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## Recovery of $\text{Co}^{2+}$ Ions from Aqueous Solutions by Froth Flotation

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### ABSTRACT

The recovery of  $\text{Co}(\text{II})$  ions from aqueous solutions under acidic conditions (pH 5) was investigated in flotation columns with inside diameters of 4.0 and 8.0 cm. Three surfactants, dodecylamine, cetyl pyridinium chloride, and sodium dodecyl sulfate, were used as collectors. Sodium dodecyl sulfate was found to be the most efficient; all three, however, produced hydrated froths, leading to rather low recoveries and separation efficiencies. The volumetric gas flow rate was found to affect the process in relation to the amount of surfactant added and the column diameter. The scale-up of the column should be done in terms of the same superficial gas velocity in order to maintain similar levels of metal ion recovery.

### INTRODUCTION

Cobalt is a strategic metal, widely applied in the manufacturing of catalysts used in the hydrocracking of crude oil, coal liquefaction, and the synthesis of fuel oil. Materials containing cobalt are also used to manufacture alloys, super alloys, ultra-high steels, tool steels, and other special alloys (1, 2).

The metal is usually obtained from various ores as a by-product when extracting such other metals as nickel, copper, gold, and lead (3). Cobalt ores exist mainly in Zaire, Zambia, and Canada (1).

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Besides the interest in its intrinsic value as an ore, there is also some interest in cobalt ions from an environmental point of view because there are reports of their toxicity to plants and animals (3). Their presence may be objectionable, and that would add one more reason to investigate its removal from aqueous solutions and/or wastewaters. Cobalt radioisotopes may also be found in PWR nuclear reactor water.

Due to the great interest of cobalt, a number of techniques have been developed to separate and recover cobalt from other valuable metals from ores, wastewaters, or other secondary sources: pyrometallurgical and hydrometallurgical processes, solvent extraction, ion exchange, distillation, reverse osmosis, chemical precipitation (3-5).

Foam flotation has also been widely used for separating or recovering ionic species from aqueous solutions (6). In recent years, various foam flotation methods have been utilized to separate or concentrate cobalt

TABLE 1  
Adsorbing Colloid Flotation<sup>a</sup>

Species	Medium	Precipitated compound	Surfactants	pH	Ref.
Co	Seawater	ln(OH) <sub>3</sub>	SDS + NaOl	8.5-9	7
Co, As, Cd, Cu, Hg, Mo, Sb, Sn, Te, Ti, U, V, W	Synthetic seawater	Fe(OH) <sub>3</sub> + Fe(APDC)	SDS + NaOl	4.0-8.0	8
Co, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Seawater	Al(OH) <sub>3</sub>	NaOl	9.5	9
Co, Cd, Cr, Cu, Mn, Ni, Pb	Wastewater, seawater	ln(OH) <sub>3</sub>	NaOl + SDS	9.5	10, 11
Co, Cd, Cu	Seawater	Fe(OH) <sub>3</sub>	ODA + SDS	9.5-9.9	12
Co, Cd, Cu, Ni	Seawater	Phenolphthalein or 2-naphthol	ODA	2-10	13
Co, Cu, Mn, Ni	Mn nodules	Fe(OH) <sub>3</sub>	HCILA	Cu, >6.9 Co, Mn, Ni 9.0	4
Co, Cu, Mn, Ni, Zn, Al	Ferromanganese nodules	Fe(OH) <sub>3</sub> + Mn(OH) <sub>2</sub>	HCILA or CTMACl + TX100	8-10	5
Co, Cu, Ni	Water	Zr(OH) <sub>4</sub>	NaOl, SDS	9.1	14
Co, Cu, Ni, Zn	Ferromanganese nodules	Na <sub>2</sub> S	SDS, CTMACl, HCILA, Triton X-100	Various	15
Co, Cu, Ni, Mn	Ferromanganese nodules	Oxine, APDC, dithizone	Stearyl trimethyl ammonium chloride		16
Co, Cd, Cr, Cu, Ni, Pb, Zn	Simulated wastewater	Fe(OH) <sub>3</sub> , Al(OH) <sub>3</sub>	SDS	4-11	17

<sup>a</sup> APDC: ammonium pyrrolidine dithiocarbamate.

CTMACl: cetyl trimethyl ammonium chloride.

HCILA: laurylamine hydrochloride.

NaOl: sodium oleate.

ODA: octadecylamine.

SDS: sodium dodecyl sulfate.

TABLE 2  
Precipitate Flotation<sup>a</sup>

Species	Medium	Precipitate nature	Surfactants	pH	Ref.
Co	Wastewater	Hydroxide	SDS	11	18
Co	Wastewater	Hydroxide	CTMABr, SDS, Tween 80	8.8	19
Co	Wastewater	Hydroxide	SDS	8.0	20
Co	Wastewater	Hydroxide	CTMABr	8.0	21
Co, Cu, Mn, Ni	—	LIX 65, LIX 63	CTMABr + TX100	Various	22
Co, Zn	Aqueous solution	Hydroxide	DBSNa, DDMBABr	8–10 11.5	23
Co, Cu, Zn	—	Hydroxide	DBSNa	5.5–11.5	24

<sup>a</sup> CTMABr: cetyl trimethyl ammonium bromide.

DBSNa: sodium dodecyl benzene sulfonate.

DDMBABr: dodecyl dimethyl benzyl ammonium bromide.

from aqueous solutions; these are summarized in Tables 1–3. However, most of this work has been performed in alkaline conditions.

In this work the flotation of cobalt ions in an acidic environment was investigated, using cationic and anionic collectors. The effectiveness of the process was examined in conjunction with the type of flotation—i.e., adsorbing colloid, precipitate, or ion flotation—and the effect of geometric

TABLE 3  
Ion Flotation<sup>a</sup>

Species	Medium	Surfactants	pH	Ref.
Co	Cyanide	CPCI and DBSNa	—	25
Co	Thiocyanate	CTMABr	2	26
Co, Cd	Thiocyanate	CTMABr	—	27
Co, Cu	Ammonium	SDS	12	28
Co, Ni	Sulfate, nitrate	HDSO <sub>4</sub> Na, DDSO <sub>4</sub> Na, DDSO <sub>3</sub> Na, Sapogenat T-180, sodium stearate	6.5	29
Co, Ag, Cd, Cr, Fe, In, Mn, Zn	Aqueous solutions	DDSO <sub>3</sub> Na, DDBSO <sub>3</sub> Na	2	30

<sup>a</sup> DDSO<sub>3</sub>Na: sodium dodecyl benzo sulfonate.DDSO<sub>4</sub>Na: sodium dodecyl sulfonate.HDSO<sub>4</sub>Na: sodium hexadecyl sulfate.

and operating parameters (column diameter, gas flow rate) on the rate of recovery of cobalt.

## EXPERIMENTAL APPARATUS AND PROCEDURE

A schematic diagram of the dispersed-air foam/froth separation apparatus is shown in Fig. 1. A column with a total height of 40.0 cm and an inside diameter of 4.0 cm was used. A side arm, located near the bottom of the column, was used for retrieving samples.

Air was fed into the column through a cylindrical ceramic gas sparger (Schott, porosity G4, with a mean pore diameter of 16–40  $\mu\text{m}$ ) which was placed at the bottom of the column for the generation of air bubbles. The air flow-rate was continuously monitored using a calibrated rotameter.

Aqueous solutions of cobalt ions were prepared by dissolving  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck) in deionized water. The solution pH was regulated using  $\text{NaOH}$  or  $\text{HNO}_3$ . Aqueous solutions of sodium dodecyl sulfate (90% Merck), cetyl pyridinium chloride (general purpose reagent, 98% BDH), and dodecylamine (98% Merck) solution in ethanol were used as collectors. Absolute ethanol and methanol were used in some experiments as frothers. All reagents, unless otherwise stated, were of pro analysi grade.

The 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 residual concentration of sodium dodecyl sulfate was determined by the methylene blue–chloroform method, using a Hitachi U-2000 Double-Beam Spectrophotometer at 652 nm (31).

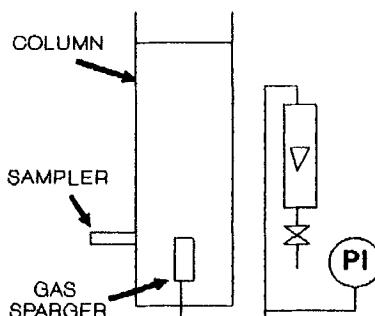


FIG. 1 Schematic diagram of experimental apparatus.

The analytical results were used to calculate the percent recovery of  $\text{Co}^{2+}$  in the froth:

$$R_{\text{Co}} = 100 \times \frac{\text{mass of cobalt recovered from solution}}{\text{mass of cobalt initially in solution}} [\%] \quad (1)$$

and the percent removal of water, where applicable:

$$R_{\text{H}_2\text{O}} = 100 \times \frac{\text{volume of H}_2\text{O removed in the froth}}{\text{initial H}_2\text{O volume in column}} [\%] \quad (2)$$

The process "efficiency" was also computed, borrowing the appropriate formula from mineral processing (32):

$$n = \left\{ \frac{\text{fraction of}}{\text{cobalt removed}} \right\}_{\text{in froth}} \times \left\{ \frac{\text{fraction of}}{\text{H}_2\text{O remaining}} \right\}_{\text{in solution}} \times 100 [\%] \quad (3)$$

## RESULTS AND DISCUSSION

### Choice of Collector

Among the various surfactants available, three were chosen in order to investigate their effectiveness as collectors in floating  $\text{Co}^{2+}$  from aqueous solution: two cationic—cetyl pyridinium chloride (CPCl) and dodecylamine (DA)—and one anionic—sodium dodecyl sulfate (SDS). All three have been widely used for such purposes. Figures 2, 3, and 4 present the results obtained with each collector under identical experimental conditions for various ratios of collector concentration to ion concentration. It was also decided to investigate their performance mainly under acidic conditions, since in alkaline conditions the cobalt ions precipitate as  $\text{Co}(\text{OH})_2$  and are separated fairly easily from solution.

Dodecylamine exhibited a steady but rather poor performance, with the percent recovery of the cobalt ions in the froth being almost insensitive to the increase in DA concentration (Fig. 2; top). Although some ions were removed into the froth phase, the residual  $\text{Co}^{2+}$  concentration remained practically constant and equal to the initial concentration.

One interesting feature of these experiments was the highly hydrated foam produced. This was not totally unexpected, since some collectors—e.g., amines (2)—are known to cause excessive foaming. However, the removal not only of ions but also of water from solution resulted in the residual ion concentration in the (remaining) solution in the column being almost equal to the initial concentration.

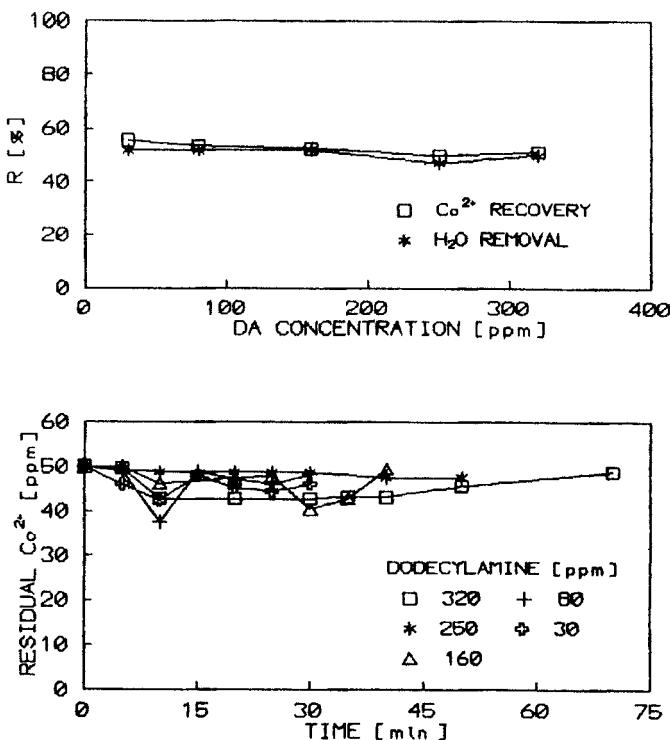


FIG. 2 Effect of dodecylamine concentration on cobalt ion recovery. Initial cobalt concentration, 50 ppm; air flow rate, 70  $\text{cm}^3/\text{min}$ ; pH, 5.0; ethanol, 0.1% v/v.

Cetyl pyridinium chloride exhibited a similar behavior, with corresponding rates of ion and water removal, resulting in residual  $\text{Co}^{2+}$  concentrations again similar to the initial one (Fig. 3). Only sodium dodecyl sulfate was able to remove substantial amounts of cobalt ions from solution (Fig. 4); however, it required considerable amounts of surfactant.

The rates of  $\text{Co}^{2+}$  recovery of all three aforementioned surfactants are presented in Fig. 5 for comparison. SDS seems to exhibit the best performance, although CPCl approaches similar levels of ion removal at high concentrations. However, it is also possible to plot the process efficiency for each surfactant against the surfactant:ion concentration ratio. This efficiency is the product of two fractions: the fraction of cobalt removed and the fraction of water remaining in solution. In an ideal separation/recovery process both these fractions should approach 1.0, hence the overall process efficiency would also approach 1.0. A lower value means

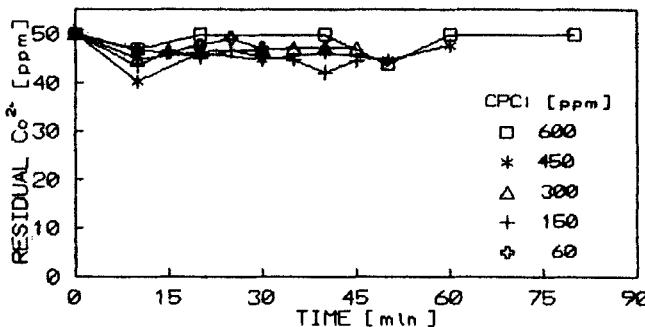
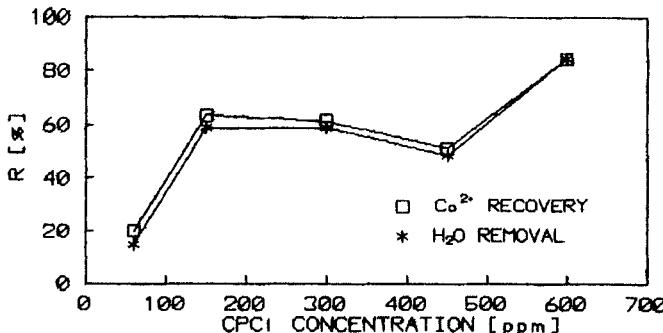


FIG. 3 Effect of cetyl pyridinium chloride concentration on cobalt ion recovery. Initial cobalt concentration, 50 ppm; air flow rate, 70  $\text{cm}^3/\text{min}$ ; pH, 5.0.

that either the particular physicochemical and/or operational conditions are not suitable for flotation of the ion or that they produce an excessively hydrated foam. In Fig. 5 (bottom), SDS is seen to be the most efficient of the three surfactants, but only for low concentration ratios; above a ratio of 1.0, SDS efficiency drops below that of DA, and CPCl efficiency eventually drops even further.

From these results, sodium dodecyl sulfate was judged to be the most efficient of these surfactants and was used for all further experiments.

#### Effect of pH

The effect of solution pH on cobalt recovery was studied for three different SDS concentrations (Fig. 6). The residual cobalt concentration remained practically stable for values of pH less than 6, whereas for pH above 8 the cobalt ions were practically totally removed. The species

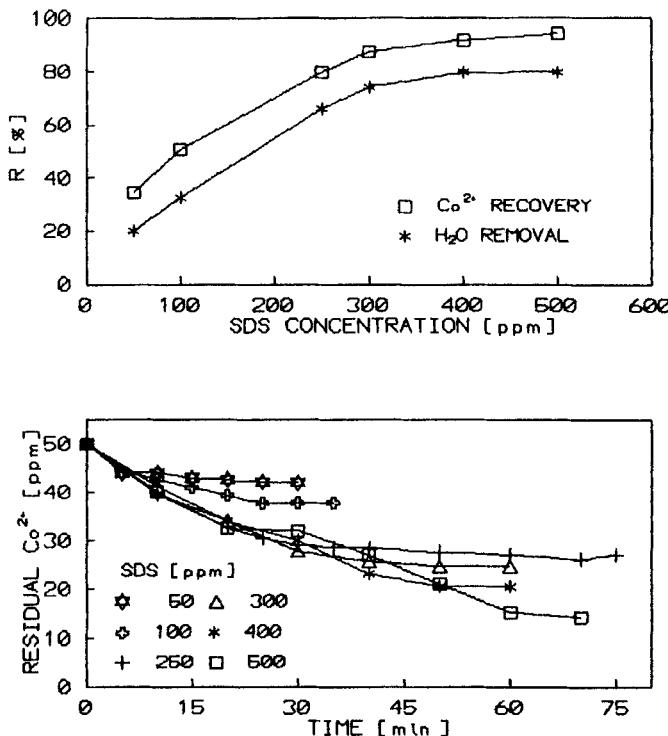
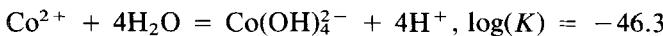
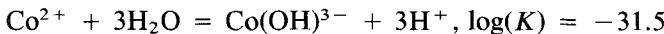
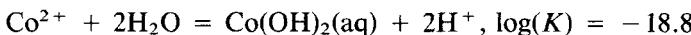
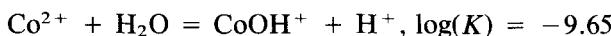


FIG. 4 Effect of sodium dodecyl sulfate on cobalt recovery and  $\text{H}_2\text{O}$  removal. Initial cobalt concentration, 50 ppm; air flow rate, 70  $\text{cm}^3/\text{min}$ ; pH, 5.0.

diagram for cobalt ions is plotted in Fig. 6 (bottom), using the following constants (33):



with other polynuclear species being also present:  $\text{Co}_2(\text{OH})^{3+}$ ,  $\log(K) = -11.2$ , and  $\text{Co}(\text{OH})_4^{2+}$ ,  $\log(K) = -30.53$ .  $\text{Co}^{2+}$  is practically the sole species present in solution in acidic conditions; at intermediate pH values (7–9),  $\text{Co}(\text{OH})^+$  appears briefly, while  $\text{Co}(\text{OH})_2$  starts precipitating at pH > 9. The latter may be adsorbed on the bubble surface; this is also facili-

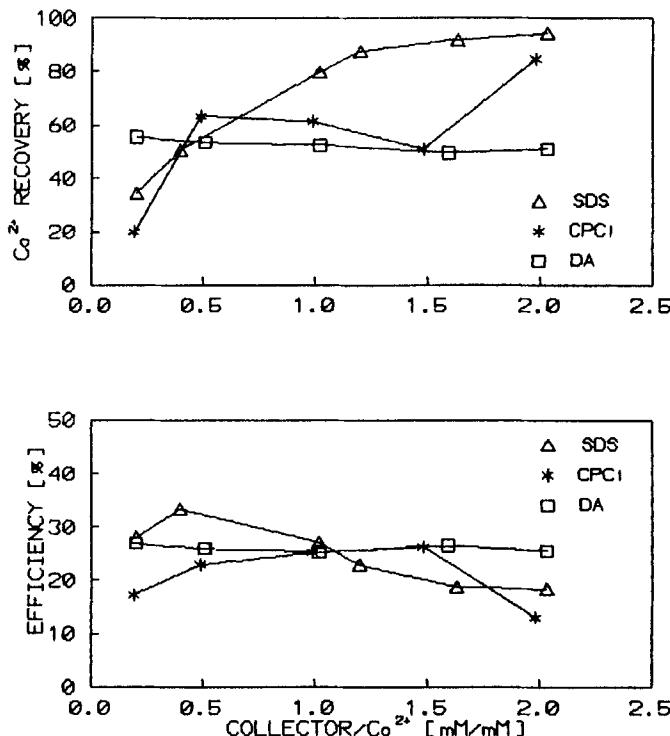


FIG. 5 Comparison of collectors' effectiveness in recovering cobalt and removing  $\text{H}_2\text{O}$  from solution. Initial cobalt concentration, 50 ppm; air flow rate, 70  $\text{cm}^3/\text{min}$ ; pH, 5.0.

tated by the presence of an anionic surfactant, and such should be the case with SDS.

Thus, for  $\text{pH} > 8$ , the process of recovering cobalt ions from solutions, even dilute ones, is highly enhanced by the presence of SDS, even at substoichiometric concentrations. In acidic conditions, on the other hand, increased SDS concentrations are required to recover  $\text{Co}^{2+}$  from solution, but this leads to a highly hydrated foam, especially at SDS concentrations higher than the stoichiometric one.

The species diagram may also help in explaining the results obtained with the other two surfactants (Figs. 2 and 3). At pH 5,  $\text{Co}^{2+}$  cations predominate; therefore, cetyl pyridinium chloride and dodecylamine become less effective in this pH range since they are both cationic surfactants and would rather float negatively-charged species.

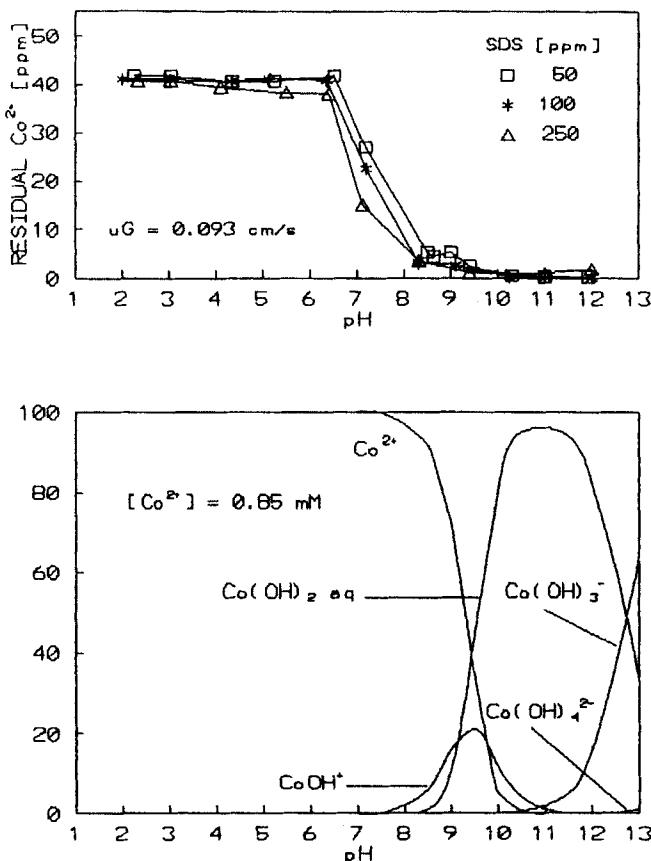


FIG. 6 (Top) Effect of sodium dodecyl sulfate concentration and pH on the recovery of cobalt from aqueous solutions. Initial cobalt concentration, 50 ppm; air flow rate, 70 cm<sup>3</sup>/min; flotation time, 10 min. (Bottom) Ionic species of Co<sup>2+</sup>; [Co<sup>2+</sup>] = 50 ppm (0.85 mM).

### Initial Metal Concentration

In order to test the effectiveness of the process for varying cobalt ion concentrations, experiments were performed with cobalt concentrations ranging from 5 to 50 ppm (Fig. 7); all these were performed at the same solution pH (~5.0) and for a constant SDS to Co<sup>2+</sup> concentration ratio (equal to 2). The recovery of Co<sup>2+</sup> increased slightly with the initial ion concentration, but the same was also true for water removal. The process efficiency therefore dropped from an initial 65% to about 20%. This may

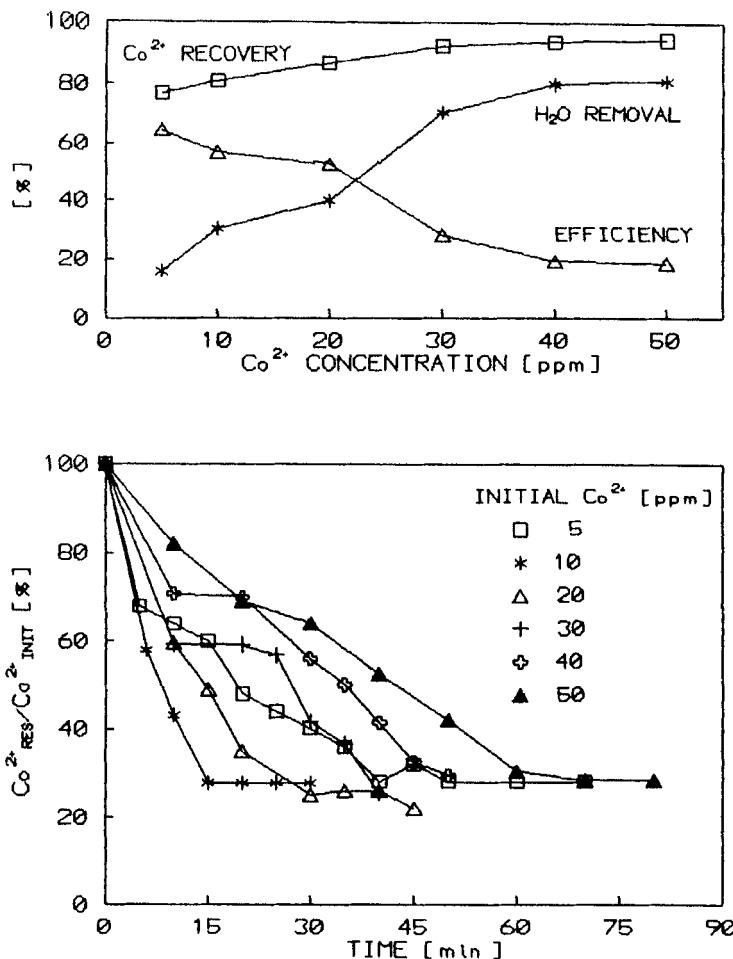


FIG. 7 Effect of initial concentration of cobalt on cobalt recovery. Air flow rate, 70  $\text{cm}^3/\text{min}$ ; pH, 5.0;  $[\text{SDS}]/[\text{Co}^{2+}] = 2.0$ .

be attributed to the increased surfactant concentration, which causes an increase in water removal exceeding the corresponding  $\text{Co}^{2+}$  recovery.

The residual cobalt ion concentration is, however, limited by the (batch) operation of the column. During the flotation experiment, the froth zone is gradually established; however, its texture is rather watery—in contrast to froths observed in mineral-processing columns—and since it is not continuously removed, its drainage probably entrains some of the floated

material back into solution. A continuous removal of the froth by some means, e.g., by suction or by overflowing, would prevent this drainage, leading to an effective depletion of the solution of cobalt ions.

### Frother

In laboratory practice, surfactants are often added as ethanolic solutions. This procedure takes place because some of them are not very soluble in water and because micelles are not easily formed in the presence of ethanol (34). An additional benefit of ethanol is that it causes a decrease in bubble size, resulting in principle in an enhanced flotation performance. However, its presence—under acidic conditions (pH 5.0)—alone is not capable of recovering cobalt ions from solution (Fig. 8), and only a substantial amount of a suitable surfactant (e.g., sodium dodecyl sulfate) leads to an appreciable reduction of residual cobalt concentration. Methanol was also used (at 0.5% v/v), with a surfactant—SDS—concentration of 50 ppm, but again gave poor results (residual cobalt concentration 45 ppm after 20 minutes of flotation). The reduction of the bubble size, which is caused by the addition of short- or long-chain alcohols, is not capable per se of floating the ions; another surfactant is necessary to impart some hydrophobicity to the ion so that it may be removed by the gas bubbles from solution.

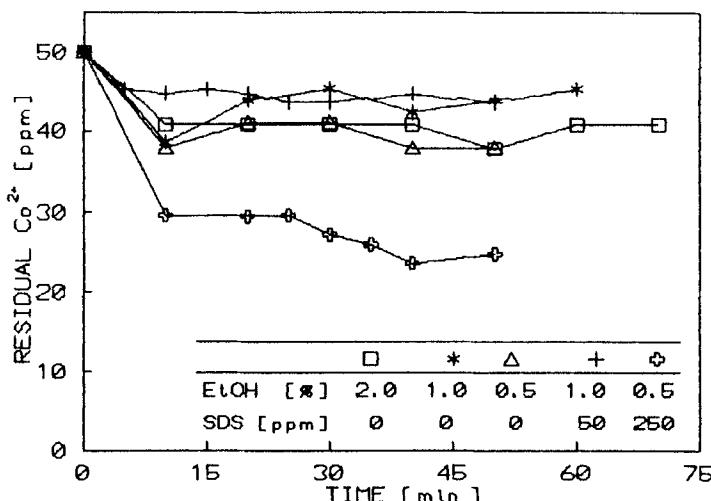


FIG. 8 Effect of frother concentration (EtOH) on flotation of cobalt. Initial cobalt concentration, 50 ppm; air flow rate, 70 cm<sup>3</sup>/min; pH, 5.0.

### Gas Flow Rate

Given the physicochemical conditions, one of the potentially important parameters in dispersed-air flotation is the gas flow-rate. Figure 9 illustrates the results obtained for several gas (air) flow rates; these are presented as superficial velocities ( $u_G$ )—i.e., volumetric flow rates ( $Q_G$ ) divided by the cross-sectional area of the column—since they are more easily used when scaling-up to larger columns. In alkaline conditions (pH 11.0), where there are no ions but mainly minute—of colloidal size— $\text{Co}(\text{OH})_2$  particles, their removal is extremely rapid and completed within a few minutes and  $u_G$  seems to have little, if any, effect on ion recovery. In acidic conditions, on the other hand, as  $u_G$  increases, a slight increase in cobalt recovery is noted, but no further effect may be seen for  $u_G$  larger than 0.2 cm/s, and the residual cobalt concentration seems unaffected by the gas flow rate.

In alkaline conditions the small particles are probably hydrophobic enough to adhere to the small gas bubbles and float in a very short time; the froth that is thus formed is reasonably stable to hold the particles and achieve a satisfactory separation. As the gas flow rate increases, the water removal is also increased, and this leads to a drop in flotation efficiency.

In acidic conditions, on the other hand, the adsorption of  $\text{Co}^{2+}$  on the surface of the bubbles is probably more gradual, hence a slight effect of  $u_G$  may be noticed. A higher gas flow rate results in more bubbles passing through the solution, removing more ion–surfactant clusters. However, the circulation velocity, which is induced by the bubble swarm rising through the column (35), increases the turbulence at the froth/collection zone interface, and some cobalt ions and water are entrained back into solution. A limit is probably reached at some gas flow rate where the two rates, the one of attachment and removal and the other of drainage and backentrainment, become equal and no more effect of  $u_G$  may be noticed.

It is thus interesting to note that the ion-floating column exhibits a behavior rather different from ore-processing ones. In the latter, as the gas flow rate increases, an enhanced solids recovery may be noticed up to a limiting  $u_G$ , after which recovery drops; the recovery curve then resembles a parabola, going through a maximum at some intermediate  $u_G$  value, typically in the 1.5–2.0 cm/s range (36). In the present case of ion flotation, the recovery seems to reach a plateau rather than a maximum. In alkaline conditions, one probably has to work in very low gas flow rates in order to distinguish the effect of the gas on cobalt ions recovery.

In our acidic conditions, the removal of water closely follows the recovery of cobalt ions, hence the efficiency of the process remains practically constant (and rather low).

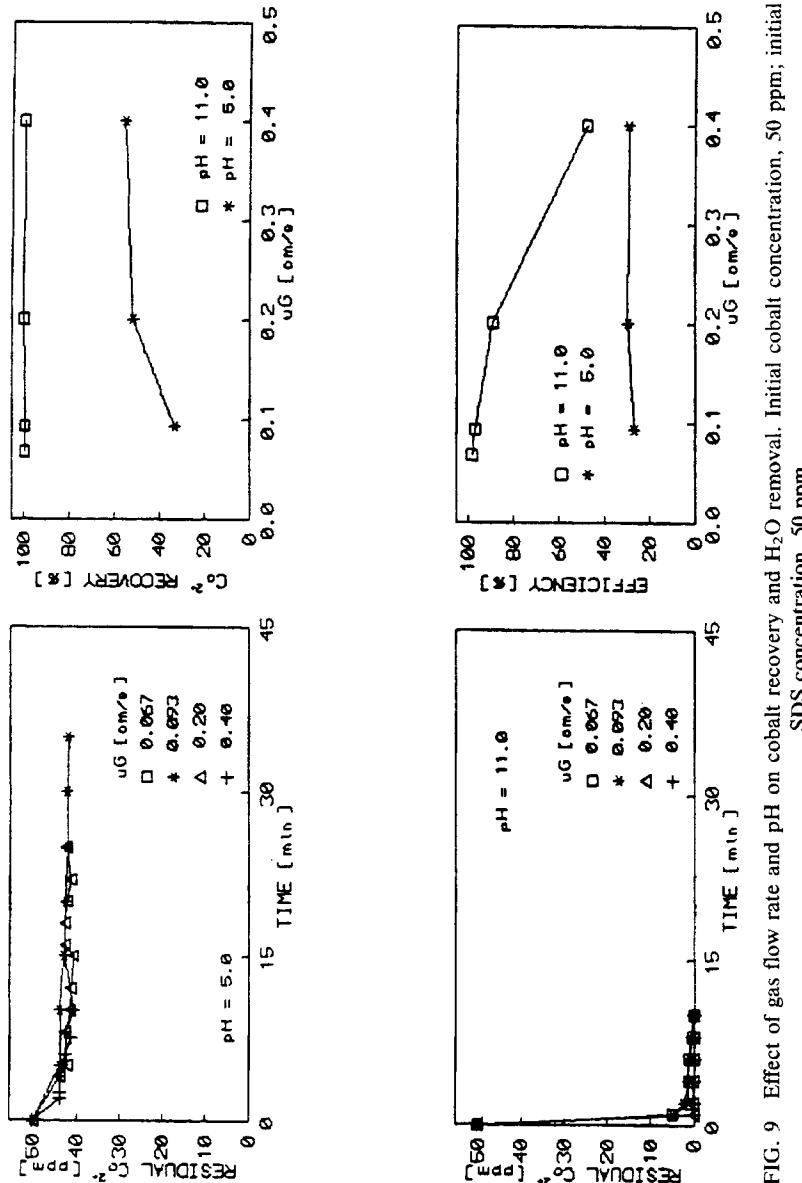


FIG. 9 Effect of gas flow rate and pH on cobalt recovery and  $\text{H}_2\text{O}$  removal. Initial cobalt concentration, 50 ppm; initial SDS concentration, 50 ppm.

It seems, however, that the effect of the gas flow rate is closely related to the amount of surfactant added to the solution (Fig. 10). For a given amount of sodium dodecyl sulfate, for example, an increase in  $u_G$  causes a rise in recovery, but only up to some limit. On the other hand, an increase in the amount of surfactant added causes higher water entrainment, and this causes a fall in the flotation efficiency, which becomes more noticeable the larger  $u_G$  is.

Therefore, from these results it seems that a combination of low gas flow rate and moderate amounts of surfactant is necessary in order to obtain satisfactory results in both ion recovery and process efficiency.

### Column Scale-Up

Finally, experiments were also performed in a larger column with an internal diameter of 8.0 cm (Fig. 11). An increase in column diameter

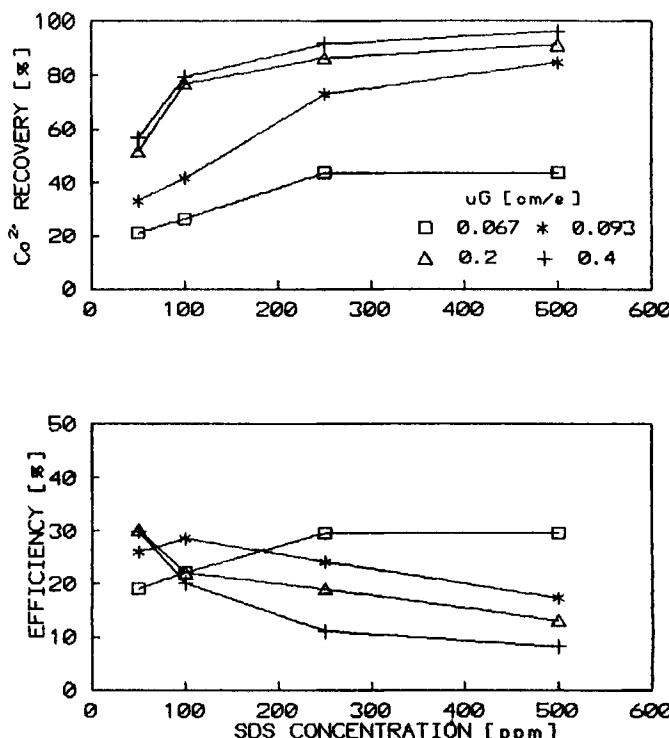


FIG. 10 Effect of sodium dodecyl sulfate concentration and gas flow rate on cobalt recovery and  $\text{H}_2\text{O}$  removal. Initial cobalt concentration, 50 ppm; pH, 5.0; flotation time, 10 min.

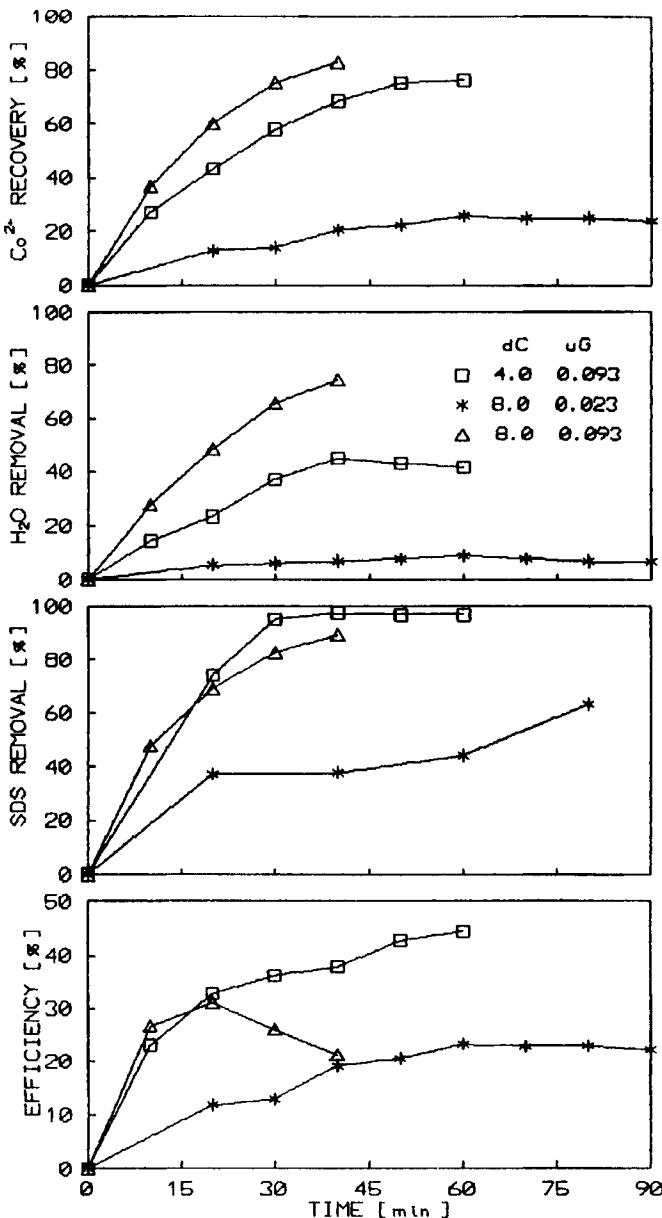


FIG. 11 Effect of gas flow rate and column diameter on cobalt recovery, H<sub>2</sub>O removal, and sodium dodecyl sulfate depletion. Initial cobalt concentration, 50 ppm; initial SDS concentration, 500 ppm; pH, 5.0.

while keeping the absolute value of the gas flow rate constant (at  $70 \text{ cm}^3/\text{min}$ , corresponding to  $u_G = 0.093 \text{ cm/s}$ ) caused a spectacular drop in performance since less gas was available for recovering the dissolved ions. As soon as the gas flow rate was increased so that the superficial velocities in both the small column ( $d_C = 4.0 \text{ cm}$ ) and the large one ( $d_C = 8.0 \text{ cm}$ ) are equal, the recovery of cobalt rose again to similar and even higher levels. However, the increase in water removal was even higher and efficiency thus decreased. This may be attributed to the unstabilized froth which is formed above the collection zone of the column, i.e., the zone beneath the froth, where the bubbles come into contact with the solution and the ion/bubble or particle/bubble aggregates are formed; the larger the column, the more easily the froth collapses and the floated ions are entrained back in solution.

It was also interesting to note that the surfactant (SDS) was almost completely removed, again depending upon the gas flow rate. This means that the process is capable not only of recovering the metal ions, albeit at a low recovery rate, but also of producing a more or less clean effluent.

## CONCLUSIONS

The recovery of cobalt ions from aqueous solutions by flotation has usually been investigated in alkaline conditions; in this work the process was carried out under acidic conditions where the ionic form of  $\text{Co}^{2+}$  is predominant and flotation is close to the ion flotation method.

Three surfactants, dodecylamine, cetyl pyridinium chloride, and sodium dodecyl sulfate, were used as collectors; of them, only SDS was found capable of floating  $\text{Co}^{2+}$  appreciably (recoveries over 90%). All of them, however, produced highly hydrated froths; part of the ion removal was due to hydraulic entrainment. The froth drainage that ensued led to considerable residual cobalt ion concentrations and low overall separation efficiencies. A means of stabilizing the froth or removing it as soon as it is formed would probably lead to a greatly improved  $\text{Co}^{2+}$  recovery.

Gas flow rate affects  $\text{Co}^{2+}$  recovery in these conditions only slightly; a gas flow rate corresponding to a gas superficial velocity of  $0.2 \text{ cm/s}$  was found to be the upper limit, after which no further effect on cobalt ion recovery was noticed. The amount of surfactant added was found to play an important role, and this should be adjusted in conjunction to the gas flow rate in order to optimize the process.

Finally, the process of recovering cobalt ions from aqueous solutions in acidic pH values by ion flotation is not very efficient; the use of a different technique, possibly involving cobalt salts insoluble at such pH values, could probably enhance the process performance.

## NOMENCLATURE

$d_C$	column diameter (cm)
$n$	efficiency (%)
$Q_G$	volumetric gas flow rate (cm <sup>3</sup> /min)
$R_{Co}$	recovery of Co <sup>2+</sup> (%)
$R_{H_2O}$	removal of water (%)
$u_G$	superficial gas velocity (cm/s)

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