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Dissolved-Air Flotation of Metal Ions

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Abstract

Metal ions (copper, nickel, zinc, and ferric ions) were separated from dilute aqueous solutions by dissolved-air flotation. The ions were either precipitated as sulfides or floated (as ions) by xanthates. Copper and nickel were selectively separated; promising results were obtained with single, binary, and ternary mixtures. The effect of several parameters (solution pH, addition of chemical reagents at varying concentrations, and the presence of other ions) on the removal of ions was studied. The collectorless flotation of copper ions was also investigated.

INTRODUCTION

Metals are often contained in industrial effluent, and since several tons of them are lost each year, there is considerable interest in recovering them. This has the additional benefit of complying with environmental conservation policies which are already being implemented.

Similar problems are faced in the hydrometallurgical recovery of metals (e.g., copper) from ores, where great volumes of aqueous solutions are often produced, and which have to be treated to recover the valuable ion.

Flotation, a rather unique case of a three phase (gas/liquid/solid) process, is one of the most significant unit operations in mineral processing, but it may also be applied to water and wastewater treatment (*1*) and to hydrometallurgy. Flotation is envisaged at present to replace both the concentration and separation processes, if feasible. In a recent review (*2*) it was suggested that one of the main advantages of flotation may be the selective recovery of ions from complex solutions with several coexisting metals.

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Previous work—in the broad field—involves, among others, the flotation as hydroxide precipitates of metal-bearing wastes mainly by amines (*3*) or by fatty acids (*4*) and as sulfide precipitates (*5*, *6*), a comparative study for a column technique and a flotation machine on copper industry wastewaters (*7*), and the application of LIX reagents (known from liquid–liquid extraction) in flotation (*8*). Adsorbing colloid flotation of metals, simultaneously for ferric or manganese hydroxides, has also been applied to deep-sea nodules (*9*). A short-chain xanthate was used as the collector for copper ions during a study of the selective separation of copper, zinc, and arsenic ions from solution by flotation (*10*). Copper and zinc ions were separated by precipitate flotation as sulfides in batch (*11*) and continuous flow (*12*) conditions.

In this work the removal of single or multiple metal ions from aqueous solutions is investigated, and conditions are determined for the removal of the ions, with or without collectors, in order to achieve total removal or selective separation.

EXPERIMENTAL

A dissolved-air flotation unit, previously described (*10*), was used for the experiments. Chemical analysis of the solution samples was carried out by AAS, and the results are expressed as the percentage of initial ion content removed (or recovered) by flotation.

The reagents used were copper nitrate, nickel sulfate, zinc nitrate, and ferric sulfate (*pro analysi* grade). The pH of the solution (deionized water) was adjusted by nitric acid or sodium hydroxide solutions.

Sodium sulfide was applied for the precipitation at a stoichiometric amount (unless otherwise stated) at a pH of approximately 3.

In the first part of this work—precipitate flotation—laurylamine (0.1% ethanolic solution), cetyl pyridinium chloride, sodium lauryl sulfate, and cetyl trimethyl ammonium bromide were used as collectors. In the second part—ion flotation—potassium *O*-ethyl-dithiocarbonate (xanthate) was used.

Several flocculants were also tested: Percol-173 (anionic), Magnafloc-351 (nonionic), and Zetag-92 (cationic), kindly supplied by Allied Colloids (UK). When these were used, the solution was agitated at 3.33 Hz for 600 s during the initial flocculation stage. The stirring was later slowed down during flotation and stopped completely when pressurized water was introduced into the cell.

Finally, microfiltration tests were conducted using membrane filters having pore sizes of 8.0, 0.45, and 0.05 μm.

RESULTS AND DISCUSSION

Precipitate flotation generally includes all processes in which an ionic species is concentrated from an aqueous solution by forming a precipitate, which is subsequently removed by flotation.

Dissolved air is often used in conjunction with precipitate flotation. Air is dissolved into water under pressure and, when the pressure is released, fine air bubbles with diameters of less than 120 μm are produced. The rising bubbles constitute the process transport medium. These have been found to float fine particles effectively (*13*). From the solubility isotherms of air in water, it has been calculated that the quantity of air released as fine bubbles from 100 cm^3 of pressurized water is roughly 7 cm^3, which we introduced into a 1-L solution of metal ions.

Collectorless Flotation of Copper Ions

Experiments were initially conducted with only copper ions in solution; sodium sulfide was used to precipitate a colloidal CuS (artificial covellite). Figure 1 illustrates the results obtained without any additional reagent. Cu removal drops to about 5% in the pH range from 3 to 6; above pH 6 it increases back to almost 100% for doses of Na_2S less or equal to the

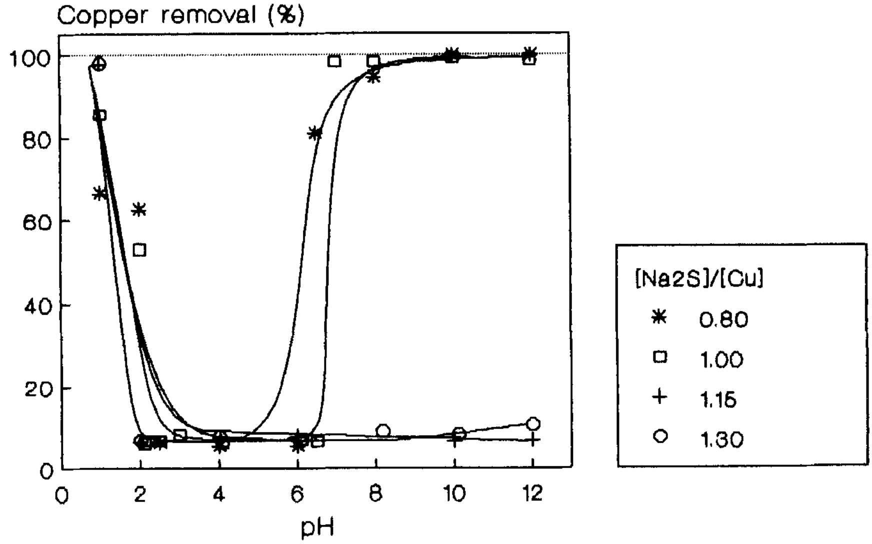

FIG. 1. Effect of sodium sulfide and pH on the removal of copper ions by dissolved-air precipitate flotation. [Cu^{2+}]: 50 mg/L. Sodium sulfide expressed as percentage equivalent to copper. Dissolved-air flotation recycle 10%.

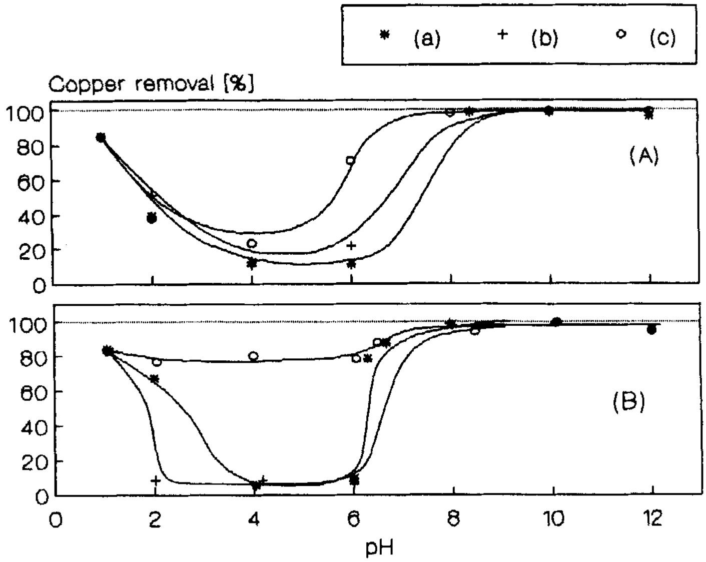

FIG. 2. Use of flocculants in the dissolved-air precipitate flotation of copper ions. (A) 5 mg/L; (B) 10 mg/L. [Cu^{2+}]: 50 mg/L. Stoichiometric amount of sodium sulfide. (a) Percol 173; (b) Magnafloc 351; (c) Zetag 92. [Na_2S]/[Cu^{2+}] = 1.0.

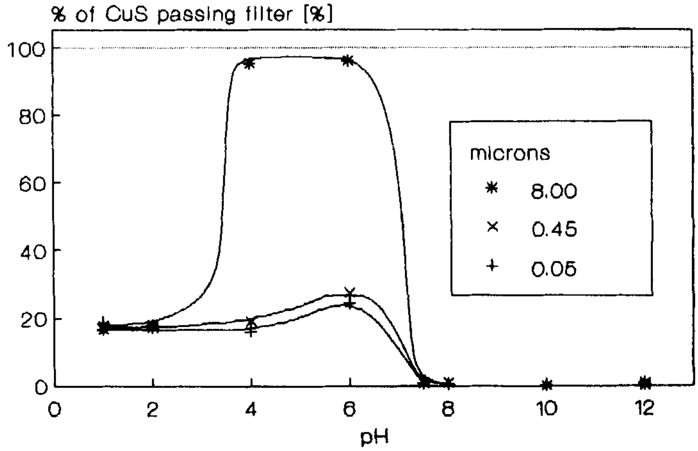

FIG. 3. Microfiltration tests; percentage of copper sulfide passing through filter. [Cu^{2+}]: 50 mg/L. [Na_2S]/[Cu^{2+}] = 1.0.

stoichiometric amount required. This seems to contradict previous results, where a 30% excess of sodium sulfide was found to be adequate (*11*), but a possible explanation can be traced to froth flotation (*14*) where sodium sulfide constitutes a depressing agent for sulfide ores.

Three different polymers [a cationic (Zetag 92), an anionic (Percol 173), and a nonionic (Magnafloc 351)] were then tested as flocculants; Fig. 2 presents the results obtained with 5 and 10 mg/L. The same flotation behavior was noticed, more or less, with the anionic and the nonionic flocculant, but with slightly higher removals. On the contrary, copper removal was always over 80% with the cationic polyelectrolyte (concentration at 10 mg/L).

As a further test of the natural floatability of the copper sulfide precipitate, the dispersion (after precipitation) was filtered through several filters having various pore sizes (from 8.00 down to 0.05 μm). Figure 3 shows that in the 3–6 pH range the precipitate particles are very fine, and this may explain why collectorless flotation is so inefficient in this pH range.

Flotation of Copper Precipitates Using Collectors

Several anionic and cationic surfactants were tested as collectors for the removal of copper precipitate: cetyl pyridinium chloride (CPCl), cetyl trimethyl-ammonium bromide (CTMABr), sodium laurylsulfate (SLS), and laurylamine (LA). The results are illustrated in Figs. 4 and 5.

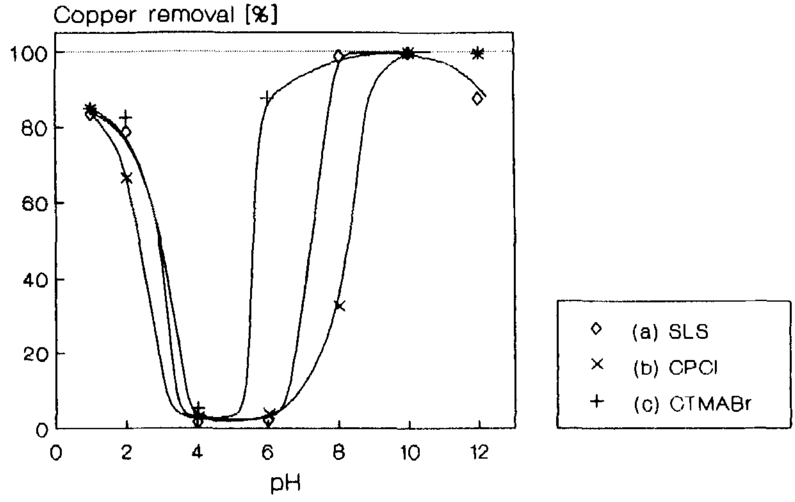

FIG. 4. Use of various collectors in copper flotation: sodium lauryl sulfate (SLS), cetyl pyridinium chloride (CPCl), and cetyl trimethyl-ammonium bromide (CTMACl). [Cu^{2+}]: 50 mg/L. Surfactant concentration: 10 mg/L. [Na_2S]/[Cu^{2+}] = 1.0.

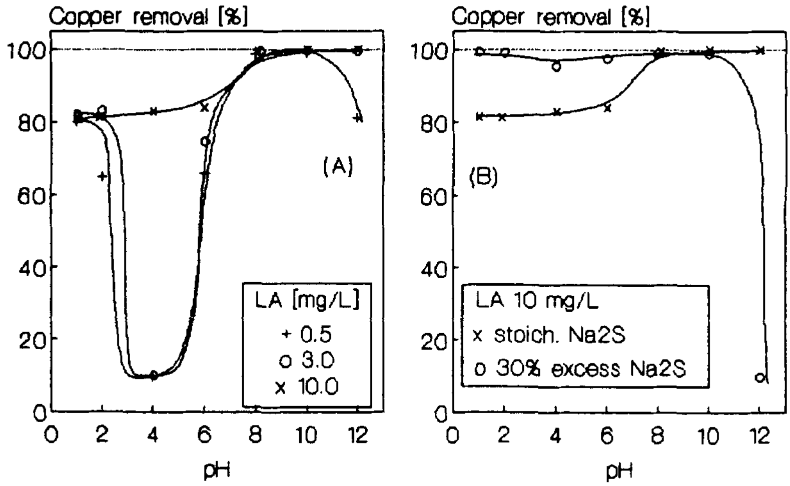

FIG. 5. (A) Effect of laurylamine (LA) on copper ion flotation. (B) Excess (30%) of Na_2S. $[Cu^{2+}]$: 50 mg/L. $[Na_2S]/[Cu^{2+}] = 1.0$.

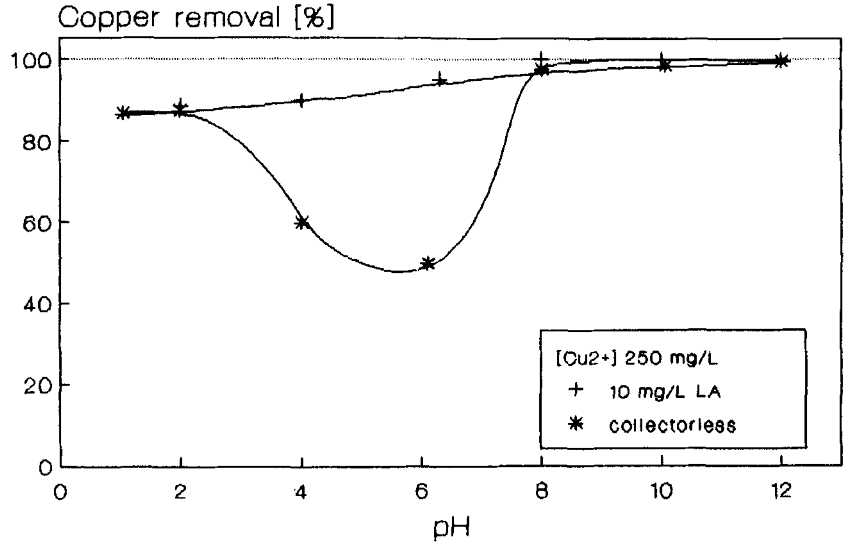

FIG. 6. Effect of increased initial copper concentration (250 mg/L) on copper ion flotation. $[Na_2S]/[Cu^{2+}] = 1.0$.

The first three surfactants display a similar behavior; they were unable to float the copper precipitate in the 3–6 pH range. Laurylamine, however, proved more efficient; it successfully removed the copper precipitate when it was added at a dosage of 10 mg/L (Fig. 5A). An excess of 30% of Na_2S further enhanced its efficiency to approximately 100% across almost the whole pH range (Fig. 5B). Laurylamine also proved to be as efficient at higher copper concentrations (250 mg/L, Fig. 6). It should be noted, however, that at this high Cu concentration, even the collectorless removal was significantly higher.

Generally, it seems most probable that flotation will be required to solve problems connected with dilute rather than highly concentrated solutions. Therefore, the observed reduction in copper ion removal in the 3–6 pH range may be corrected by adding some suitable cationic reagent (surfactant).

Collectorless Floatation of Multi-Ion Solutions

The removal of the copper precipitate in the presence of other ions was also investigated. The analysis of an actual scrubber wastewater from a copper smelting plant (6) was used as a guide for the ionic species and the respective concentrations that may be found in an industrial effluent.

Zinc ions often coexist with copper. Figure 7 illustrates the effect of adding 50 mg/L of zinc ions to the copper ion solution (at pH 5). It seems

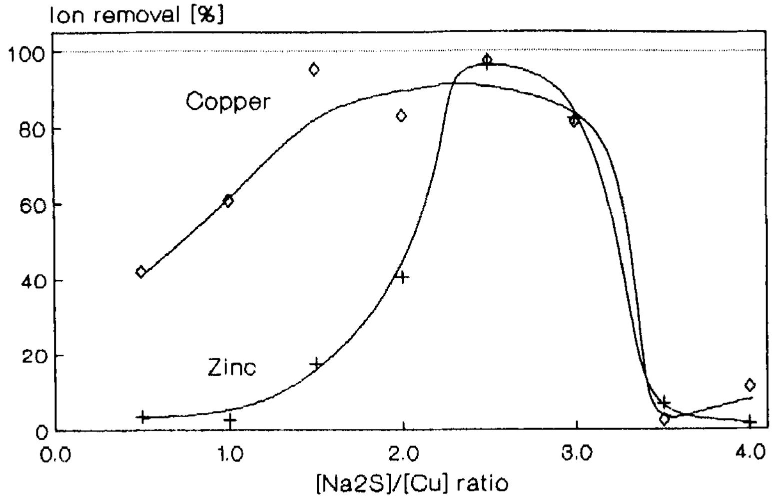

FIG. 7. Effect of sodium sulfide and zinc ions (50 mg/L) on copper ion flotation (pH approximately 5). $[Cu^{2+}]$: 50 mg/L.

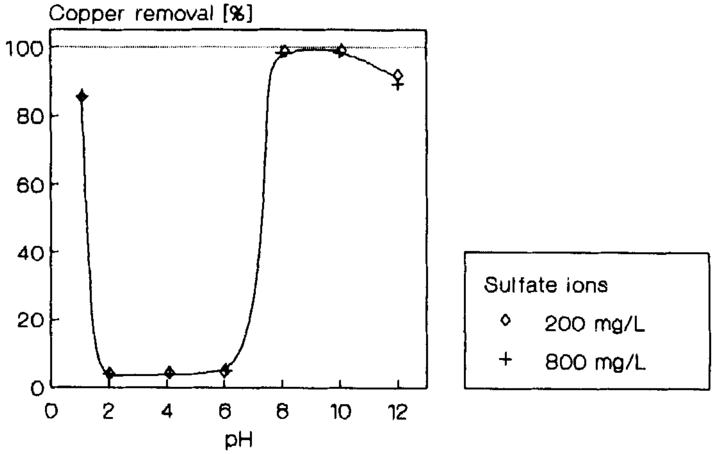

FIG. 8. Effect of SO_4^{2-} ions on copper ion flotation. [Cu^{2+}]: 50 mg/L. [Na_2S]/[Cu^{2+}] = 1.0.

that the presence of Zn^{2+} enhances the collectorless removal of the copper ion.

It should be remembered (from Fig. 1) that, at pH 5, there is very little removal of Cu^{2+}, even with an excess of 30% of Na_2S. When Zn is added, a 60% removal is achieved for a stoichiometric amount of Na_2S. A selective separation of the two species is achieved at this dosage. A similar selective separation has been achieved at pH 2 by using laurylamine (*11*).

If, on the other hand, a total removal of the ionic species is required, then an excess of over 150% of Na_2S is required to remove both Cu^{2+} and Zn^{2+}.

The addition of sulfate ions (200 or 800 mg/L SO_4^{2-}) had no effect on the (collectorless) flotation of copper (Fig. 8).

The addition of Fe^{3+} had, however, a noticeable effect (Fig. 9). The removal of Cu^{2+} was enhanced in the 3–6 pH region (compared with the single ion behavior—Fig. 1), but then dropped dramatically. At pH over 6, heavy flocs appeared in the cell due to the precipitation of $Fe(OH)_3$ which could not be floated under these collectorless conditions. However, at pH < 3 the selective separation of Cu^{2+} from Fe^{3+} is apparent, with recoveries of Cu^{2+} over 80%.

Metal Ions Flotation as Xanthates

Thiol reagents, such as the xanthates, are common collectors in froth flotation of sulfide minerals (*15*) and have been extensively studied (*16*). Here, potassium *O*-ethyl-dithiocarbonate (KEX) was used for the dissolved-air flotation of several ions.

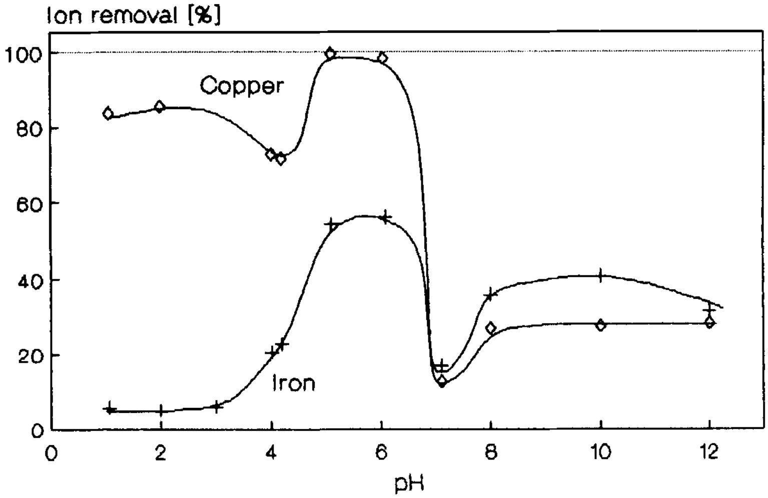

FIG. 9. Effect of iron ions (150 mg/L) and pH on removal of ions. [SO_4^{2-}] = 800 mg/L. [Cu^{2+}]: 50 mg/L. [Na_2S]/[Cu^{2+}] = 1.0.

Copper ions were previously floated with KEX as a yellow precipitate in the pH range from 2 to 6, displaying satisfactory rates of removal (*10*). When Cu^{2+} reacts with xanthate anions, it yields an unstable complex which decomposes, producing dixanthogen and cuprous xanthate, CuEX.

Trivalent iron was also floated with KEX; the conditioning time was 300 s at an agitator speed of 5 Hz. Stirring was then slowed down to 1.33 Hz for another 300 s to help flocculation. A stoichiometric amount of KEX was used. Removals of almost 100% were observed for pH values over 4.5 (Fig. 10A), where one (or more) of the xanthate anions in the reaction product, $Fe(EX)_3$, was expected to be replaced by OH^-.

Iron, depending upon the conditions, precipitates out of solution at around pH 3.5 and, due to hydrolysis, ferric hydroxo-complexes are formed. When ferric ions come in contact with a xanthate solution, a dark brown precipitate forms. This is possibly ferric xanthate, because ferrous xanthates have considerable solubility in water (*16*). It is interesting to note that a stable ferric xanthate was formed in the case of iron, even though (under the same conditions) cupric xanthate is reduced to the cuprous state.

Experiments with Ni^{2+} gave similar results (Fig. 10B) for a 10% excess of KEX over the stoichiometric amount. Removals of over 90% were obtained for pH values over 4. Even better results, with removals of almost 100%, occurred at pH over 8, where nickel precipitation (as hydroxide)

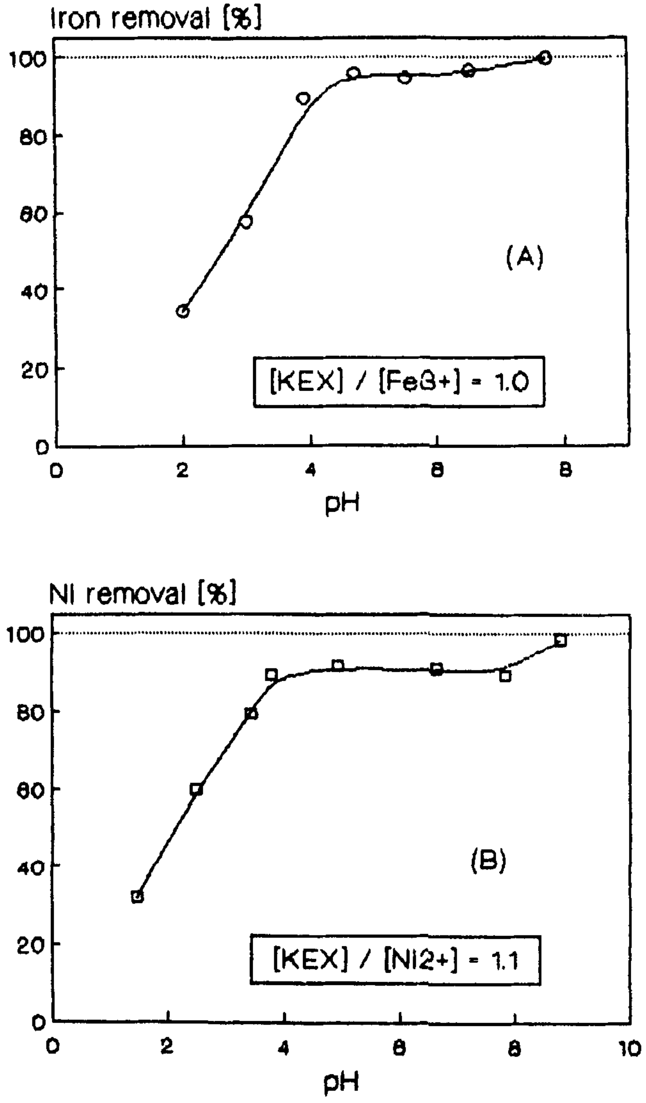

FIG. 10. Flotation of single metal (Fe^{3+}, Ni^{2+}) solutions using potassium-*O*-ethyl dithiocarbonate (KEX).

starts. Nickel xanthate, $Ni(EX)_2$, was yellow and colloidal initially; an activity product of 1.4×10^{-12} has been reported for nickel ethyl xanthate (*17*).

The above dissolved-air flotation experiments covered a wide pH range. Thiol anions, which exhibit a high reactivity for heavy metal ions, may hydrolyze in acidic conditions, forming free acids; the latter are normally short-lived and decompose rapidly. For example, at pH 2.5 the half-life of ethyl xanthate is only 120 s (*18*). In an alkaline medium, xanthate can be considered as stable during any normal flotation operation.

Tests were performed with binary systems (Cu-Fe, Ni-Fe, Ni-Cu). Figure 11 illustrates the results with the Cu-Fe system; equal concentrations of the ions were used and the amount of KEX was that stoichiometrically required for the copper ion only. At pH values over approximately 6, nearly complete flotation was obtained due to the precipitation of metal hydroxides. In the more acidic region, copper removal was of the order of 50%, since part of the xanthate was consumed by the ferric ions. Since even at low pH values both ions exhibit some percentage of removal, no appreciable separation may be achieved.

The results with the Ni-Fe system are shown in Fig. 12(A); similar behavior was noticed for pH values over 7, with total removal of both ionic species. The experiments were repeated without any xanthate collector

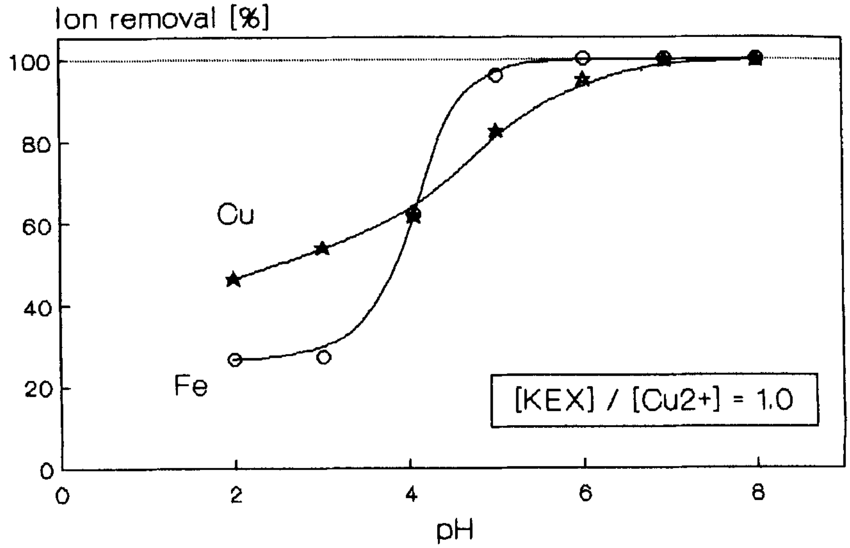

FIG. 11. Flotation of Cu-Fe solution using potassium-*O*-ethyl dithiocarbonate (KEX). $[Cu^{2+}] = [Fe^{3+}] = 50$ mg/L.

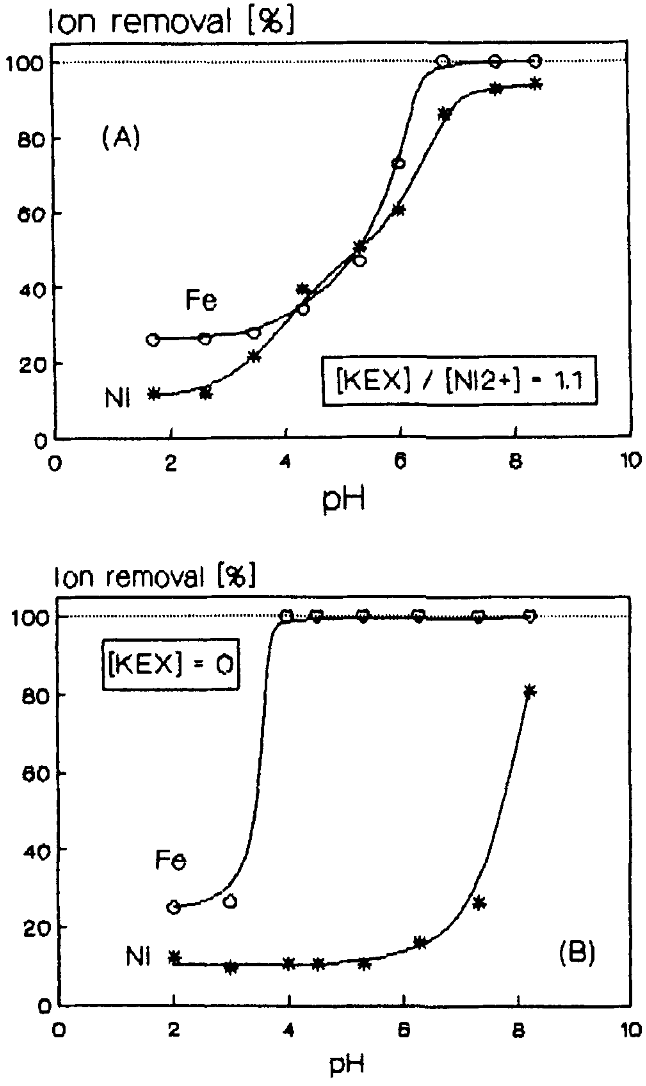

FIG. 12. Flotation of Ni-Fe solution with and without KEX. $[Ni^{2+}] = [Fe^{3+}] = 50$ mg/L.

(Fig. 12B) in order to check whether there was any adsorption of nickel on ferro-hydroxo complexes. The results showed that Ni^{2+} floats only in the pH region where its hydroxide forms.

When the binary solution Ni-Cu was examined at equal concentrations, shown in Fig. 13(A), the xanthate was more easily tied to Cu^{2+} than to

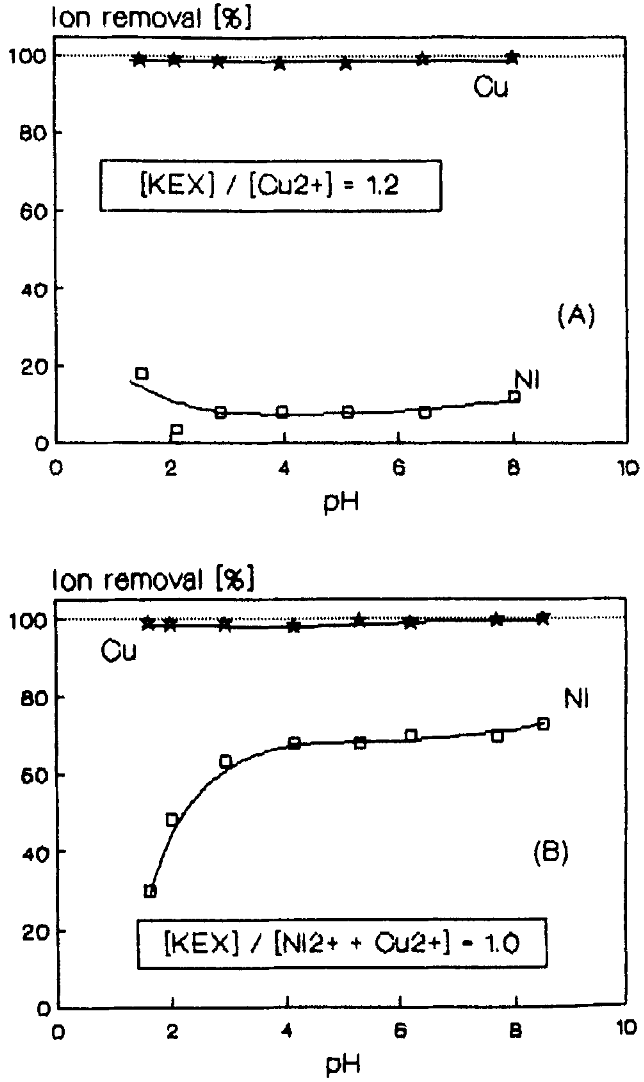

FIG. 13. Flotation of Ni-Cu solution. $[Ni^{2+}] = [Cu^{2+}] = 50$ mg/L.

Ni^{2+}, probably as a result of its lower solubility (1.54×10^{-5} g/L) as compared to the solubility of nickel xanthate (2.07×10^{-1} g/L). Copper was completely removed over the entire pH range. An increase in the amount of KEX added resulted in higher nickel removals (Fig. 13B). From these results it was inferred that an excess of collector would be detrimental

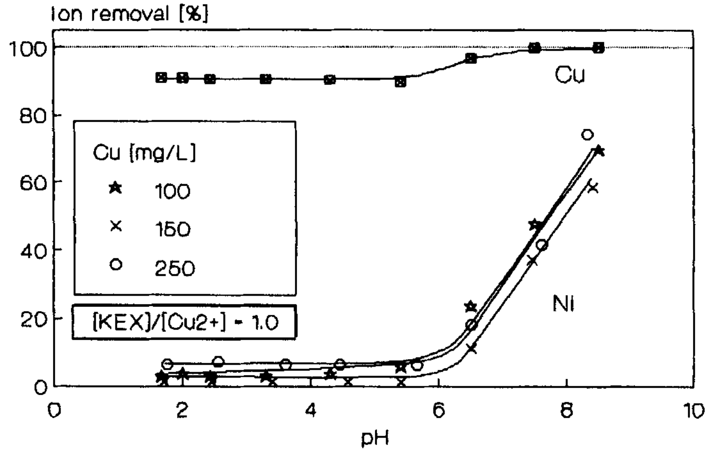

FIG. 14. Flotation of Ni-Cu solution ([Ni] = 50 mg/L). Effect of Cu concentration.

to the process because it lowered the selectivity of the separation process; hence, the amount of xanthate used in all subsequent experiments was stoichiometric toward copper alone.

Figure 14 shows the results with increased copper concentrations ranging from 100 to 250 mg/L for the same binary Cu-Ni system. Nickel usually occurs in lower concentrations than copper in the effluents from metal-producing plants. In all cases a similar behavior was observed. Copper removals were steadily high; at pH over about 7, a 100% removal was reached due to the simultaneous precipitation of copper hydroxide. On the other hand, Ni remained in solution; it started floating only when $Ni(OH)_2$ was formed.

It should be noted that in hydrometallurgy the separation of Ni-Cu mixtures is conventionally accomplished by liquid-ion exchange (*19*). Therefore, flotation may be regarded as an alternative process, especially for dilute solutions.

Finally, a ternary Ni-Cu-Fe system was tested. At low initial Cu concentrations (Fig. 15A), copper and iron floated more or less together, except at very low pH (<3) where removals of copper reached 50% whereas iron reached only 25%. Nickel, however, remained in solution until the pH was high enough for the nickel hydroxide to precipitate. Thus, some separation may be achieved, especially at pH around 6, with copper and iron in the foam and nickel remaining mainly in solution. At higher copper concentrations (Fig. 15B), however, the copper removal was greatly enhanced. Even at pH 2 its removal was over 80%, while the removals of iron and nickel remained practically the same as before. Therefore, it

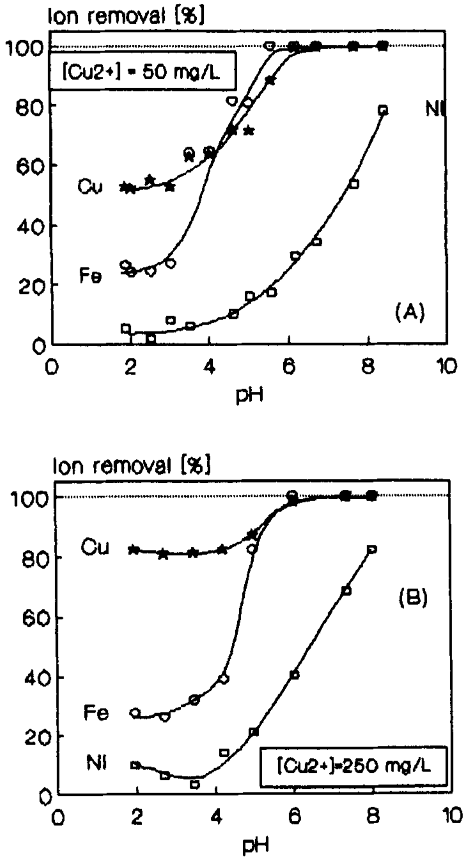

FIG. 15. Flotation of Ni-Cu-Fe solution. $[Ni^{2+}] = [Fe^{3+}] = 50$ mg/L.

should be possible, in principle, to separate the ternary system into two binary ones, which may be processed as before in order to separate all three species.

CONCLUSIONS

It is known that flotation presents some advantages over other, more conventional processes, such as sedimentation, because of its better effluent quality and, mainly, its appreciably lower residence time, which implies a lowering of plant costs, including the need for less floor space.

The present work demonstrated that dissolved-air flotation may achieve two goals: concentration and separation of metal ions. Conditions for the collectorless flotation of Cu^{2+} precipitates have been determined, and they permit the selective separation and removal/recovery of this ionic species from a complex metal-containing effluent.

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REFERENCES

1. A. I. Zouboulis, K. A. Matis, and G. A. Stalidis, in *Innovations in Flotation Technology* (P. Mavros and K. A. Matis, eds.), Kluwer Academic Publishers, Dordrecht, 1992, p. 499.
2. K. A. Matis and P. Mavros, *Sep. Purif. Methods, 20,* 1 (1991).
3. D. Pearson and J. M. Shirley, *J. Appl. Chem. Biotechnol., 23,* 101 (1973).
4. L. D. Skrylev and V. A. Borisov, *Zh. Prikl. Khim., 51,* 434 (1978).
5. M. C. Kuhn, M. J. Noakes, and A. D. Rovig, *CIM Bull.*, p. 103 (June 1975).
6. D. Bhattacharyya, A. B. Jumawan, and R. B. Grieves, *Sep. Sci. Technol., 14,* 441 (1979).
7. W. Charevicz and W. Walkowiak, *Environ. Protect. Eng., 8,* 67 (1982).
8. N. A. Mumallah and D. J. Wilson, *Sep. Sci. Technol., 15,* 1753 (1980).
9. E. H. De Carlo, B. D. Bleasdell, H. Zeitlin, and Q. Fernando, *Ibid., 17,* 1205 (1982).
10. G. A. Stalidis, K. A. Matis, and N. K. Lazaridis, *Ibid., 24,* 97 (1989).
11. G. A. Stalidis, K. A. Matis, and N. K. Lazaridis, *Int. J. Miner. Process., 24,* 203 (1988).
12. G. A. Stalidis, N. K. Lazaridis, K. A. Matis, and I. N. Papadoyannis, *Sep. Sci. Technol., 24,* 1033 (1989).
13. K. A. Matis and G. P. Gallios, in *Mineral Processing at a Crossroads* (B. A. Wills and R. W. Barley, eds.), Nijhoff, Dordrecht, 1986, p. 37.
14. S. M. Bulatovic and D. M. Wyslouzil, in *Complex Sulfides—Processing of Ores, Concentrates and By-Products* (A. D. Zunkel, R. S. Boorman, A. E. Morris, and R. J. Wesely, eds.), TMS/AIME, Pennsylvania, 1985, p. 101.
15. I. Bayraktar, U. A. Ipekoglu, and R. Tolun, in *Innovations in Flotation Technology* (P. Mavros and K. A. Matis, eds.), Kluwer Academic Publishers, Dordrecht, 1992, p. 307.
16. G. W. Poling, in *Flotation—A. M. Gaudin Memorial Volume* (M. C. Fuerstenau, ed.), SME/AIME, New York, 1976, p. 334.
17. D. W. Fuerstenau and R. K. Mishra, in *Complex Sulphide Ores,* IMM Symposium, London, 1980, p. 271.
18. I. Kakovsky, in *Proceedings, 2nd International Conference on Surface Activity,* Vol. 4, Butterworths, London, 1957, p. 225.
19. J. C. Agarwal, N. Beecher, G. L. Hubred, D. L. Natwig, and R. R. Shrab, *Eng. Min. J.*, p. 74 (December 1976).

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