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Recovery of Co^{2+} Ions from Aqueous Solutions by Froth Flotation. Part II. CoS Precipitation

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ABSTRACT

Cobalt ions have been recovered from aqueous solutions by dispersed-air flotation in acidic conditions. The preliminary step of precipitation as cobalt sulfide using Na_2S is kinetically limited, with only approximately 70% of the cobalt ions being recovered. Recoveries increase considerably under alkaline conditions, where $Co(OH)_2$ is also precipitated. Several collectors have been tested: cetyl trimethyl ammonium bromide, sodium dodecyl sulfate, cetyl pyridinium chloride, and dodecylamine; dodecylamine was found to be the most efficient. The gas flow rate was found to affect the process, with a flow rate corresponding to a superficial gas velocity of 0.1 cm/s yielding maximum recoveries; any further gas flow rate increase resulted in lower recoveries. An increase in column height was found to have an adverse effect on CoS recovery.

Key Words. Precipitate flotation; Column flotation; Cobalt ions; Dodecylamine; Cobalt sulfide

INTRODUCTION

The recovery and/or removal of metals from wastewaters or aqueous solutions may be achieved by applying a variety of methods, e.g., chemical precipitation, complexation, solvent extraction, cementation, reverse os-

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mosis, adsorption, flotation, ion exchange, and evaporation, among others (1). Of these, flotation presents some advantages: simplicity; flexibility and effectiveness of operation; low space requirements; the production of small, concentrated volumes of sludge; and the fact that it may be applied at a small, intermediate, or large scale.

Precipitate flotation is a subcategory of the flotation techniques. It involves a preliminary step where the ionic species under consideration is precipitated and the precipitate is then floated by using an appropriate collector to render the minute solid particles hydrophobic. Precipitation is usually achieved by pH regulation, since most metal ion hydroxides are insoluble at some range of pH values (2–5). However, this technique has its limitations:

The pH at which each metal ion exhibits its minimum solubility is not the same for all metals; therefore, in cases when removing the totality of metal ions from a given solution is required, it is possible that for a particular pH, only some of these may be precipitated, necessitating a series of steps for the total removal of the metal ion load.

Hydroxides tend to resolubilize when the solution pH is changed, making the process pH-sensitive.

Metal hydroxides precipitate mostly at alkaline pH values, making this ion removal technique either inoperative in cases of acidic solutions, or requiring a shift of solution pH to the appropriate alkaline region by using large amounts of the reagent $Ca(OH)_2$ or NaOH.

An alternative to hydroxide precipitation involves sulfide precipitation (6, 7). This offers certain advantages, such as:

The low solubility of metal sulfides over a broad pH range. For example, the stability constant of CoS at 18–25°C is 3.0×10^{-26} (8); thus, most metals may be precipitated fairly easily as sulfides (9). Sulfides of Ag, Pb, and Zn are even insoluble in the presence of strong complexing agents (10, 11).

The high reactivity of sulfide species (S^{2-}, HS^-) with metal ions.

Better sludge thickening (7, 10).

In most cases the amount of a particular ionic species removed from solution as hydroxide is usually less than the amount removed as sulfide, under comparable conditions (Fig. 1). Its single major disadvantage is the potential discharge of the noxious H_2S which, however, is avoided by controlled addition of the appropriate sulfide (e.g., H_2S, Na_2S) in fairly stoichiometric quantities. Another disadvantage is the small size of the particles produced, which causes problems in removal by filtration or sedimentation of the precipitate.

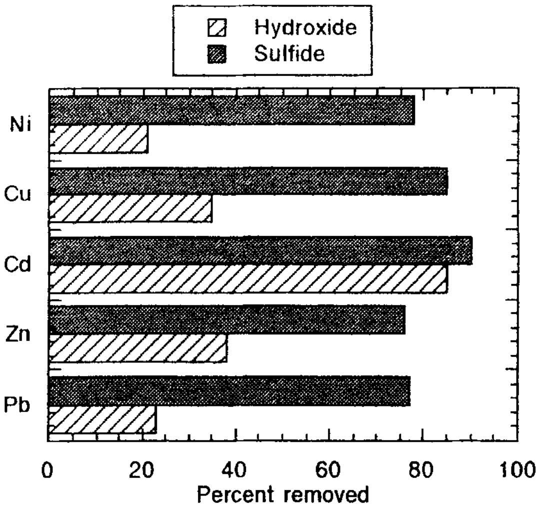

FIG. 1 Removal of metal ions as precipitated hydroxides or sulfides (adapted from Ref. 12).

Sulfide precipitation has been applied as a removal method for various metals (see Ref. 1 for a detailed review of the metal ions investigated up to 1984, and Refs. 13–15 for work later than 1984). Table 1 presents a selective list of metal ion removal by sulfide precipitation followed by flotation (see also Ref. 20). The recovery of cobalt ions from solutions has recently attracted considerable attention because it is a metal of industrial importance. It has been floated mainly as a hydroxide precipitate using a variety of mainly cationic surfactants (see Ref. 21 for a list of relevant references). Its flotation in acidic conditions by applying ion flotation with anionic surfactants has also been reported (21).

The objective of the present work was to investigate the recovery of cobalt ions by applying flotation after they were precipitated as sulfides, a process which has received little attention so far. The effectiveness of this process was then compared to Co^{2+} recovery by anionic-surfactants flotation. Both dispersed- and dissolved-air flotation have been applied, and the effects of several parameters (e.g. gas flow rate, column height) were studied.

EXPERIMENTAL APPARATUS AND PROCEDURE

A column made of Plexiglas, with a total height of 40.0 cm and an inside diameter (i.d.) of 4.0 cm, was used for the dispersed-air experiments. The

TABLE 1
Application of the Ion Removal/Recovery by Sulfide Precipitation and Flotation

Ion	Collector-frother[a]	pH	Precipitating agent	Ref.
CuS/ZnS	DA-CPCl	1.7	Na_2S	16
Cu	CL-pine oil	2.0	H_2S	17
	CL-Dow Z200	2.0	H_2S	18
Cu, Fe	Dow Z-200	2.2, 8.0	NaHS	4
	Minerac A	2.2, 8.0		
	Minerac 1331	2.1		
	KEthX	9.7		
Cu, Ni	Lauroseptol	3.2, 10.0	NaHS	3
Cu, Ni, Fe, Co, Mn	CTACl, LACl, NaLS, Triton X-100	3–9	Na_2S	19

[a] DA: dodecylamine; CPCl: cetyl pyridinum chloride; CL: collectorless; CTACl: cetyl trimethylammonium chloride; LACl: lauryl ammonium chloride; NaLS: sodium lauryl sulfate

total volume of the column was 0.5 L. A side arm, located near the bottom of the column, was used for sample retrieval (for a schematic diagram of the experimental apparatus, see Ref. 21).

Air was fed into the column through a cylindrical ceramic gas sparger (Schott, porosity G_4, with a pore diameter ranging from 16 to 40 μm) which was placed at the bottom of the column for the generation of the necessary air bubbles. The air flow rate was controlled and continuously monitored using a calibrated rotameter.

The dissolved-air flotation experiments were carried out in a larger, 8.0 cm i.d. column, with a side sampling point and a drain, and it had a slightly conical bottom (Aztek, UK). The total volume of the column was 1.5 L. Water was saturated with air under a gauge pressure of 0.4–0.5 MPa in a 10 L-saturator, and it was introduced at the base of the column through a suitable nozzle.

Aqueous solutions of cobalt ions were prepared by dissolving $Co(NO_3)_2 \cdot 6H_2O$ (Merck) in deionized water. The solution pH was regulated using NaOH or HNO_3, and it was monitored throughout the experiments. An aqueous solution of sodium sulfide hydrate (Merck; $Na_2S \cdot xH_2O$, $x = 7–9$, 35% Na_2S) was used as the precipitating compound. The initial cobalt ion concentration of the solution, prior to precipitation, was always 50 mg/L, and all experiments were performed at ambient temperature (20 ± 2°C).

Cetyl-trimethyl-ammonium bromide (Merck, pro analysi grade), sodium dodecylsulfate (Merck, 90% grade), cetyl-pyridinium chloride (BDH, 98% grade), and dodecylamine (Merck, 98% grade) were used as surfactants. All collectors were directly dissolved into the cobalt ion solution except dodecylamine which, being insoluble in water, was added in the Co^{2+} solution dissolved in a small amount of (pro analysi grade) EtOH, resulting in a 0.1% (v/v) concentration of ethanol (EtOH) in the Co^{2+} solution (except in those experiments where the effect of the EtOH concentration on the recovery of CoS was investigated).

The residual concentration of cobalt ions in bulk solution and in the samples was determined by AAS, using a Perkin-Elmer Model 2380 atomic absorption spectrophotometer. The amount of water removed from solution by the surfactants used in this work was minimal as compared to the copious hydraulic entrainment caused by the anionic surfactants used previously (21). Therefore, the percentage recovery of cobalt from solution could be calculated from the initial (C_i) and final or sample Co^{2+} concentrations (C_f):

$$R_{Co} = 100 \times \frac{C_i - C_f}{C_i} \quad (\%) \tag{1}$$

For the dissolved-air flotation experiments, 200 mL of air-saturated water were introduced into an initial solution volume of 1 L; this corresponded to a 20% "recycle" (a term used in continuous-apparatus plants to describe the percentage of the incoming flow being pressurized before being introduced into the flotation cell).

RESULTS AND DISCUSSION

For the removal of a particular ion from solution by precipitation, three separate subprocesses have to be studied:

1. The precipitation step itself, and in particular the amount of precipitating agent required for the maximum removal or recovery of the given ionic species.
2. Closely connected to Process 1 is the flocculation of the minute precipitate particles into larger flocs.
3. The actual separation process, be it flotation or filtration.

I. Precipitation of CoS

The precipitation of cobalt ions was accomplished using Na_2S. Filtration through a 0.45-μm microfilter was used to determine the effect of the amount of Na_2S added on CoS recovery (Fig. 2). Experiments were per-

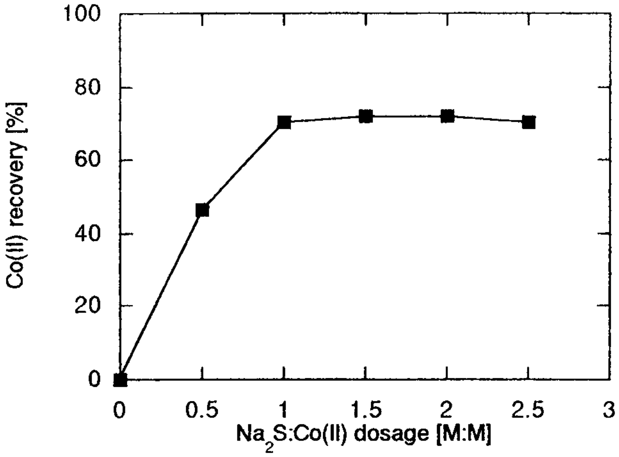

FIG. 2 Effect of Na_2S dosage on CoS precipitation. Conditions: [dodecylamine], 5 mg/L; pH 6.5; agitation, 150 + 50 rpm (15 + 15 minutes).

formed at the natural Co^{2+} solution pH (6.5), and after Na_2S was added, the solution was agitated for an initial rapid-mixing period of 15 minutes (at 150 rpm) and a subsequent slow-mixing 15-minute period at 50 rpm. This double-period agitation (as will be explained later) was found in preliminary studies to yield better results than uniform agitation (dodecylamine was also present during these experiments for reasons explained later).

A stoichiometric amount of Na_2S was found sufficient to provide the maximum recovery. It is interesting to note that any further increase in the amount of Na_2S dosage did not result in further CoS precipitation and seemed, in fact, to be deleterious to the precipitation process (Fig. 3). Altering the pH of the solution (Figs. 3 and 4) increased CoS precipitation, reaching 100% recoveries at pH values over 10, where $Co(OH)_2$ also precipitates, as illustrated in the cobalt ion species diagram (21, 22).

It seems, therefore, that the recovery of cobalt ions from solution by precipitation as sulfides is limited by some complex reaction scheme equilibrium. Similar results have been reported by DeCarlo et al. (19), who also worked under acidic conditions (pH 3) with Co-bearing ferromanganese nodules.

Figure 4 also shows that an agitation period of 30 minutes was sufficient to achieve terminal CoS precipitation. This agitation time was used in all further experiments.

Regarding the agitation process, it was found that when precipitation was allowed to occur in a single agitation period, the agitation speed had

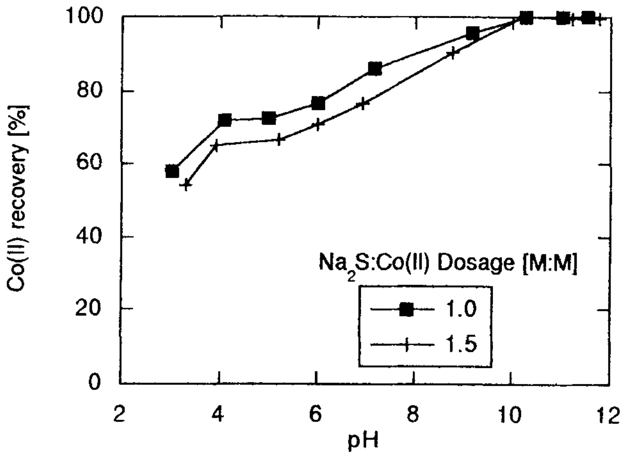

FIG. 3 Effect of pH on CoS precipitation. Conditions: [dodecylamine], 5 mg/L; agitation, 150 + 50 rpm (15 + 15 minutes).

no noticeable effect on Co^{2+} recovery (Fig. 5). When precipitation was done in two periods, an initial one with rapid mixing (for 15 minutes) and then a subsequent one with slow mixing (for another 15 minutes), a considerable increase in CoS precipitation was found (Fig. 6), this double agitation period, typical of the flocculation process, was then followed in all further experimentation.

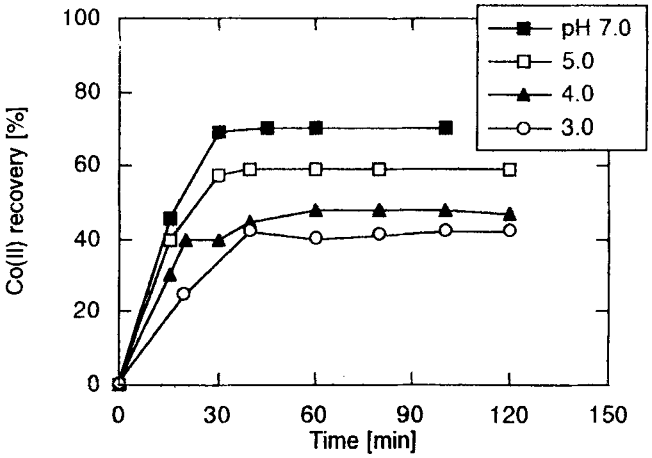

FIG. 4 Effect of pH on precipitation of cobalt. Conditions: [Na$_2$S]:[Co^{2+}] = 1:1 (M:M).

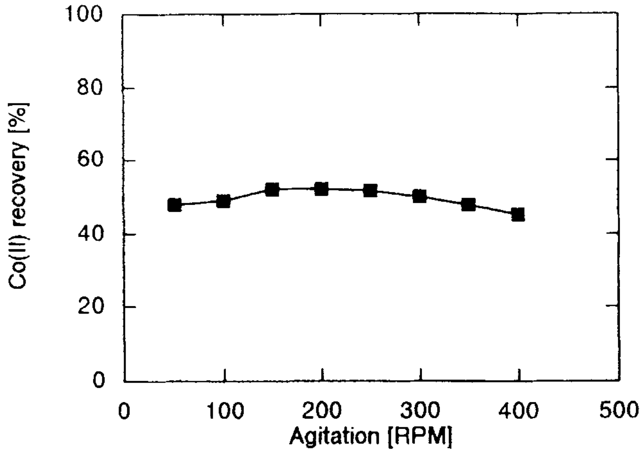

FIG. 5 Effect of agitation speed on CoS precipitation. Conditions: $[Na_2S]:[Co^{2+}]$ = 1:1 (M:M); agitation time, 30 minutes; pH 5.0.

It is interesting to note at this stage that the precipitation process was beneficially affected by the presence of one of the surfactants used for the subsequent flotation stage, dodecylamine (DA). As illustrated in Fig. 7, 5 mg/L DA was sufficient to increase the recovery (by filtration) of CoS from 30 to 60% (in the pH 3 region), with the effect gradually diminish-

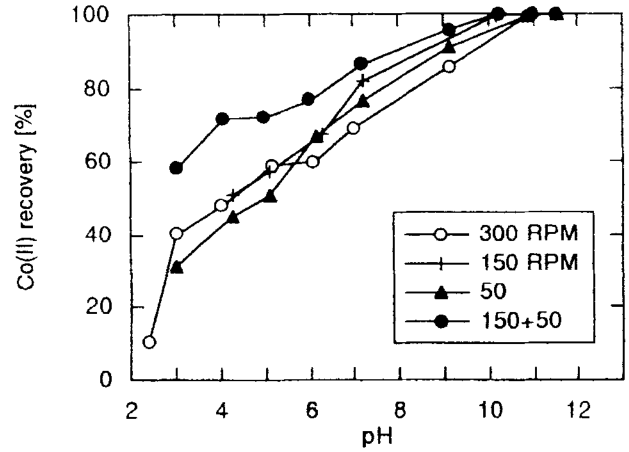

FIG. 6 Effect of agitation on CoS precipitation. Conditions: $[Na_2S]:[Co^{2+}]$ = 1:1 (M:M); agitation time, 30 minutes; [dodecylamine], 5 mg/L.

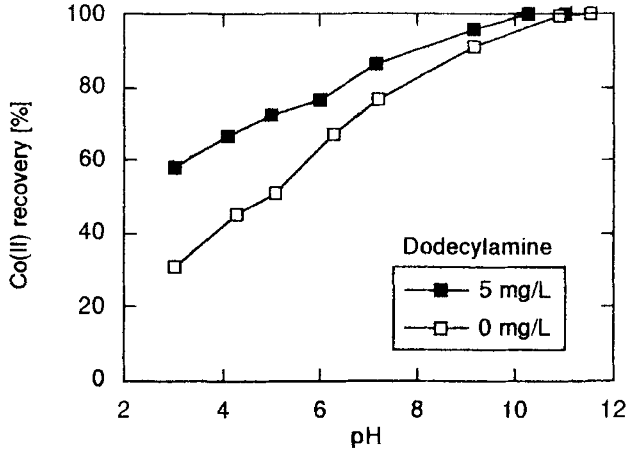

FIG. 7 Effect of dodecylamine on CoS precipitation. Conditions: $[Na_2S]:[Co^{2+}] = 1:1$ (M:M); agitation, 150 + 50 rpm (15 + 15 minutes).

ing as the solution pH increased. This can be explained by a flocculating effect that DA may have on minute CoS particles since it is practically insoluble in water. Thus, the size of the particles is increased and, therefore, their retainment by the microfilter is enhanced, with a corresponding decrease in the amount of Co^{2+} found in the residual solution.

II. Dispersed-Air Flotation

Flotation is a complex process which depends not only upon the chemistry of the solution (like its pH and the chemicals added to cause the necessary precipitation) but also on several other parameters as well, e.g., the choice and amount of surfactant added to render the precipitate particles and flocs hydrophobic, the gas flow rate, the column dimensions, and the hydrodynamics, among others.

Surfactant Choice

Four commonly used (23) surfactants were chosen to investigate their effectiveness in floating CoS from aqueous solution: cetyl pyridinium chloride (CPCl), cetyl trimethylammonium bromide (CTMABr), and dodecylamine (DA)—all cationic—and sodium dodecyl sulfate (SDS), which is anionic. Results from these experiments are reported for the same flotation time (10 minutes). The gas flow rate in all cases was $Q_G = 70\ cm^3/min$. Figure 8 presents the results obtained with each collector under identical

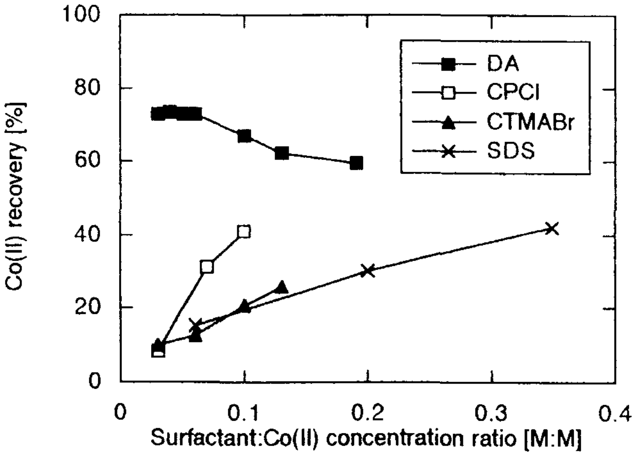

FIG. 8 Effect of surfactant concentration on CoS flotation. Conditions: [Na_2S]:[Co^{2+}] = 1:1 (M:M); agitation, 150 + 50 rpm (15 + 15 minutes); pH 5.0; Q_G = 70 cm³/min.

experimental conditions for various ratios of surfactant to ion concentration under acidic conditions (pH 5.0).

Sodium dodecyl sulfate exhibited a rather poor performance; at concentrations lower than the stoichiometrically necessary one, an unstable foam formed on top of the solution, resulting in redispersion of the floated particles. Higher SDS concentrations yielded highly hydrated foams. The increased recovery in such cases is due to hydraulic entrainment rather than flotation itself.

Cetyl trimethylammonium bromide and cetyl pyridinium chloride also exhibited poor performance as surfactants, similar to that of SDS, but they both produced relatively more stable foam layers.

Dodecylamine was found to be much more effective than the other surfactants, even at surfactant-to-metal concentration ratios much lower than the stoichiometric ones. Interestingly, increasing the amount of surfactant led to a decrease in the recovery of CoS. All further experiments were therefore performed with a dodecylamine concentration of 5 mg/L.

Because dodecylamine is insoluble in water, it was added after being dissolved in a small amount of EtOH, resulting in an EtOH concentration of 0.1% (v/v). An additional benefit of ethanol is that it causes a decrease in bubble size, resulting, in principle, in an enhanced flotation performance. The EtOH presence was therefore tested for its effect on the flotation of the CoS particles (Fig. 9), but it was not found to have a significant effect at the 0.1% concentration on the process. Similar tests

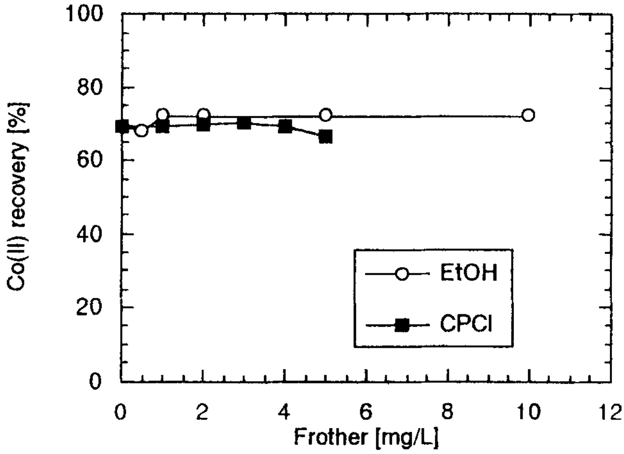

FIG. 9 Effect of CPCl and EtOH used as frothers on CoS flotation. Conditions: $[Na_2S]:[Co^{2+}] = 1:1$ (M:M); [dodecylamine], 5 mg/L; agitation, 150 + 50 rpm (15 + 15 minutes); pH 5.0; $Q_G = 70$ cm^3/min; flotation time, 10 minutes.

were also performed with cetyl pyridinium chloride (Figs. 9 and 10). It produced stable foams but, again, its presence in conjunction with 5 mg/L DA did not yield any additional benefit to the process.

Increasing the pH of the solution resulted in a gradual increase in the amount of Co^{2+} recovered in the froth (Figs. 11 and 12), but this may be attributed to a correspondingly increasing amount of cobalt ions being precipitated either as CoS or $Co(OH)_2$. In Fig. 12 the cationic DA is compared to the anionic SDS. As expected, the latter exhibits an overall low effectiveness, with both providing comparable performances in term of Co^{2+} recovery at alkaline pH values, where $Co(OH)_2$ is expected to prevail.

Figures 10 and 11 also show that within a relatively short period of about 10 minutes all floatable CoS particles were removed to the froth; any further time did not improve CoS recovery.

Gas Flow Rate

In a process driven by the presence of a swarm of bubbles, like flotation, it is obvious that the interfacial area of the bubbles present in the gas–liquid dispersion is important for its effectiveness. This, in turn, is related to the amount of gas being held up in the dispersion, and is regulated by its volumetric flow rate.

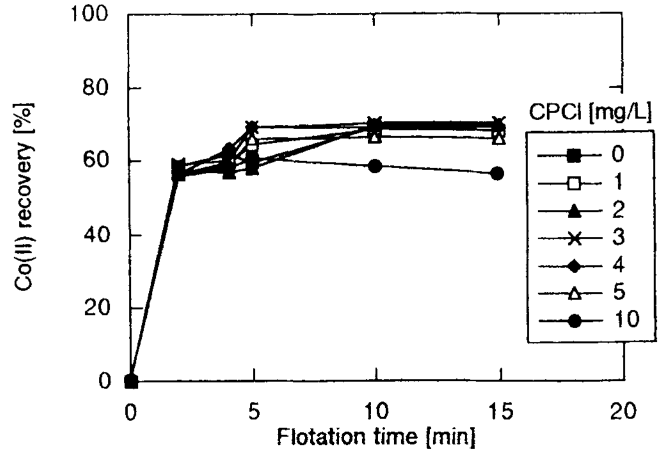

FIG. 10 Effect of CPCl concentration on CoS flotation. Conditions: [Na$_2$S]:[Co^{2+}] = 1:1 (M:M); [dodecylamine], 5 mg/L; agitation, 150 + 50 rpm (15 + 15 minutes); pH 5.0; Q_G = 70 cm^3/min.

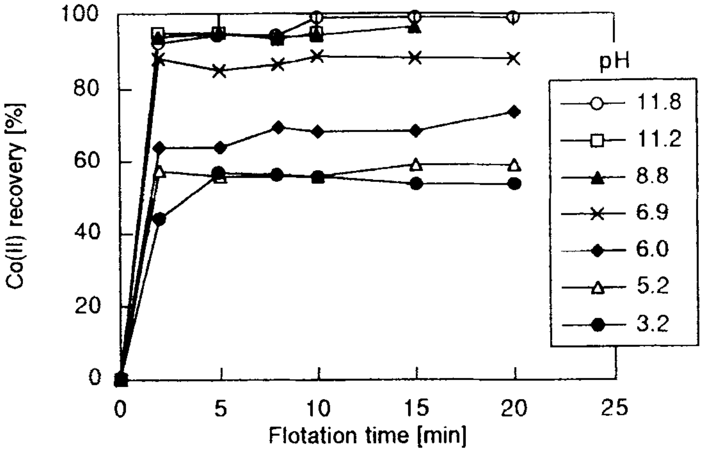

FIG. 11 Effect of pH on precipitate flotation of cobalt. [Co^{2+}], 50 ppm; [Na$_2$S]:[Co^{2+}] = 1.5:1 (M:M); agitation, 50 rpm (30 minutes); [dodecylamine], 5 mg/L; Q_G = 70 cm^3/min.

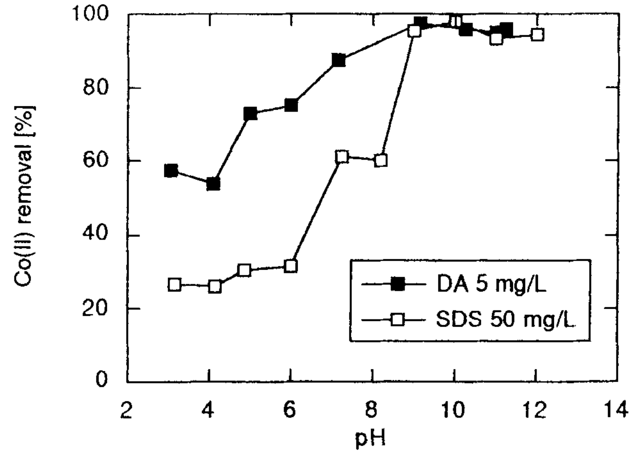

FIG. 12 Effect of pH and type of surfactant on the removal of Co^{2+} from aqueous solutions. Conditions: Q_G = 70 cm^3/min; flotation time, 10 minutes.

Figures 13 and 14 illustrate the results obtained for several gas (air) flow rates.* In these experiments, a small amount of CPCI (4 mg/L) was added to the solution in order to increase stabilization of the foam layer. As u_G increased, cobalt recovery went through a maximum—at approximately 0.1 cm/s—and then steadily decreased at higher superficial gas velocities. As the gas flow rate increased, however, so did the water removal by hydraulic entertainment, and this led to a drop in overall flotation efficiency.

Another possible reason for this recovery loss may be attributed to the turbulence induced by the stream of bubbles rising through the column; the well-known "Gulf stream" effect establishes an internal recirculation loop, with liquid velocities often much higher than those of the gas stream (24), resulting in a shearing disruption of the lower part of the foam layer and a potential redispersion of the floated CoS particles.

Under alkaline conditions (pH 11.0; Fig. 14) the superficial gas velocity was not found to affect CoS recovery appreciably; it may be postulated that froth stability becomes more stable, influenced either by the surfactant species and/or the precipitated particle in such pH conditions, hence the effect of superficial gas velocity will become evident only at extremely low or very high gas velocities.

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* Results are presented as superficial velocities (u_G)—i.e., the volumetric flow rates (Q_G) divided by the cross-sectional area of the column—since these permit results obtained on columns of various sizes to be compared.

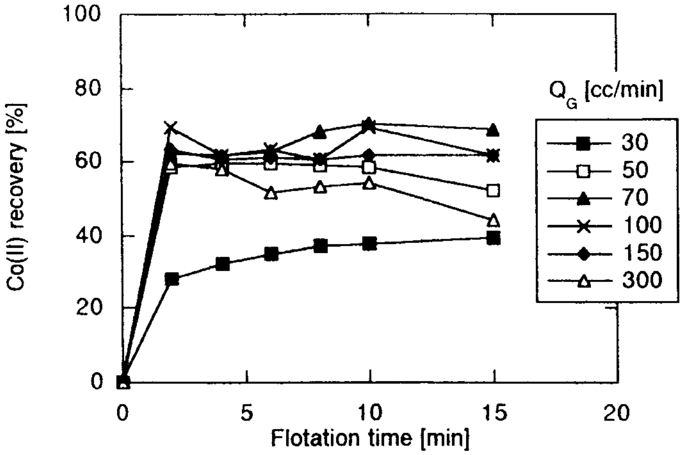

FIG. 13 Effect of air flow rate and flotation time on CoS flotation. Conditions: $[Na_2S]$: $[Co^{2+}]$ = 1:1 (M:M); agitation, 150 + 50 rpm (15 + 15 minutes); pH 5.0; [dodecylamine], 5 mg/L; [CPCl], 4 mg/L.

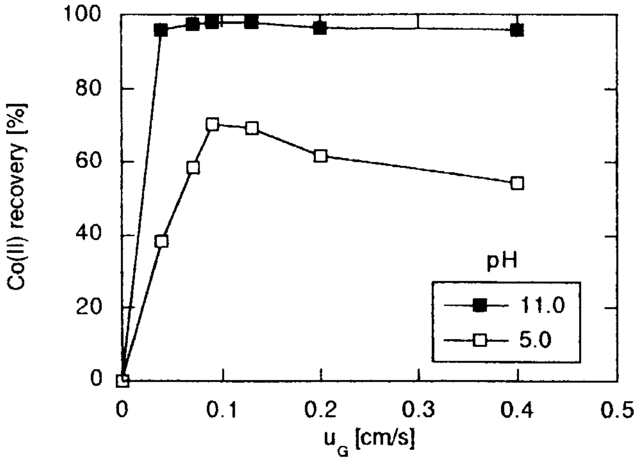

FIG. 14 Effect of air flow rate on CoS flotation. Conditions: $[Na_2S]$:$[Co^{2+}]$ = 1:1 (M:M); agitation, 150 + 50 rpm (15 + 15 minutes); [dodecylamine], 5 mg/L; [CPCl], 4 mg/L; pH 5.0; flotation time, 10 minutes.

Column Scale-up

Experiments were also carried out in taller columns in order to determine the effect of dispersion height on Co^{2+} recovery. Besides the initial experiments at h_C = 40.0 cm, two more heights, h_C = 100.0 and 150.0 cm, were investigated, all of them having a 4.0 cm internal diameter. The results are illustrated in Fig. 15.

An increase in column height was found to cause a drop in effectiveness of the flotation process, in marked contrast with mineral processing where columns up to 12 m in height are common (25). Such heights are necessary in the latter in order to increase the probability of the downflowing solid particles colliding with and possibly adhering to the rising bubbles. The height increase, in this case, resulted in longer retention times for the gas bubbles: the mean residence time of the gas (τ_G), which may be calculated from the dispersion height h_C and the superficial gas velocity u_G ($\tau_G = h_C/u_G$), is directly proportional to h_C. It seems, therefore, that the longer a floc-laden bubble takes to reach the foam layer, the more probable it is for the floc to detach itself from the bubble surface, thereby lowering cobalt ion recovery.

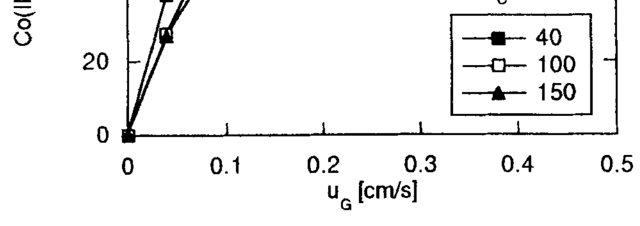

FIG. 15 Effect of gas flow rate and column height on CoS flotation. Conditions: $[Na_2S]:[Co^{2+}]$ = 1:1 (M:M); [dodecylamine], 5 mg/L; [CPCl], 4 mg/L, agitation, 150 + 50 rpm (15 + 15 minutes); pH 5.0; flotation time, 10 minutes.

III. Dissolved Air Flotation

Flotation of ionic species is often carried out in dissolved-air cells. Minute air bubbles, with a mean diameter between 40 and 100 μm (depending upon the specific operating conditions) are released as soon as pressurized water is fed into the cell.

Results from experiments performed with a dissolved-air apparatus are illustrated in Fig. 16; these are compared to the results obtained with a dispersed-air flotation column (see the Appendix I for a discussion about the conditions for a valid comparison). The slightly superior performance of the dispersed-air process over the dissolved-air process is probably due to the size of the CoS flocs and possibly their weight. At pH values where $Co(OH)_2$ is precipitated, the two processes are found to give similar Co^{2+} recoveries.

Interestingly, the surfactant dosage was found to be of minor importance to dissolved-air CoS recovery at both acidic and alkaline conditions (Fig. 17) as compared to dispersed-air flotation (Fig. 8). It seems that the CoS precipitate particles are sufficiently light and hydrophobic to be floated by the minute bubbles even under surfactant-less conditions, and the presence of the dodecylamine that is precipitated out, when its ethanolic solution is dispersed into the CoS dispersion, has no visible effect on the process.

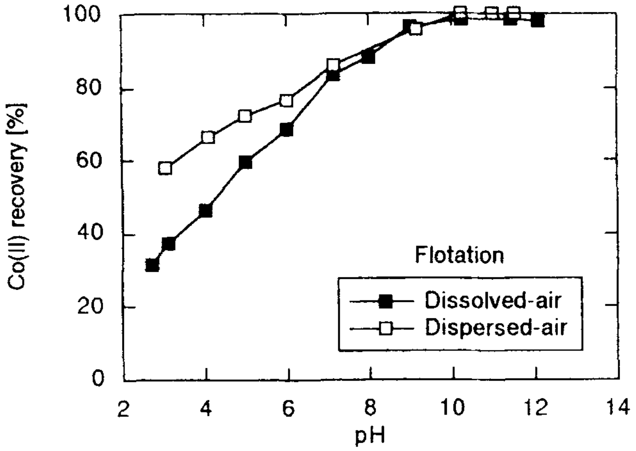

FIG. 16 Comparison between dispersed- and dissolved-air flotation. Conditions: $[Na_2S]:[Co^{2+}] = 1:1$ (M:M); [dodecylamine], 5 mg/L; pH 5.0.

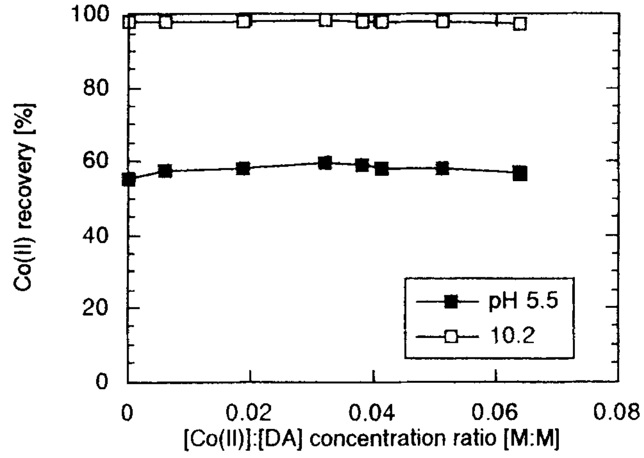

FIG. 17 Effect of pH on dissolved-air flotation of CoS. Conditions: $[Na_2S]:[Co^{2+}]$ = 1:1 (M:M); [dodecylamine], 5 mg/L.

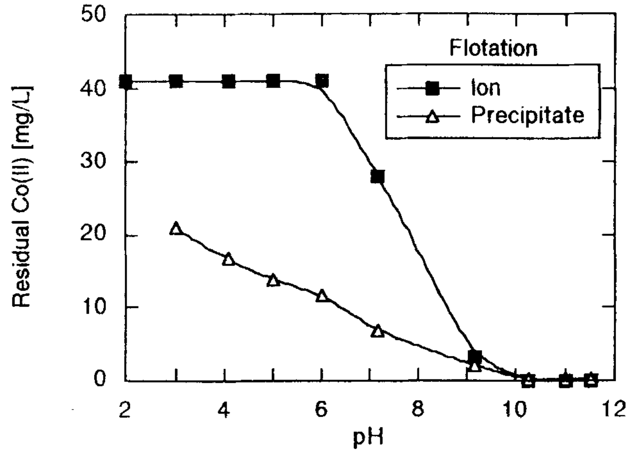

FIG. 18 Comparison between ion and precipitate flotation for the recovery of Co^{2+} ions from aqueous solutions. Precipitate flotation conditions: $[Na_2S]:[Co^{2+}]$ = 1:1 (M:M); [dodecylamine], 5 mg/L; u_G = 0.1 cm/s. Ion flotation conditions: [sodium dodecyl sulfate], 50 mg/L; u_G = 0.093 cm/s (data from Ref. 21, Fig. 6).

IV. Ion vs Precipitate Flotation

The recovery of Co^{2+} was achieved in this work through precipitate flotation and was shown to yield acceptable but not totally satisfactory results (see Fig. 7) when performed under acidic conditions. Co^{2+} ions were recovered through ion flotation in a previous publication (21), and sodium dodecyl sulfate was found to yield the relatively best although not totally satisfactory results. The two processes are compared in Fig. 18, where the residual Co^{2+} concentration is illustrated for various pH values. It is obvious that precipitate flotation is a more efficient process than ion flotation for the recovery of these ions at acidic conditions.

CONCLUSIONS

The recovery of cobalt ions from aqueous solutions by flotation has been investigated.

The ions were first precipitated as CoS using Na_2S, and it was found that the process is kinetically limited, resulting in only partial CoS precipitation, yielding maximum recoveries of approximately 70%. Higher recoveries, reaching 100%, are possible only in alkaline conditions, where cobalt ions are also precipitated as $Co(OH)_2$.

Dispersed-air flotation in a column was applied for the recovery of CoS particles. Several collectors were tested: dodecylamine was found to give the best results, and cetyl pyridinium chloride helped by providing a more stabilized foam layer.

The volumetric flow rate of gas (in this case, air) being fed into the column and the height of the latter were found to affect the flotation process:

An optimum gas flow rate, corresponding to a superficial gas velocity of 0.1 cm/s, yields maximum CoS recovery. Higher and lower flow rates result in poorer performances.

The higher the column, the worse its performance, indicating that the process of floc attachment onto gas bubbles is sensitive to turbulence inside the dispersion caused by the rising gas bubbles.

Dissolved-air flotation was found to give inferior results to those of dispersed-air flotation. Finally, the recovery of cobalt ions from solution is higher when ion flotation rather than precipitate flotation is applied.

APPENDIX: CONDITIONS FOR VALID DISSOLVED- VS DISPERSED-AIR FLOTATION COMPARISONS

The amount of dissolved air released when pressurized water is fed into a flotation cell may be calculated by the equations published recently by Edzwald and coworkers (26). In the present case, some reworking is necessary since the equations have been formulated for a continuous (recycle) process whereas the present work corresponds to a batch process.

The concentration of air in water (C) in equilibrium with the surrounding pressure (P) is given by the simple equation

$$P = K_H C \tag{A1}$$

where K_H is Henry's law constant (P in kPa, C in mg/L). When air is dissolved in water under pressure in a saturator, an efficiency factor (f) is used:

$$P_s = \frac{K_H C_s}{f} \tag{A2}$$

where P_s is now the (absolute) saturator pressure and C_s is the corresponding saturation concentration. Packed saturators have efficiencies up to 90% whereas unpacked ones reach ~70%.

By using these equations, it is possible to deduce the amount of air, m_a, released into a solution when an amount V_p of pressurized water is injected into it:

$$m_a = V_p(C_s - C_a) \tag{A3}$$

where C_a is the concentration corresponding to ambient conditions. m_a corresponds to an air volume:

$$V_a = m_a/\rho_{sat} \tag{A4}$$

where ρ_{sat} is the density of air saturated with water. From Eq. (A4) the number of bubbles (N_b) released may be calculated:

$$N_b = 6V_a/\pi d_b^3 \tag{A5}$$

where d_b is the bubble diameter. The surface of these bubbles (A_b), which constitutes the interfacial area available in principle for the flotation process, may also be calculated:

$$A_b = \pi d_b^2 N_b \tag{A6}$$

Thus, for (atmospheric) pressure P_a = 101.3 kPa, C_a = 24.2 mg/L, and for a gauge saturator pressure P_g = 450 kPa, with K_H (at 20°C) = 4.18 kPa·L·mg^{-1} (26), and with a saturator efficiency of 70%, C_s = 92.3 mg/L. From this it may be calculated that an amount of m_a = 13.6 mg is released when 200 mL of pressurized water are injected into the CoS dispersion, corresponding to a volume (V_a) of 11.4 cm^3 [at 20°C, ρ_{sat} = 1.19 kg/m^3 (26)].

Therefore, in the dissolved-air experiments, for bubbles having an average diameter of $d_b = 40$ μm, the number of bubbles released into the CoS dispersion is $N_b \cong 3.4 \times 10^8$, with a total interfacial area of $A_b \cong 1.71$ m^2.

In dispersed-air flotation, gas is bubbling through the column throughout the whole experiment, and the bubbles produced are usually rather large, with diameters typically $d_b \cong 1$ mm. The interfacial area determined for dissolved-air bubbles corresponds in this case to an air volume $V_a \cong 285$ cm^3, which for a gas flow rate of 70 cm^3/min is obtained after approximately 4 minutes from initiation of the experiment. Thus, in terms of interfacial area, a single 0.2 L shot of pressurized water is equivalent to 4 minutes of dispersed-air gas bubbling.*

The effectiveness of the two processes may be compared if the values for the dispersed-air case correspond to this running time. But, as illustrated in Fig. 11, the dispersed-air flotation process in the case of CoS is rather fast, probably because of flocculation of the sulfide particles; thus final recoveries are reached within a very short time, approximately 2.5 to 3 minutes from the beginning of the experiment, which is less than the time deemed necessary—as calculated above—for a valid comparison. It is possible, therefore, to use the final recoveries in dispersed-air flotation for comparison with dissolved-air flotation.

NOTATION

A_b	gas–liquid interfacial area (cm^3) (Appendix)
C	concentration (mg/L) (Appendix)
C_a	dissolved-air concentration (ambient conditions) (mg/L) (Appendix)
C_i	cobalt concentration before flotation (mg/L)
C_f	cobalt concentration after flotation (mg/L)
C_s	(dissolved-air) saturator air concentration (mg/L) (Appendix)
d_b	bubble diameter (cm) (Appendix)
f	(dissolved-air) saturator efficiency factor (Appendix)
h_C	column height (cm)
K_H	Henry's law constant (Appendix)
m_a	(dissolved) air released into solution (mg) (Appendix)
N_b	bubble number (Appendix)
P	pressure (kPa) (Appendix)
P_s	(dissolved-air) saturator pressure (kPa) (Appendix)

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* It is assumed in this analysis that the effectiveness of both dissolved- and dispersed-air bubble surfaces in capturing the CoS particles and/or flocs is similar.

Q_G	volumetric gas flow rate (cm^3/min)
R_{Co}	recovery of Co^{2+} (%)
u_G	superficial gas velocity (cm/s)
V_a	air volume (cm^3) (Appendix)
V_p	pressurized water volume injected into dispersion (Appendix)

Greek Letters

ρ_{sat}	(air-saturated) water density (g/cm^3) (Appendix)
τ_G	mean gas residence time in the column (min)

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