides are further classified into "simple" and "complex," the latter resulting from the ability of the CN moiety to form stable complex ions with various metals. These complexes are important from solubility and toxicity considerations. The cyanide anion, CN^-, cannot permeate cellular membranes because it is charged. Entry into the cell is achieved by molecular HCN. Equilibrium is then reestablished, liberating CN^- ions within the cell; these combine with the Fe^{3+} present in the porphyrin molecule. This causes inhibition of the processes which effect oxygen metabolism. Asphyxiation of affected tissues results. Natural cyanide detoxification occurs by the enzyme conversion of CN^- into thiocyanate, SCN, which is eventually eliminated in the urine. The literature contains many assessments of acute cyanide poisoning of various aquatic organisms (*2*), semiaquatic and terrestrial organisms (e.g., Refs. *2* and *3*), and humans (e.g., Ref. *4*).

There are several sources of cyanide in our environment. Wastewaters from the following industries are known to contain cyanide: ore extracting and mining, photographic processing, coke making and coal chemicals, synthetic fiber making, case hardening and pickling of steel, and electroplating (*5*). The concentration of total cyanide in industrial discharges permitted under Public Law 92–500 by July 1, 1977 ranges from 0.01 to 0.5 mg/l (*6*). The recreational water quality criterion for cyanide is 0.005 mg/l (*7*). There are no water quality criteria for cyanide in public water supplies. The previous value of 0.2 mg/l was rescinded because such concentrations would result from a spill. As such, regulation falls under other auspices (*8*). The greatest sensitivity for the determination of cyanide concentration according to the U.S. EPA is 0.02 mg/l (*9*).

Various treatment technologies (physical, chemical, and biological) exist for the removal of cyanide from wastewaters. These include alkaline chlorination, electrolytic decomposition, ozonation, complexation with metals, ion exchange, reverse osmosis, dialysis, irradiation, permanganate oxidation, peroxide oxidation, complexation with polysulfides, the Kastone process, liquid–liquid extraction with primary and secondary amines, copper-catalyzed activated carbon adsorption, and biological oxidation using trickling filters and activated sludge (*5*, *10*). Many of these processes are well adapted to treating waste streams of low volume and high concentration (e.g., wastewater from an electroplating facility). Some exhibit technical difficulties, while others at present lack full-scale demonstration. The alkaline chlorination process is most commonly employed.

The iron cyanide complexes are so stable (see Table 1) that standard alkaline chlorination does not affect them. Since they exhibit little dissociation, they have acquired "nontoxic" labels. Table 2 lists the solubilities of some complex cyanide salts. However, Doudoroff has found the toxicity of the zinc, cadmium, and copper cyanide compounds to be greater than an equal concentration of sodium cyanide. Also, synergistic toxic effects occur in the combination of zinc and copper with cyanide (*11*). Iron complexes are capable of releasing cyanide ion through photodissociation in strong sunlight. Ten milligrams per liter of an iron cyanide, expressed as CN^-, may release 1 mg/l HCN in 1 hr (*11*). Also, bacterial decomposition of the complex in the receiving water to form CN^- is

TABLE 1

Stability Constants for Cyanide Complexes[a]

Complex	K_s (25°C)
$Co(CN)_6^{4-}$	1×10^{19}
$Cu(CN)_4^{2-}$	1×10^{25}
$Fe(CN)_6^{4-}$	1×10^{24}
$Fe(CN_6)^{3-}$	1×10^{31}
$Ni(CN)_4^{2-}$	1×10^{22}
$Zn(CN)_4^{2-}$	8.3×10^{17}

[a] From A. J. Bard, *Chemical Equilibria*, Harper and Row, New York, 1966.

TABLE 2

Solubilities of Cyanide Compounds[a]

Compound	Solubility (g/l)	Temperature (°C)
$Ni(CN)_2$	5.92×10^{-2}	18
$Zn(CN)_2$	5.8×10^{-3}	18
$Fe_4[Fe(CN)_6]_3$	2.5×10^{-4}	22
$Zn_2Fe(CN)_6$	2.6×10^{-3}	NA
$Zn_3[Fe(CN)_6]_2$	2.2×10^{-5}	NA
$Cu(CN)_2$	0.014	20

[a] From ASTM, 1975 and Linke, 1958, 1965.

possible as well as increased solubility under alkaline conditions. Consequently the deliberate complexing of simple cyanides with iron salts as an economical wastewater treatment should be unacceptable. The insoluble iron cyanide in a solid waste can best be treated by burial or landfill in an area where acid conditions are common (*12*). The other metallo-cyanide complexes are susceptible to chlorine oxidation but proceed at different rates (*13*).

There has been much continuing activity in the theory and application of separation of foam flotation techniques (*14*). Because its roots lie in extractive metallurgy, much of this interest is in the removal of metals. Comparatively little has been done on the removal of anion contaminants (*15–17*). Grieves, Bhattacharyya, and co-workers, however, have devoted much effort to applying flotation techniques to anionic waste treatment problems (e.g., Refs. *18* and *19*). They also studied the removal of iron-complexed cyanide by foaming with a cationic surfactant, ethylhexadecyldimethylammonium bromide (*20, 21*). After treatment, the free residual cyanide averaged 7.5 mg/l; residual complexed cyanide, 2.9 mg/l. The reduction in free cyanide ranged from approximately 80 to 90%. Other studies involving metallo-cyanide complexes include batch foam fractionation experiments concerning the selectivity of several chloride vs cyanide complex ions (*22*, *23*), and a similar determination of the selectivity coefficients for Ag $(CN)_2^-$ and Au $(CN)_2^-$ vs I^- (*24*).

In this paper we investigate the removal of metallo-cyanide complexes using the anionic surfactant sodium lauryl sulphate, NLS. We consider the precipitate and/or adsorbing colloid flotation of cobalt, copper, chromium, iron, nickel, and zinc systems, individually and in combination. Removal is addressed from two aspects: (1) the removal of cyanide ion itself and (2) the removal of complexes which could be present or readily formed in the wastewater. Particular interest was paid to iron–iron cyanide systems because of their low toxicity and low cost.

EXPERIMENTAL

Batch foam separations were carried out in 90 cm long Pyrex columns described earlier (*25*, *26*). Metals analyses were performed on acidified aqueous samples on an Aztec Mark II atomic absorption spectrophotometer. Cyanide determinations were performed on basic (pH 13) solutions with an Orion specific ion probe electrode, model 94–06. The standard curves were linear in the range studied, 0.05 to 10.0 mg/l. The average correlation coefficient (for the first-order fit of log concentration vs MV) was 0.9970.

A semiquantitative method was developed for the determination of a residual iron-cyanide complex in solution. A solution was prepared as described below, but not foamed. The first metal added was Fe^{2+} (100 mg/l); the second, Fe^{3+} (150 mg/l). The additional pH adjustments to prepare for the cyanide and metals analyses were also performed on the sample. This insured comparable ionic strength of the solutions. The solution was then permitted to stand, covered, to simulate the oxidation experienced in the column. Aliquots were diluted to yield a series of standards representing 0 to 20% of the initial concentration. Absorbance vs percent of initial concentration were run on a Beckman DB spectrophotometer at a wavelength of 732 mμ. The results were linear in the range studied with a correlation coefficient of 0.9996 for a first-order fit.

Stock solutions of cyanide (50 mg/l) from KCN were prepared daily. Two hundred milliliters were placed in a beaker and the appropriate amount of the "first metal" was added. In all cases 1 ml of stock metal solution resulted in a 50 mg/l concentration. It was presumed that the "first metal" forms the metal-cyanide complex anion. The stock metal solutions were prepared from the corresponding nitrate salts except for the Fe^{2+} solution, for which ferrous ammonium sulfate was used. All metal solutions were kept at acidic pH. The metal cyanide solution was stirred for approximately 5 min. pH was monitored throughout. The "second metal" was added and the solution stirred for approximately 10 min. Longer stirring periods were tested but yielded no increase in CN removal (see the "Results and Discussions" section). The pH was adjusted to the desired value by adding NaOH or HNO_3 as necessary. Five milliliters of 1000 mg/l NLS were added before the test solution was poured into the column. Additional surfactant was added in a series of 5 ml injections throughout the run as required. Air flow rate in the column was approximately 60 ml/min.

RESULTS AND DISCUSSIONS

A series of runs was performed to determine the optimum operating parameters for the foam removal of cyanide. Optimization required the assessment not only of residual cyanide concentrations but also residual levels of cyanide complex and iron. The parameters which were varied were Fe(II) concentration, Fe(III) concentration, NLS concentration, pH, and duration of foaming. The manner of NLS addition was also studied. Second-order effects were also briefly assessed. These included the effect of increased stirring time after iron addition and use of dry weight iron salts additions (instead of acidified stock solutions). The latter was tried in an effort to maintain ionic strength as low as possible. Both second-order effects produced no more than minor variations well within the experimental precision of the results.

Table 3 shows the results of preliminary tests in which precipitate flotation was employed to remove cyanide. (Earlier runs determined optimum pH for removal.) The precipitation with Fe(III) effected no removal. The hydroxide was formed and an odor of HCN was noticed escaping from the column, so the run was terminated. Precipitation with Fe(II) produced better results. Foaming effected an average 82.8% free CN reduction and a 91.1% iron reduction.

Table 4 presents a summary of required molar ratios and milligrams per liter equivalents for the iron cyanide complexes and precipitated compounds. Similar information for the heavy metals studied (and dis-

TABLE 3

Precipitate Flotation Runs

Run	Initial concentration Fe(II) (mg/l)	Initial concentration Fe(III) (mg/l)	pH	Foaming time (min)	Residual CN (mg/l)	Residual Fe (mg/l)
A	50	0	4.9	40	8.6	4.1
B	50	0	4.9	40	8.6	4.8
C	0	50	4.9 → 6.5	[a]	17.1	NA

[a] Aborted, see text.

TABLE 4

Molarity and mg/l Conversions[a]

Species	at	mg/l	yields	Molarity ($\times 10^5$)	solution
CN		50		19.2	
Fe		50		8.95	
Cu		50		7.87	
Cr		50		9.61	
Co		50		8.48	
Ni		50		8.52	
Zn		50		7.65	

Species	Ratio of Fe/CN (mg/l)	Ratio of Fe/CN (mole)
$Fe(CN)_6^{3-}$	0.358	0.167
$Fe(CN)_6^{4-}$	0.358	0.167
$Fe[Fe(CN)_6]$	0.716	0.333
$Fe_4[Fe(CN)_6]_3$	0.835	0.389
50 ppm Fe and 50 ppm CN	1.00	0.466

[a] For 50 ppm CN, total conversion to $Fe_4[Fe(CN)_6]_3$ yields 9.45 mg/l complex salt or 1.1×10^{-5} mole complex salt.

cussed later) is also included. It was assumed that the Fe(II) formed the stable complex $Fe(CN)_6^{4-}$ and excess iron formed $Fe_4[Fe(CN)_6]_3$—the excess Fe(II) being oxidized to Fe(III) upon stirring and/or foaming.

In an effort to increase the removal of cyanide, a series of runs was made using adsorbing colloid flotation. The precipitate formed was still assumed to be predominantly $Fe_4[Fe(CN)_6]_3$ (see Ref. *27*, p. 195). This was then adsorbed onto ferric hydroxide floc and foamed with pulsed NLS additions. For 60 min runs, 5 ml (25 mg/l) additions of NLS were added at times of 0, 10, 25, and 40 min. Table 5 shows the results of these runs which determined the standard operating conditions. A fresh ascarite air filtering system adequately removed CO_2 so that initial and final pH on the columns were essentially the same. Two additional pH considerations were included in this study: (1) ferric hydroxide floc floated best with NLS over a pH range of 5 to 7 (*25*), and (2) most discharge regulations require the pH of plant effluent to be between 6 and 9 (*6*).

The first series of runs (1–6) employed 100 mg/l Fe(II) to form the ferrocyanide complex and precipitate and 200 mg/l excess Fe(III) to form the adsorbing floc. Overall best results were obtained in the pH 5.3 to 5.5 range considering the duration of foaming and amount NLS required.

It should be noted that according to Grieves and Bhattacharyya (*20*), as suggested by Legros (*28*, *29*), complete conversion of "free" cyanide to complexed cyanide is impossible. A "reasonable" percentage of non-complexed cyanide was reported to be 20%. This results from the hydrolysis of the ferrocyanide complex ion to form a ferro aquo penta cyanide complex, $[Fe(CN)_5H_2O]^{3-}$, and free cyanide, CN^-.

The next series of runs (7–14) optimized the iron concentration and foaming time. On the basis of the results of Series 1, the pH employed was 5.3 to 5.5. An initial pH of 5.5 was used to accommodate a decrease in pH with minimal reduction in removal efficiency should the quantity of the ascarite prove insufficient. Runs at a somewhat lower pH (suggested by the results from Series 1) were performed to verify this during this optimization study.

At pH 4.2 the average percent CN removal was 88.0. The average iron removal was 87.7%. There was evidence of trace residual iron complex at this pH. At pH 5.5 the percent CN removal was 92.2 (3.9 ppm average residual) and the average percent iron removal was 97.8 (5.4 ppm average residual). There was no evidence of residual iron complex when the samples were analyzed as described in the previous section. Extended foaming did not decrease the residual free cyanide concentration but did reduce the iron concentration from 5.0 mg/l at 60 min to 3.0 mg/l at 90 min. The foamate volume at the end of the 60-min runs was 5 to 6% of the initial sample volume for one system; this quantity was 7 to 8% in another column.

As mentioned previously, the iron cyanide complex is known to photodecompose. A run was made which was shielded from the laboratory fluorescent lights. No decrease in free cyanide concentration was noted. However, there was an increase in percent residual complexed cyanide, 0.76. (Operating conditions as in Runs 12–14.)

TABLE 5

Standard Operating Conditions—Determining Runs

Run	Initial concentration		Operating conditions			Residuals		
	Fe^{2+} (mg/l)	Fe^{3+} (mg/l)	pH	Foaming duration (min)	Total NLS added (mg/l)	Free CN (mg/l)	Fe (mg/l)	Complex (% initial concentration)
1	100	200	3.85	45	75	3.9	7.7	0.8
2	100	200	4.7	45	100	3.2	7.5	0
3	100	200	5.3	60	100	2.8	2.4	0.5
4	100	200	5.5	60	100	4.1	5.9	0
5	100	200	5.7	120	175	1.9	4.0	0.5
6	100	200	6.0	Aborted—poor floc removal				
7	100	150	4.2	60	125	6.5	13.1	0
8	100	150	4.2	90	125	5.9	21.2	0.2
9	100	150	4.2	90	125	6.5	20.3	0
10	100	150	4.2	120	150	5.9	20.3	0
11	100	150	4.2	120	150	5.1	17.4	0.2
12	100	150	5.5	60	100	3.6	4.8	0
13	100	150	5.5	60	100	4.1	6.6	0
14	100	150	5.5	60	100	4.1	4.9	0

The operating conditions from Runs 12–14 were selected as the standard operating conditions. Another series of runs using these conditions investigated the effect of increasing ionic strength on residual concentrations. The results are seen in Table 6. As anticipated, the residual concentrations of iron and complex increased with increasing salt concentration. The concentration of free cyanide at the end of the run was found to decrease with increasing salt concentration.

Next the standard operating conditions were used in a study of cyanide removal in the presence of various heavy metals, singly and in combination. The metals selected for study were cobalt, copper, chromium, nickel, and zinc. Cobalt was included since it also forms a very stable cyanide complex (see Table 1). The other metals are commonly used in electroplating facilities and are found in the wastewater. Cyanide can be used as a major anion in the plating baths (*30*) for zinc, nickel, and copper. These plated metals often form the basis surface for subsequent chromium plating. The average results for cyanide removal are given in Table 7.

In a Type A run, one first adds the metal of interest, M, to the free cyanide solution to form the complex and then adds the Fe(III). This is completely analogous to the standard runs. In a Type B run the complex is made with Fe(II) and then the metal, M, is added. The operating pH was selected as optimum from an earlier series of test runs. A Type C run reverses the order of the addition used in Type B runs. It is run at the standard pH. The Type D runs combine the five metals in equal con-

TABLE 6

Ionic Strength Runs[a]

Run	$NaNO_3$ molarity	Residuals CN (mg/l)	Residuals Fe (mg/l)	Complex (% initial concentration)
Average of standard runs	0	3.9	5.4	0
18	0.01	8.8	11.3	0.2
19	0.01	8.8	19.5	0
20	0.1	7.3	44.3	NA
21	0.1	6.2	54.8	32
22	0.25	3.4	73.6	100
23	0.50	3.2	145.6	100

[a] Standard operating conditions: pH 5.3–5.4, 100 mg/l Fe^{2+}, 150 mg/l Fe^{3+}, duration of foaming 60 min, total NLS added, 100 mg/l.

TABLE 7

Heavy Metal Runs—Residual Concentrations—Average

	Cobalt			Copper			Chromium			Nickel			Zinc		
Run Type	Co (ppm)	Fe (ppm)	CN (ppm)	Cu (ppm)	Fe (ppm)	CN (ppm)	Cr (ppm)	Fe (ppm)	CN (ppm)	Ni (ppm)	Fe (ppm)	CN (ppm)	Zn (ppm)	Fe (ppm)	Cn (ppm)
A[a]	70.2	0.4	0.08	34.6	1.6	7.6	0.3	0.3	19.2	41.8	0.4	0.23	80.0	0.4	43.4
B[b]	~100	39.1	0.13	29.2	0.4	0.06	~100	34.3	7.4	38.7	NA	0.23	91.0	33.8	10.4
C[c]	68.6	30.3	0.07	14.1	5.0	0.69	40.0	25.8	45.4	99.1	43.1	0.43	89.0	74.9	40.3
D[d]	8.2	0.2	1.5	4.9	0.2	1.5	0.1	0.2	1.5	8.7	0.2	1.5	15.0	0.2	1.5

[a] M + Fe^{3+}, [M] = 100 ppm, [Fe^{3+}] = 150 ppm, [CN] = 50 ppm, pH 5.4–5.5.

[b] Fe^{2+} + M, [Fe^{2+}] = 100 ppm, [M] = 100 ppm, [CN] = 50 ppm, pH 4.7–4.8.

[c] M + Fe^{2+}, [M] = 100 ppm, [Fe^{2+}] = 100 ppm, [CN] = 50 ppm, pH 5.4–5.5.

[d] M1 + M2 + M3 + M4 + M5 + Fe^{3+}, [M1] etc. = 20 ppm, [Fe^{3+}] = 150 ppm, [CN] = 50 ppm, pH 5.4–5.5.

TABLE 8

Percent Residual Metals, Run Types A and D

Run Type	Co	Cu	Cr	Ni	Zn
A	70.2	34.6	0.3	41.8	80.0
D	41.0	24.5	0.5	43.5	75.0

centrations, 20 mg/l each for a total concentration of 100 mg/l metal. Runs of Type D are then handled identically to Type A runs.

For the cobalt study, Type B was the least effective method, although the residual free cyanide is low. It is assumed that the overall lower free cyanide concentration (cf. standard runs) reflects the absence or reduction of the hydrolysis reaction. Run Types A and C give comparable results in cobalt and cyanide residual concentrations but not iron. This could be attributed to the only partial oxidation of Fe(II) to Fe(III). For cobalt and the other metals there is general agreement in the percent residual metal between run Types A and D (see Table 8).

Copper, however, gave generally better results with Type B runs. Nickel and chromium gave generally better results with Type A runs. Studies using zinc gave the worst removals of the five metals. This was expected because of zinc's amphoteric character and the comparatively small stability constant of the zinc cyanide complex (see Table 1). Again the increased residual iron concentrations obtained from the Type A and C runs most likely reflect incomplete conversion of Fe(II) to Fe(III) during the stirring and foaming periods.

The residual concentrations of iron and cyanide in the mixed metal runs are lower than those obtained in the standard runs. The average 0.2 mg/l Fe residual is a 99.9% reduction. The average 1.5 mg/l CN residual is a 97% reduction.

CONCLUSIONS

The adsorbing colloid flotation of free cyanide by Fe(II)/Fe(III) results in roughly 92.2% removal of free cyanide, and 100% removal of iron/cyanide complex and 97.8% removal of iron after 60 min at a pH of 5.5. NLS was the surfactant used. Increased ionic strength reduces the percent removal of the complex and iron but decreases the presence of free cyanide after the initial increase. Removal of cyanide in the presence of heavy metals, other than iron, can be effected by the addition of Fe(III) to provide the adsorbing precipitate of $Fe(OH)_3$. The concentration of heavy metal is also reduced. Optimum removal conditions must be determined for each metal or combination.

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