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Precipitate Flotation of Complexed Cyanide

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Summary

Precipitated cyanide, complexed with Fe(II) at a molar Fe/CN ratio of 0.550, can be floated readily from aqueous suspension with a cationic surfactant, ethylhexadecyldimethylammonium bromide. The effects of three distinct mixing times of significance in preparing the precipitate and contacting it with surfactant, of pH, of initial cyanide concentration, of initial surfactant concentration, and of ionic strength have been established experimentally. Mixing times and the initial cyanide concentration have little influence on the flotation, while increases in pH and ionic strength have a most pronounced influence, part of which can be overcome with increased surfactant concentrations. At pH 6.0, 95% of the complexed cyanide can be foam separated from distilled water suspensions 1.5 to 3.1 m*M* in total cyanide. About 0.04 mole surfactant/mole complexed cyanide is required; about 0.08 mole/mole is required to increase the flotation to 99% or to overcome ionic strength effects.

INTRODUCTION

Inorganic precipitates can be floated to the surface of a suspension and physically removed in a foam rising above the suspension. A surface-active agent of opposite charge to the precipitate is adsorbed on the surfaces making the particulates hydrophobic and susceptible to gas bubble attachment. The initial charge of the precipitate (and thus the type of surfactant to be used) is determined by exchange of ions from solution with ions of the outermost layer of the crystal and/or with ions of the interior, especially interstitial ions and "vacancies" (*8*). The ion preferentially exchanged is generally the constituent ion of the precipitate present in excess in the solution phase. Coordination between ionic species present in the precipitate and the surfactant may be significant and can explain the flotation of a precipitate by an ionic surfactant of the same charge (*17*). A single surfactant can be utilized as both a collector and a frother.

Research on precipitate flotation has been limited to the past decade, beginning with that of Skrylev and Mokrushin (*21*) and that of Baarson and Ray (*1*). A number of studies have been carried out (*2,15,20,23*), including an excellent group of papers by Pinfold and Mahne (*10–14,19*) and another by Rubin et al. (*16–18*).

A series of investigations has been conducted of the foam separation of cyanide complexed by ferrous iron. With a molar iron to cyanide ratio of 0.206 mole Fe/mole CN, the soluble ferrocyanide ion reacts with a cationic surfactant to form a surface-active, particulate complex that is readily floatable at pH 7. Upon increasing the iron to cyanide ratio to 0.351, colloidal particulates are immediately formed (Prussian blue), probably consisting of polynucleated $[FeFe(CN)_6]^-$ and $[FeFe(CN)_6]^{2-}$, which can be floated more efficiently than $[Fe(CN)_6]^{4-}$, considering the quantities of Fe(II) and of surfactant that are required. With both Fe/CN ratios, the effects have been investigated of pH, of initial cyanide concentration, and of initial surfactant concentration (*4,5*). Complexed cyanide has been included in a discussion of the use of foam separation as a technique for qualitative analysis (*7*). A series of rate studies has been made, indicating that the rate of removal of $[FeFe(CN)_6]^{2-}$ can be fit by an approximately first-order, reversible rate expression (*4*).

Upon increasing the Fe/CN ratio to 0.50, particulates become visible to the naked eye. With a constant initial surfactant concentration of 0.132 *mM* (1.32×10^{-4} *M*), 98% flotation of complexed cyanide can be achieved from an initial solution 1.54 *mM* in CN, at an Fe/CN ratio of 0.550; while at Fe/CN = 0.455, the flotation is only 38%, and at Fe/CN = 0.351, the flotation is only 22% (*6*).

Only two fundamental studies have been made of the flotation of an inorganic precipitate by an oppositely charged surfactant (*17,19*). The objective of this investigation is to establish the effects on the precipitate flotation of cyanide complexed by ferrous iron of the following independent variables: (1) mixing times of Fe(II) with CN, both before and after pH adjustment, and of the precipitate with surfactant; (2) pH; (3) initial cyanide concentration and surfactant concentration; and (4) ionic strength. Throughout the study, a distinction is made between complexed and "free" (noncomplexed) cyanide, and the surfactant concentration is monitored. The applicability of the separation process is to the treatment of cyanide wastes from such industries as metal plating, steel pickling and producing, and coking.

EXPERIMENTAL

Initial (feed) solutions in distilled water were prepared containing from 1.54 to 3.08 *mM* NaCN. In a few cases (detailed below), tap water was used instead of distilled water. The cyanide was complexed and precipitated by $FeSO_4 \cdot 7H_2O$ or $FeCl_2 \cdot 4H_2O$, with the molar Fe/CN ratio always maintained at 0.550. In the few experiments with tap water, the $FeSO_4 \cdot 7H_2O$ had to be initially dissolved in slightly acidified tap water. For some experiments the ionic strength was modified by adding varying quantities of NaCl or Na_2SO_4, before addition of Fe(II). The reaction was promoted by mixing with a magnetic stirrer for a predetermined time period (2 to 15 min). The pH was then adjusted within the range 5.0 to 8.9 by a mixture of 0.50 *M* NaOH and 0.60 *M* $NaHCO_3$. The mixing time after pH adjustment was varied from 0 to 20 min. The cationic surfactant, ethylhexadecyldimethylammonium bromide (EHDA–Br), was then added and was mixed with the suspension for an additional time period from 0 to 20 min. The initial surfactant concentration was varied from 0.053 to 0.132 *mM*.

Two liters of the suspension were then placed in the foam separation column. The apparatus has been detailed previously (*5*,*7*). The foam separation column was made of Pyrex and was 82 cm in height and 9.7 cm in diameter. Nitrogen gas was saturated with water, metered with a calibrated rotameter, and dispersed through twin, sintered glass diffusers of 50-μ porosity at a rate of 1300 ml/min (at one atmosphere and 25°C). The suspension was foamed for 25 min, with continuous foam removal from a port located 7.0 cm above the initial solution level. Temperature was maintained at 25°C (±1°C). After each experiment was terminated, the volume of the residual suspension was measured, and the concentartion of surfactant in the residual suspension was determined by a two-phase titration technique, using sodium tetraphenylboron (*3*). The residual concentration of total cyanide (*22*) and of noncomplexed cyanide (*9*) were determined. The cyanide analysis techniques were very satisfactory and gave consistently accurate results with cyanide solutions of known concentration.

A typical, average bubble size during the course of an experiment was determined photographically. A Speed Graphic lens and bellows, connected to a 35-mm adapter and in turn to a Hieland-Pentax 35-mm single-lens reflex camera, was focused on a wire of known diameter located about 2.5 cm above the surface of the gas diffusers in the center of the column. Tri-X film was used at *f*/22, with an electronic flash. Average bubble size was determined by direct measurement on the positive prints, using the wire of known diameter for calibration.

RESULTS AND DISCUSSION

For each experiment the following material balances can be written:

$$V_i = V_r + V_f \tag{1}$$

$$(Z_t)_i V_i = (Z_t)_r V_r + (Z_t)_f V_f \tag{2}$$

$$X_i V_i = X_r V_r + X_f V_f \tag{3}$$

The volumes in liters of initial solution, residual solution, and collapsed foam are represented by V_i, V_r, and V_f, respectively. V_i was always maintained at 2.0 liters. The same subscripts apply also to the cyanide and surfactant concentrations, Z and X (both mM), respectively. Free (noncomplexed) cyanide is designated by Z_{nc}, complexed cyanide by Z_c, and the sum of the noncomplexed plus complexed by Z_t, all mM.

$$(Z_t) = (Z_{nc}) + (Z_c) \tag{4}$$

Results of the flotation experiments are generally given in terms of R_c, the removal ratio of complexed cyanide. R_c is defined as:

$$\frac{[(Z_t)_i - (Z_{nc})_r]V_i - (Z_c)_r V_r}{[(Z_t)_i - (Z_{nc})_r]V_i}$$

The term $[(Z_t)_i - (Z_{nc})_r]V_i$ represents the quantity of cyanide "available" for foam separation; $(Z_{nc})_r$ was always less than but about equal to $(Z_{nc})_i$. The reason for the inequality was not the foam separation of the noncomplexed cyanide but rather the shift in the equilibrium between the complexed and noncomplexed forms during an experiment, as the complexed cyanide was floated. The average value of $(Z_{nc})_r$ for the 56 experiments discussed below was 0.27 mM (with $(Z_t)_i$ ranging from 1.54 to 3.08 mM); $(Z_{nc})_r$ ranged from 0.18 to 0.36. None of the independent variables produced significant variation in $(Z_{nc})_r$. In discussing R_c and the flotation of complexed cyanide for a particular experiment with $(Z_t)_i = 1.54$ mM, for example, there is considered the flotation of $1.54 - 0.28 = 1.26$ mM complexed cyanide that is "available." A value of R_c of 1.0 corresponds to complete flotation of 1.26 *mM* and a value of 0.0 to no flotation.

The addition of a small amount of Fe(II) to a solution of CN^- resulted in the formation of $[Fe(CN)_6]^{4-}$. However, as more Fe(II) was added, several species of complexed cyanide were present (*24,25*). Above Fe/CN = 0.50, where a precipitate was formed, possible forms for units polynucleated into the crystal structure are $Fe^{2+}[Fe(CN)_6Fe]_2^-$ and $Fe^{2+}[Fe(CN)_6Fe]^{2-}$. Some complexed cyanide, as $[FeFe(CN)_6]^-$ or $[FeFe(CN)_6]^{2-}$, may also have been absorbed onto the surfaces of the precipitated particles.

The negative charge on the precipitated particles was probably produced by noncomplexed cyanide (CN^-) "exchanged" from the bulk solution phase and/or by the adsorption of $[FeFe(CN)_6]^-$ and $[FeFe(CN)_6]^{2-}$. The noncomplexed cyanide persisted in solution even in the presence of substantial excesses of Fe(II).

Effect of Mixing

Three mixing times were involved: in the precipitation of the cyanide (contact between NaCN and $FeSO_4 \cdot 7H_2O$), designated as t_1; in pH adjustment, designated as t_2; and in contact between the precipitated complexed cyanide and the cationic surfactant just prior to foaming, designated as t_3. An initial series of experiments was conducted with $(Z_t)_i = 1.54$ *mM* and an initial EHDA-Br concentration, X_i of 0.053 *mM*. First, with the pH not adjusted from the value of 5.0 resulting from adding $FeSO_4 \cdot 7H_2O$ to the NaCN solution and thus $t_2 = 0$, and with t_3 maintained at 5 min, the initial contact time, t_1, was varied from 2 to 15 min. The removal, R_c, ranged from 0.80 to 0.87, increasing somewhat and then decreasing again as t_1 was increased. An increase in t_1, which might tend to promote growth in particle size, did not appear to improve the flotation, although $(Z_{nc})_r$ was reduced somewhat, indicating more complete complexing of the cyanide.

Second, with t_1 maintained at 5 min and t_3 maintained at 5 min, the contact time after pH adjustment from 5.0 to 6.0, t_2, was varied from 0 to 20 min. The removal R_c ranged only from 0.88 to 0.91, indicating again that an increased opportunity for particle growth or charge modification by equilibration with the bulk solution phase did not enhance the flotation of the precipitated complexed cyanide.

Third, with t_1 maintained at 5 min. the pH adjusted to 6.0, and t_2 maintained at 0 min (thus the surfactant was added just after pH adjustment), t_3 was varied from 0 to 20 min. The results are tabulated as follows:

t_3, min	R_c
0	0.78
5	0.87
10	0.82
20	0.75

An increase in t_3 provided additional time for surfactant adsorption onto the precipitate, which tended to promote flotation at short times but reduced the flotation at longer times, perhaps due to adsorption of surfactant in a second layer on the particles (with the charged head groups pointing outward) producing decreasing hydrophobicity of the particles.

For all later experiments, described below, t_1 was held at 5 min, t_2 at 0 min, and t_3 at 5 min.

Effect of pH and of Initial Surfactant and Cyanide Concentrations

A second series of experiments was carried out in an effort to establish the optimum pH for the flotation of precipitated complexed cyanide. Figure 1 shows the effect of pH on R_c, with $(Z_t)_i = 1.54$ *mM* and three values of X_i. At $X_i = 0.053$ *mM*, efficient flotation was achieved over pH 5–6, at $X_i = 0.079$ *mM* over pH 5–6.5, and at $X_i = 0.132$ *mM* over pH 5–7. The reason for the lengthening of the effective pH range with increasing surfactant concentration is believed to be due to a modification in the varying demands for the surfactant. Surfactant was adsorbed onto the precipitated complexed cyanide, adsorbed onto the excess Fe(II) and Fe(III) precipitated as $FeCO_3$ and $Fe(OH)_3$ (or FeOOH, etc.), respectively, and some had to be present in a free, nonadsorbed state to act as a frother. As the pH was increased, more excess Fe(II) was precipitated as $FeCO_3$ and more was oxidized by dissolved O_2 to Fe(III) and precipitated as $Fe(OH)_3$; consequently more surfactant was "demanded" by the precipitated iron and less was available to act as a frother and as a collector for the precipitated complexed cyanide. Clearly, this effect would be evidenced at a lower pH with a lower value of X_i. The loss of frother was shown by the fact that at $X_i = 0.132$ *mM*, the collapsed foam volume, V_f, went to zero over the pH range $7.0 \rightarrow 7.3$; at $X_i = 0.079$ *mM*, $V_f \rightarrow 0$ over pH $6.3 \rightarrow 6.6$; and at $X_i = 0.053$ *mM*, $V_f \rightarrow 0$

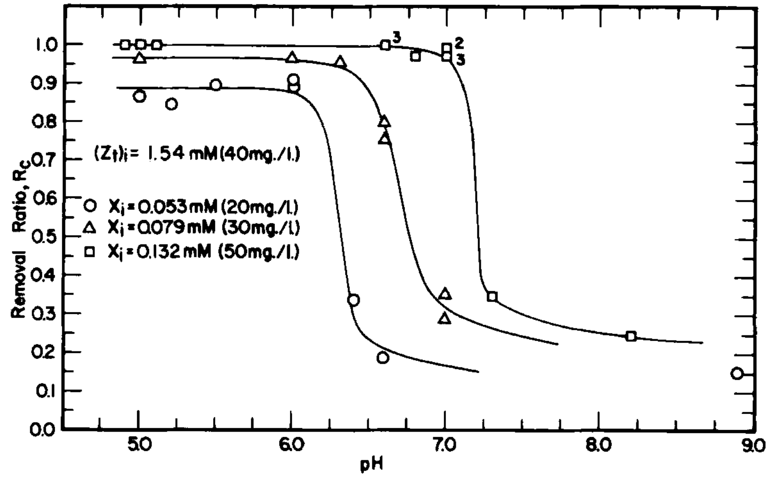

FIG. 1. Effects of pH and initial surfactant concentration on the removal ratio of complexed cyanide.

over pH 6.0 → 6.4. These ranges corresponded precisely to the sharp drops in the three curves in Fig. 1. As long as a certain minimum quantity was present to act as a frother, the flotation was efficient. For example, at $X_i = 0.079$ *mM*,

pH	V_f, liter	R_c
5.0	0.34	0.97
6.0	0.22	0.97
6.3	0.07	0.96
6.6	0	0.76

From all of the experiments, the optimum pH appeared to be 6.0, with $X_i = 0.079$ *mM* yielding $R_c = 0.97$ and $X_i = 0.053$ *mM* yielding $R_c = 0.91$. Three additional experiments were made at pH 6.0 with $(Z_t)_i = 1.92$, 2.31, and 3.08 and initial surfactant concentrations, X_i, equivalent to 0.053 at $(Z_t)_i = 1.54$. The results are given below:

$(Z_t)_i$, *mM*	X_i, *mM*	R_c
1.54	0.053	0.91
1.92	0.066	0.95
2.31	0.079	0.97
3.08	0.11	0.95

Flotation appeared to improve with $(Z_t)_i$ at a constant ratio of surfactant to cyanide. Over the full range of $(Z_t)_i$, about 95% flotation could be expected at pH 6.0 with a molar surfactant to complexed cyanide ratio of 0.04 mole EHDA–Br/mole CN. The collapsed foam volume, V_f, was independent of $(Z_t)_i$.

The ionic strength was increased as the pH was increased, but the increase was small. For example, in going from pH 6.0 to pH 7.0 the increase in the in the "anionic" strength $\Delta\mu^*$, with μ^* defined as

$$\mu^* = \frac{1}{2}\sum_i (\text{Concentration Anion}_i)(\text{Charge of Anion}_i)^2$$

was 0.11 *mM*. As shown below, this increase would produce virtually no effect on R_c. Thus the pH effects were not produced by the concommitant increases in μ^*.

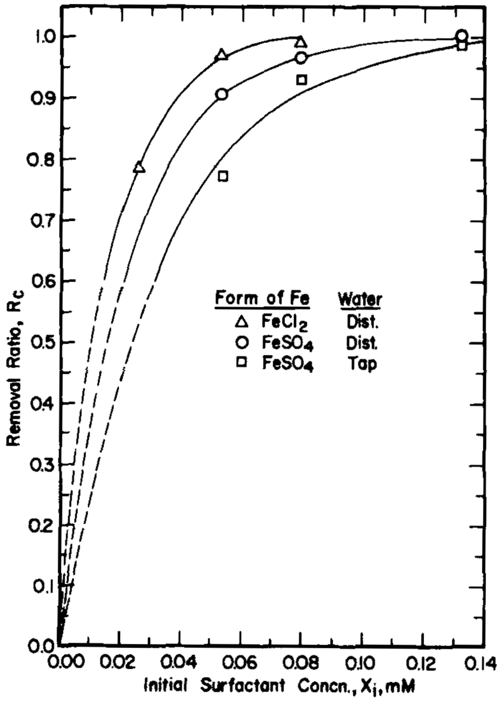

FIG. 2. Effects of initial surfactant concentration and of competing ions on the removal ratio of complexed cynanide.

Effect of Ionic Strength

All of the above experiments were conducted with distilled water suspensions. Figure 2 gives results at pH 6.0 with $(Z_t)_i = 1.54\ mM$, contrasting Lexington tap water to distilled water. The tap water had a conductivity of 405 μmho/cm (at 23°C); this may be compared with the conductivity 478 μmho/cm, of a distilled water solution 2.11 *mM* in Na_2SO_4 and with the conductivity of the distilled water itself, 3.5 μmho/cm. The tap water produced a decrease in the flotation that was more clearly evidenced as the initial surfactant concentration was reduced. The effect was due to other anions competing for the surfactant plus the increased ionic strength produced by both cations and anions. This was further indicated by the upper curve in Fig. 2, in which $FeCl_2 \cdot 4H_2O$ replaced $FeSO_4 \cdot 7H_2O$ as the precipitant, in distilled water suspension.

Rubin (*16–18*) has indicated no effect of ionic strength on precipitate flotation, while Sheiham and Pinfold (*19*) found a pronounced effect. A final series of experiments was conducted at pH 6.0, with $(Z_t)_i = 1.54\ mM$ and $X_i = 0.053\ mM$. Either $FeSO \cdot {}_4 7H_2O$ or $FeCl_2 \cdot 4H_2O$ was used as the precipitant, each together with NaCl

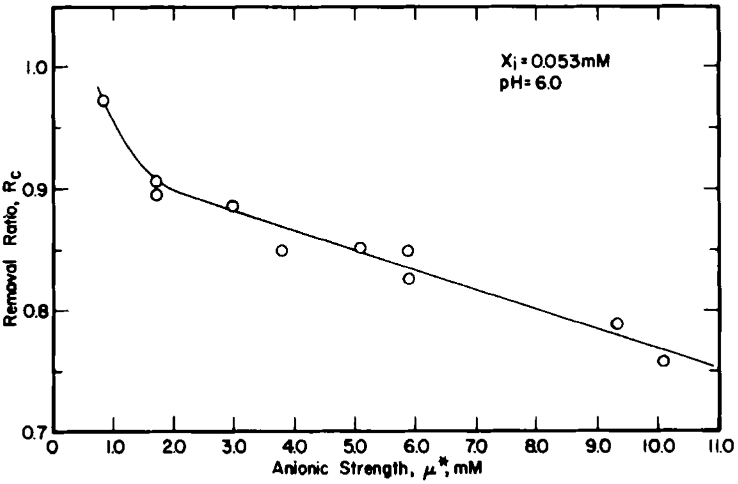

FIG. 3. Effect of anionic strength on the removal ratio of complexed cyanide.

or Na_2SO_4 for added ionic strength. For each run the ionic strength due to both Cl^- and SO_4^{2-}, μ^*, was computed and is plotted on the abscissa of Fig. 3. The removal ratio, R_c, decreased rapidly with μ^*, and then declined less rapidly and approximately linearly. As suggested by Sheiham and Pinfold (*19*), R_c decreased as μ^* was increased, first because of slower precipitation of the cyanide by the iron, produced by increased ion competition, second because of decreased adsorption of the surfactant on the precipitate, produced by a reduction in the potential on the precipitate particles, and third because of greater competition for surfactant by the other anions present. The increased ionic strength may also have promoted the exchange of some of the $[FeFe(CN)_6]^-$ and $[FeFe(CN)_6]^{2-}$ adsorbed on the precipitate, returning to solution those species which had a greater surfactant demand than the precipitate. With the 25-min foaming times that were used throughout, the ionic strength had no apparent influence on the flotation of the surfactant, with both the collapsed foam volume and residual surfactant concentration being independent of ionic strength.

Residual Surfactant Concentration

The concentration of $EHDA^+$ in the residual suspensions was monitored throughout the study. Except for the experiments shown in Fig. 1 at the higher pH values and low values of R_c, the maximum value of X_r for all experiments was 4.3 mg/liter (0.01 *mM*). Values of X_r approaching X_i were obtained at the higher pH's corresponding to low R_c. In general, X_r increased as X_i was increased, increased somewhat with pH over pH 5.0 → 6.5, increased as $(Z_t)_i$ was increased, and was independent of ionic strength. Because of the long foaming times, no really significant variation in X_r would be expected.

Bubble Size

Photographs were taken at several times during the course of an experiment. They could not be taken for about the first three minutes because of the presence of the dense bluish-green precipitate. At a given gas rate and with a given diffuser porosity, bubble size should vary with surfactant concentration and with ionic strength and thus should vary with time. The effect of surfactant concentration should not be too significant, however, as long as it remains appreciable enough for a reasonably stable foam to be formed. A "typical" photograph taken after a foaming time of 5 min was used and the sizes of

200 bubbles were measured. The bubble sizes could be represented by a normal distribution with an average bubble diameter of 660 μ and a standard deviation of 66 μ.

CONCLUSIONS

Precipitated complexed cyanide can be floated readily from aqueous suspension. At an Fe/CN ratio of 0.550 with the pH adjusted to 6.0, 95% of the complexed cyanide can be foam separated from distilled water suspensions 1.5 to 3.1 *mM* in total cyanide using about 0.04 mole of a cationic surfactant/mole complexed cyanide. The residual noncomplexed cyanide, about 0.27 *mM*, can be removed by other means, such as alkaline chlorination or granular carbon adsorption. The collapsed foam volume in which the cyanide is concentrated is about 11% of the initial suspension volume, and about 90% of the surfactant is carried into the foam. An increase in ionic strength decreases flotation, but this can be overcome readily by increasing the molar surfactant/complexed cyanide ratio, again achieving 95% flotation.

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