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G. A. Stalidis[a]; N. K. Lazaridis[a]; K. A. Matis[a]; I. N. Papadoyannis[b]
[a] LABORATORY OF GENERAL AND INORGANIC CHEMICAL TECHNOLOGY, [b] LABORATORY OF ANALYTICAL CHEMISTRY UNIVERSITY OF THESSALONTKA THESSALONIKA, GREECE

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G. A. STALIDIS, N. K. LAZARIDIS, and K. A. MATIS

LABORATORY OF GENERAL AND INORGANIC CHEMICAL TECHNOLOGY

I. N. PAPADOYANNIS

LABORATORY OF ANALYTICAL CHEMISTRY

UNIVERSITY OF THESSALONIKA
THESSALONIKA, GREECE

Abstract

The precipitate flotation of copper and zinc as sulfides in dilute aqueous solutions (50–250 ppm metal ion concentration) was investigated in the laboratory in continuous flow. The dispersed-air flotation technique was followed, leading to a selective recovery of copper sulfide of the order of 95% in a high acidic pH region (of 1.7) by a laurylamine ethanolic solution as collector and with the addition of cetyl-pyridinium chloride as frother. The precipitate flotation of zinc sulfide was then accomplished with the same method at pH 5.0 as a second separation stage (in the presence of minor amounts of copper).

INTRODUCTION

Precipitate flotation is a process that involves all those steps where an ionic species is concentrated, forming initially some kind of precipitate, and removed from a dilute aqueous solution (usually wastewater) transferred to the surface by gas bubbles (*1*). Among the advantages of precipitate flotation over ion flotation is the lower surfactant requirement

(*2, 3*). In this way, heavy metals can be removed or separated by flotation, in most cases in the form of their hydroxides, as for instance the precipitate flotation of chromium (*4*), copper (*5*), and zinc hydroxides (*5, 6*).

Precipitate flotation has been studied and applied in most cases on hydroxides of heavy metals. However, limitations of the latter method are the added capital and operating costs of the system, since one must conduct the precipitation at high pH, and the nonexistence of a unique pH for hydroxide precipitation, where all metal hydroxides are at their minimum solubility. Hence, it cannot often meet stringent standards for metal removal (*7*).

Besides the conventional hydroxide precipitation process, the sulfide precipitation process exists and has been studied, among others, by Beitelshees et al. (*8*). This is known to offer certain advantages, such as the low solubility of metal sulfides, better sludge thickening, and reduced leaching (*9*). Nevertheless, metal sulfide precipitates are very fine in some cases, which makes their removal by filtration or by flotation difficult. This is a problem that can possibly be overcome by adding a coagulant and/or generating fine bubbles for the flotation. The method has been also applied for deep-sea ferromanganese nodules treatment (*10*). In continuous flow, the precipitate (foam) flotation of trivalent chromium hydroxide (*11*), as well as of cuprous sulfide (*8*), has been reported.

In a previous paper a statistical approach was attempted for the precipitate flotation of copper and zinc sulfides in batch (*12*). From the results of this paper it was obvious that selective separation from dilute solutions of high acidity was possible by the dissolved-air flotation technique. The selective separation of copper, zinc, and arsenic ions from dilute solutions was also investigated by ion flotation, as was copper xanthate and also zinc diethyl-dithiocarbamate, and, by adsorbing colloid flotation, pentavalent arsenic (*13*). In this paper the results of the selective separation of copper and zinc ions as sulfides by precipitate flotation in a continuous mode are presented. Dodecylamine was used both as coagulant and collector, while the addition of small amounts of cetyl-pyridinium chloride was necessary for better stabilization of the froth.

EXPERIMENTAL

The continuous flow flotation system generates fine bubbles by dispersed air produced mechanically by such means as passing air

through porous media. The basic parts of the arrangement, built in the laboratory, are shown in Fig. 1. The feed tank was approximately 30 L on volume and was cylindrical (295 mm internal diameter by 485 mm height). A four-blade impeller (of 85 mm diameter) for mixing was situated about 80 mm from the bottom of the tank. When four baffles were added in the mixing tank, no improvement was observed. The pH values of solutions measured in the tank were previously adjusted by nitric acid or sodium hydroxide solution. The liquid rotameters were controlled so that the solution height in the column remained steady.

The flotation cell was a cylindrical perspex column with a volume of about 2100 cm^3 (80 mm internal diameter by 420 mm height); its bottom consisted of a Schott No. 4 diaphragm with a porosity of 10–16 μm used as the air disperser. The air compressor (60 L, 0.75 hp) had an outlet excess pressure set at 1 atm. The feed of the column was performed about

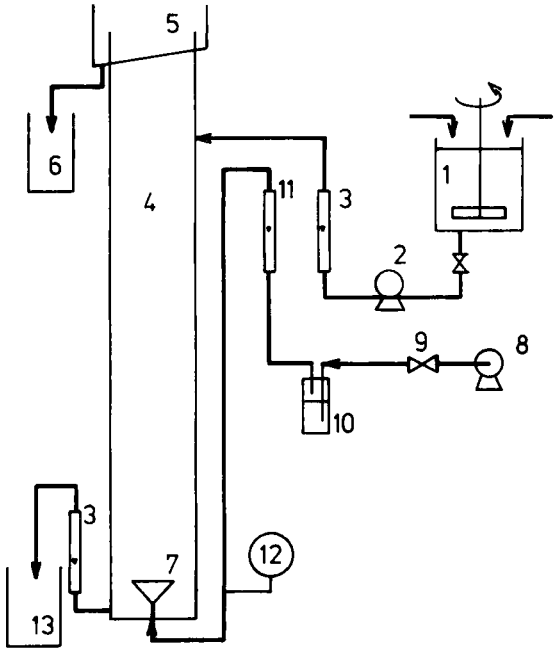


FIG. 1. Continuous flow laboratory flotation arrangement. 1: Conditioning and feed tank. 2: Peristaltic pump. 3: Liquid rotameters. 4: Flotation column. 5: Weir. 6: Foam collection tank. 7: Porous plate. 8: Air compressor. 9: Needle valve. 10: Washing trap. 11: Air rotameter. 12: Mercury U-tube manometer. 13: Effluent tank.

30 mm below the down level of the froth. Sampling was conducted at the flotation cell exit for chemical analysis by atomic absorption in the normal way.

A soluble sulfide method was followed for the initial precipitation; sodium sulfide was used because it is easily handled. Initial copper and zinc addition, as a synthesized wastewater, was in the form of their nitrate salts. The collector was laurylamine (dodecylamine), denoted hereafter as RNH_2; it was introduced as an ethanolic solution. After 300 s mixing, cetyl-pyridinium chloride (CPCl) was added as needed as a foam stabilizer, which was checked from batch experiments. The CPCl alone, under the conditions used, did not supply sufficient flotation.

Under the experimental conditions used, the flotation column behaved as a completely mixed flow vessel, which was checked from the residence time distribution of KCl determined conductometrically (see also Ref. *18*).

RESULTS AND DISCUSSION

Flotation of CuS

In industrial wastewater treatment, sulfide precipitation is usually accomplished by Na_2S (or NaHS) solutions, FeS (the insoluble method), CaS, etc. It is known that the reactivity of sulfide species S^{2-} and HS^-, which are soluble chemical reactants in aqueous solutions, with heavy metal ions is high (*14*).

From preliminary precipitation experiments followed by filtration through a Sartorius 0.05 μm microfilter, it was found that a 30% excess of the stoichiometric amount of sodium sulfide for the quantitative precipitation of copper was required. The precipitate produced was almost colloidal, indicating that a second-stage sedimentation or filtration would have problems. Indeed, the removal of the precipitates by batch flotation experiments was limited although sulfides are normally hydrophobic, which suggests the fine size of the precipitates. Coagulation was accomplished by the addition of small amounts of laurylamine, which also acted as a collector. From experimental work in continuous flow, followed by preliminary flotation tests in batch, it was found out that an initial mixing was necessary in the feed tank for approximately $t_M = 600$ s with a stirring speed of 200 rpm; the pH of the solution was 1.7 $\pm$ 0.1. In this highly acidic medium, iron, if it is present, is not expected to

be precipitated. The influences of pH on precipitate flotation are similar to those for ion flotation (*15, 16*).

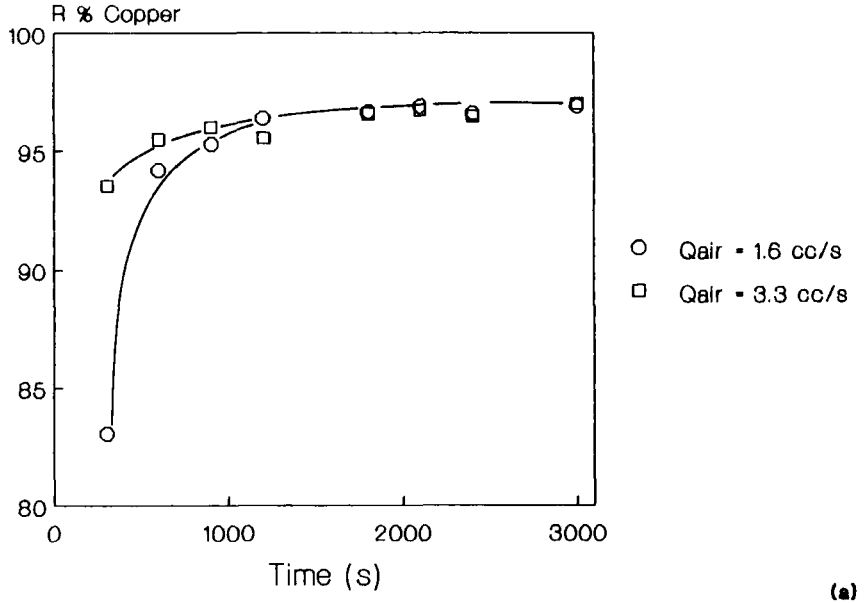
The first round of experiments was carried out on a copper feed of 50 ppm at two air flow rates and by the addition of laurylamine plus CPCl, as presented in Fig. 2. Four different liquid flow rates (ranging from 1.6 to 8.3 cm^3/s) were tested. Since only small differences were observed, only the two extreme cases are given for comparison. The RNH_2 collector in these experiments (at a concentration of 5 ppm) was added as an ethanolic 0.1% solution; the latter was also found as optimum from batch tests. The CPCl surfactant concentration was increased to 5 ppm (in the batchwise experiments it was 1 ppm) in order to produce a stable foam layer. It was observed that copper recoveries reached 95% even at residence times of the order of 5 min, although a better recovery could be achieved with the smaller feed rate of the column. The gas flow rates used had little or no influence on the removal of precipitate, although in some cases of ion flotation gas flow rates have been observed to have a kind of influence (*17*).

It is noted that the process could be classified, according to Pinfold (*1*), as "precipitate flotation of the first kind"—meaning one which involves the flotation of precipitate particles by a surface-active species; the latter is not a chemical constituent of the precipitate substance and occurs only on the surface of the particles. However, to our knowledge, this terminology is not widely adopted.

A higher feed concentration of 250 ppm in copper was also tried and the results are shown in Fig. 3. An air flow rate of 3.3 cm^3/s was used this time, and a higher CPCl concentration (20 ppm) was tested to avoid redispersion. The effect of collector and colligend concentrations on precipitate flotation have been discussed by others elsewhere (*1*).

Experiments were also conducted with reduced amounts of ethanol, down to 0.025%, but keeping the laurylamine concentration the same (5 ppm) in the final solution; liquid flow rate was 1.6 cm^3/s, air flow rate 3.3 cm^3/s, and the other operating conditions as before. The results are shown in Fig. 4. No real effect of ethanol concentration on flotation recovery was observed, so the lower ethanol concentration was chosen for the subsequent work. The addition of collector in the form of an ethanolic solution is generally convenient, as many collectors are not very soluble and it is preferable to maintain them in solution until they can come in contact with colligend ions.

The ratio of collector to colligend (often denoted as ϕ) existing at the commencement of flotation is low in precipitate flotation. In the present work this was varied from 0.02 to 0.1, which is in agreement with the range given in Pinfold's review (*1*).



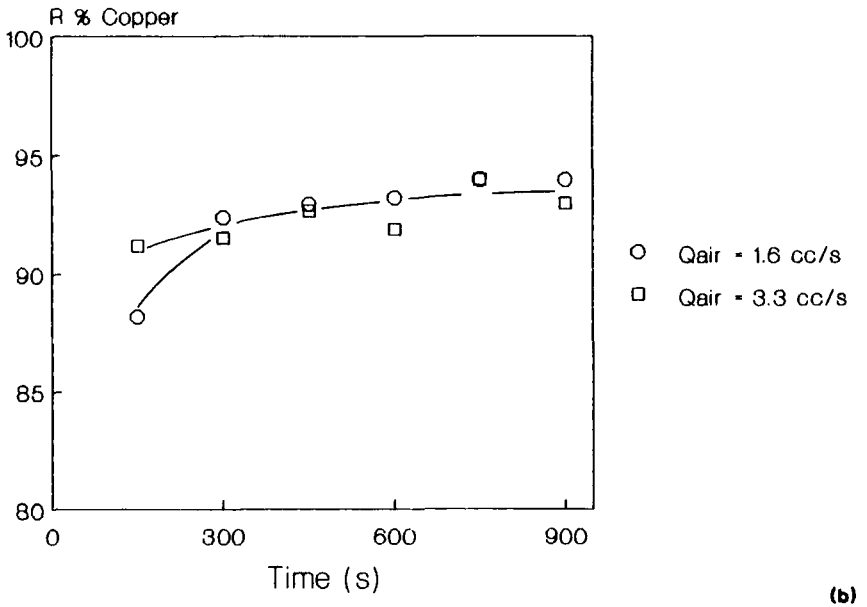
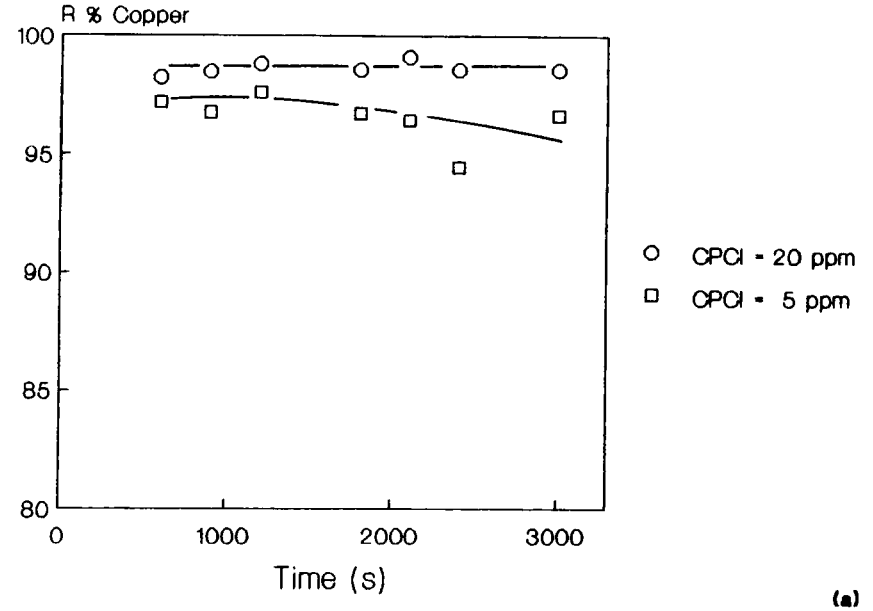


FIG. 2. Continuous-flow flotation experiments of 50 ppm Cu^{2+} solution as sulfide, showing copper recovery with flotation time; t_M = 600 s, 200 rpm, pH = 1.7 ± 0.1, {R−NH_2} = 5 ppm, CPCl = 5 ppm: (a) t_f = 1.2 ks, (b) 0.24 ks.



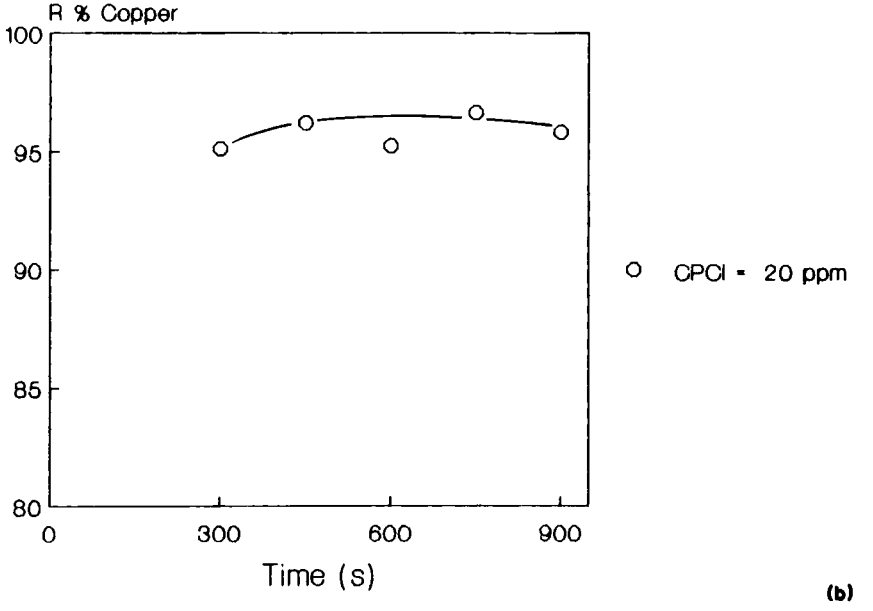
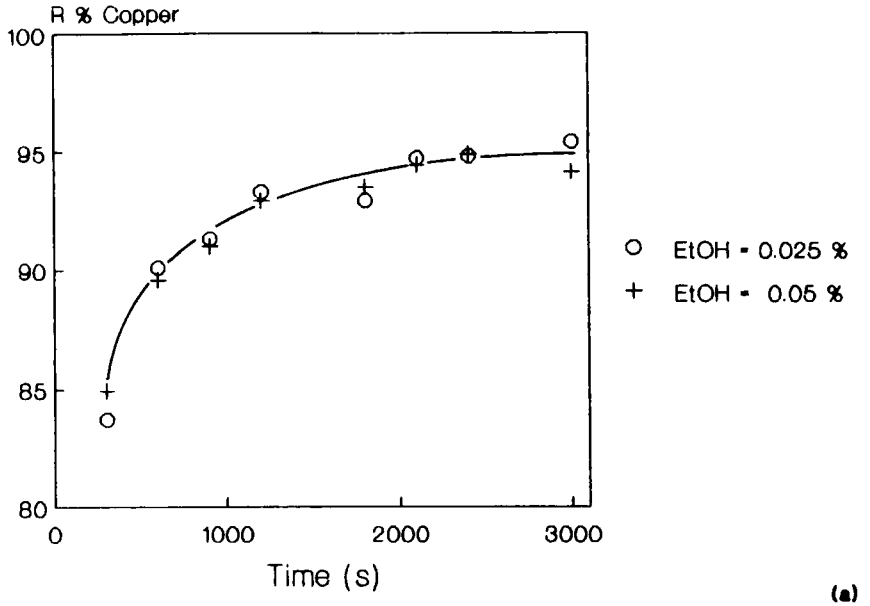


FIG. 3. Continuous-flow flotation experiments of 250 ppm Cu^{2+} solution; Q_{air} = 3.3 cm^3/s: (a) $\bar{t}_f$ = 1.2 ks, (b) 0.24 ks (the other conditions as in Fig. 2).



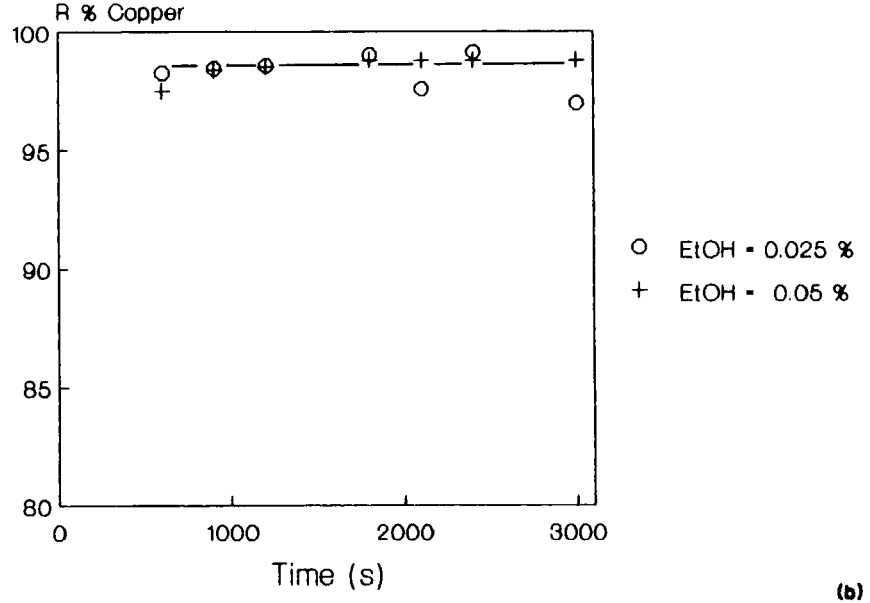


FIG. 4. Experiments decreasing the amount of alcohol of collector solution: (a) 50 and (b) 250 ppm Cu^{2+}

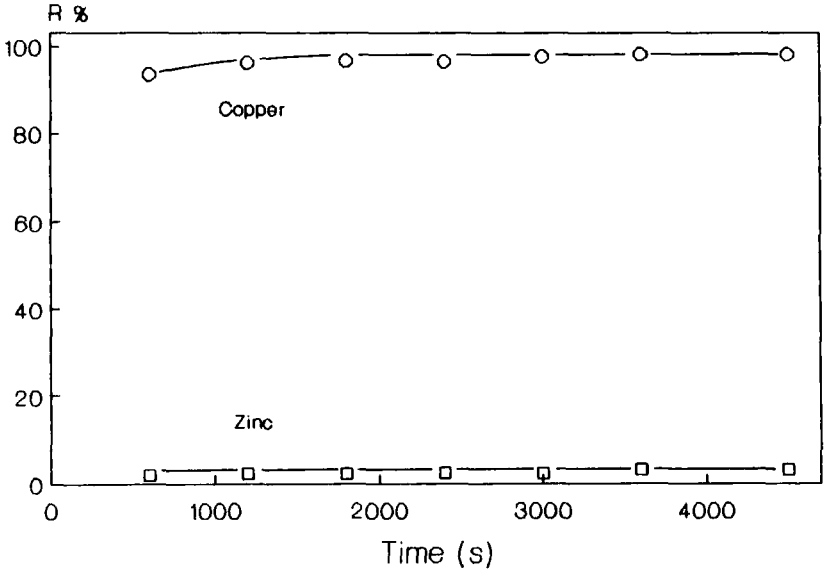
Selective Separation of Cu-Zn

The zinc-copper separation was shown to be achieved by changing the pH of the solutions (*19*); at pH values above 10.5 the copper-surfactant (dodecylimminodipropionic acid) complex was stable while the zinc complex was less stable. In another publication (*20*) it was said that, with ion and precipitate flotation of metal ions as their hydroxides, high recoveries are generally associated with high froth volumes; the removal of copper and iron ions from aqueous solutions was examined there with sulfhydryl collectors.

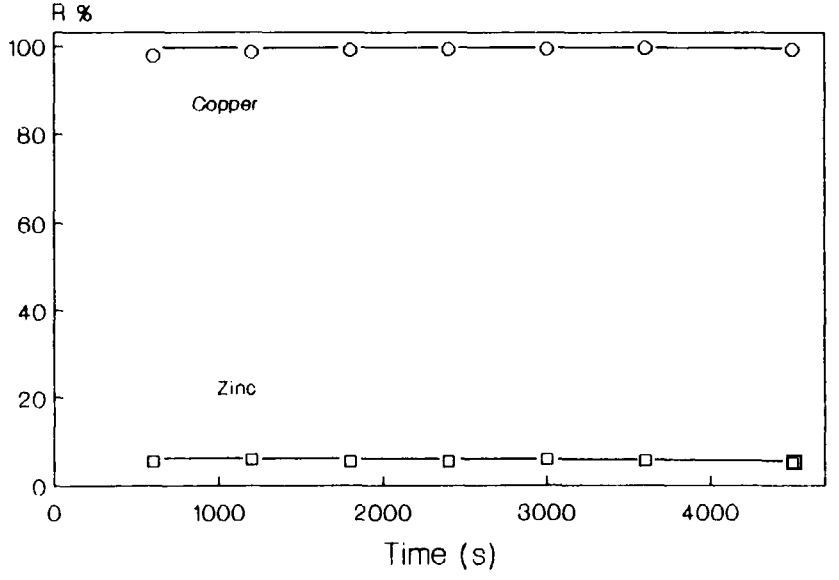
The separation of copper and zinc ions as sulfides in a continuous way was studied under the aforementioned conditions; i.e., pH = 1.7 ± 0.1, t_M = 600 s at 200 rpm, [RNH_2] = 5 ppm in a 0.025% ethanolic solution, [CPCl] = 5 ppm, and liquid flow rate of 1.6 cm^3/s. Some of the results are shown in Fig. 5, where zinc ion initial concentration was constant at 250 ppm and copper either 50 or 250 ppm. Na_2S amounts were added in 30% excess of the stoichiometric concentration of Cu ions. Even more excess of Na_2S at this pH causes no real ZnS precipitation because of its solubility product in correlation with hydrogen sulfide dissociation constants. Zinc recovery in the foam layer was always under 6%, being in the second case a little higher, while copper recovery surpassed 95% after a flotation time (t_f) of about 1.2 ks, twice the residence time of the flotation cell, and was also higher in the case of 250 ppm concentrations. It appears that a selective separation of CuS can be achieved by regulating only the pH and the Na_2S concentration.

Following copper removal, a second flotation stage was then sought for the removal of zinc ion. For this reason, the flotation behavior of zinc sulfide was examined in a separate series of experiments. Again, sulfide precipitation was used. Precipitation was observed to start at approximately pH 4.5. A 20% excess of Na_2S over the stoichiometric amount was selected from batch tests. Coagulation and flotation were performed without any CPCI present and with a mixing speed of 50 rpm (for 600 s). The results in continuous flow are presented in Fig. 6 for a liquid flow rate of 1.6 cm^3/s. Due to the absence of CPCI, an increased ethanol concentration (0.1%) was found necessary to give stable foam and recoveries well over 95%; reduced stirring is noted.

As was observed in the selective separation experiments (Fig. 5), a minor amount of copper ions was left behind in solution after the concentrate was removed. So the next attempt, shown in Fig. 7, was to float in continuous flow zinc (50 ppm) and copper (5 ppm) at pH 5.0 with Na_2S calculated for both. At this pH value both metals are precipitated as sulfides, so they can be cofloated. Zinc and copper were removed in these cases almost quantitatively with concentrate (over 95% recovery). In the



(a)



(b)

FIG. 5. Separation of Cu/Zn in continuous flow at gas flow rate 3.3 cm^3/s and residence time 1.2 ks: (a) $\{Cu^{2+}\} = 50$, $\{Zn^{2+}\} = 250$ ppm and (b) $\{Cu^{2+}\},\{Zn^{2+}\} = 250$ ppm (Na_2S in 30% excess).

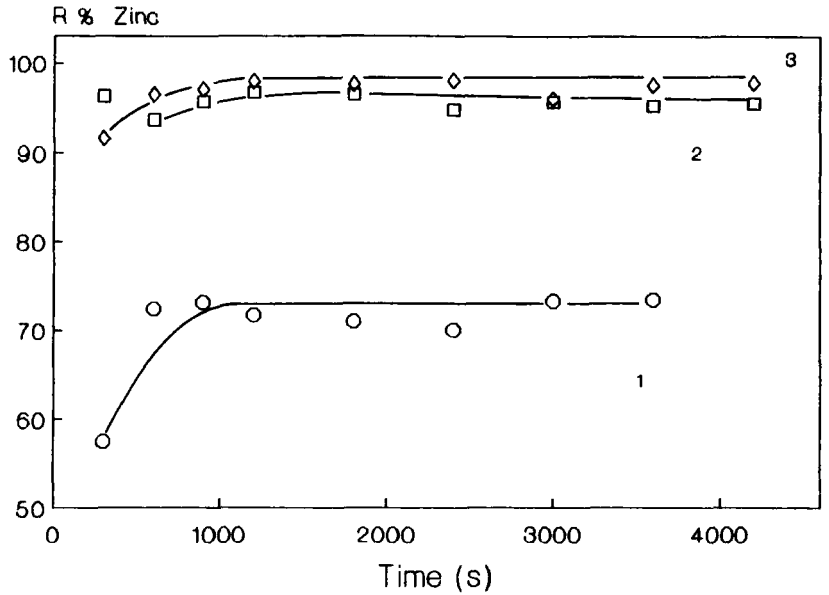


FIG. 6. Influence of ethanol concentration on precipitate flotation of 50 ppm Zn^{2+} as sulfide at pH = 5.0 ± 0.1; t_M = 600 s at 50 rpm, Q_{air} = 1.6 cm^3/s, $\bar{t}_f$ = 1.2 ks {R−NH_2} = 5 ppm in: (1) 0.025, (2) 0.05, and (3) 0.1% C_2H_5OH solution (Na_2S in 20% excess).

first case (Fig. 7a), at 50 rpm with increasing flotation time (t_f), zinc recovery was noticed to slightly decrease, as did copper recovery; this observation was more noticeable when no CPCl was added. The phemomenon of redispersion, discussed elsewhere (*1*), could be responsible for this observation. This was improved, however, at higher mixing speeds, as shown in Fig. 7(b). The same result was also obtained by increasing the RNH_2 concentration. It was generally found that zinc sulfide was floated under conditions suitable for cofloating copper.

The promising results obtained in continuous flow exhibit the possibility for this process to operate at industrial, as well as bench, scale.

CONCLUSIONS

Precipitate flotation, in contrast to other wastewater treatment processes (perhaps more conventional), was shown to be a selective separation method in dilute aqueous solutions. In particular, copper and zinc as sulfides can be separated by flotation, contributing in this way in metals

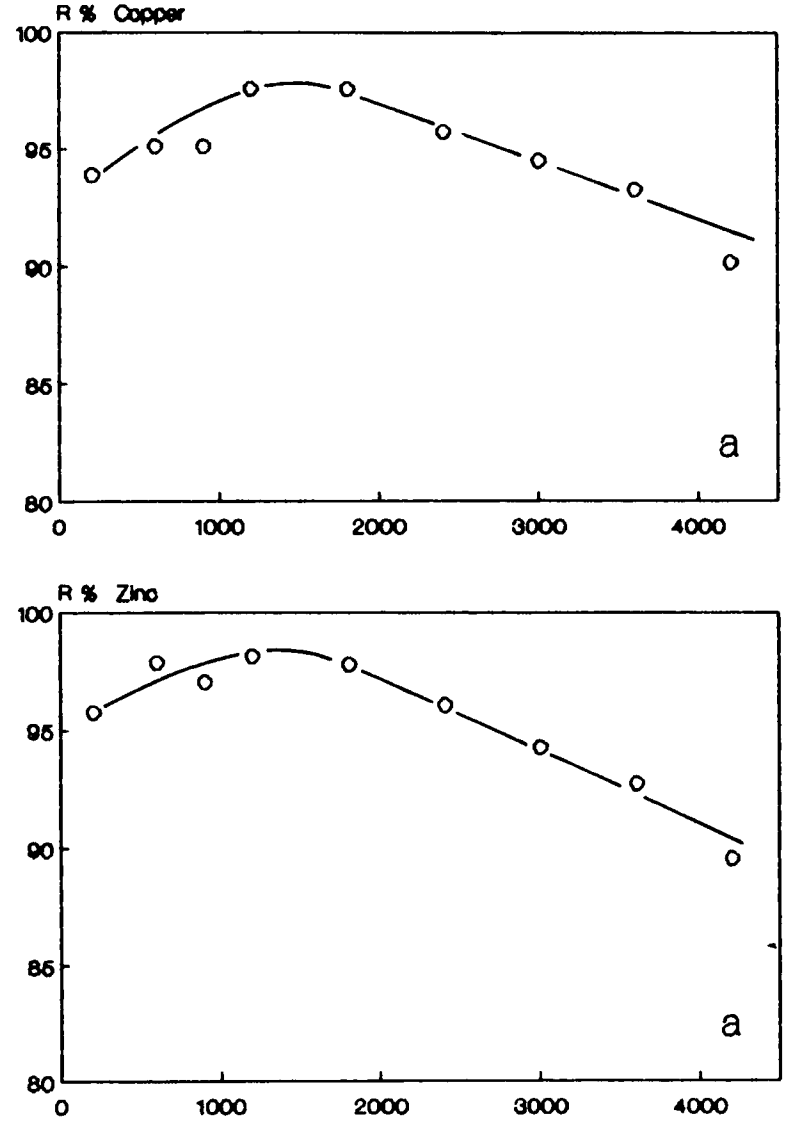
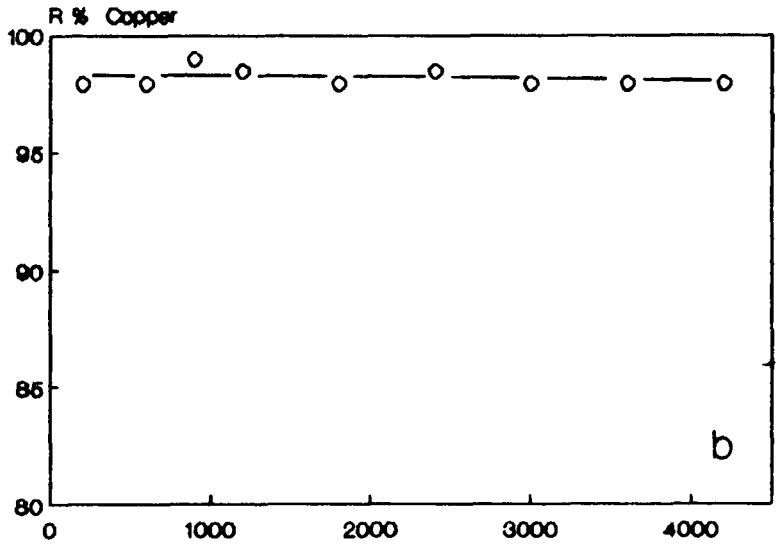
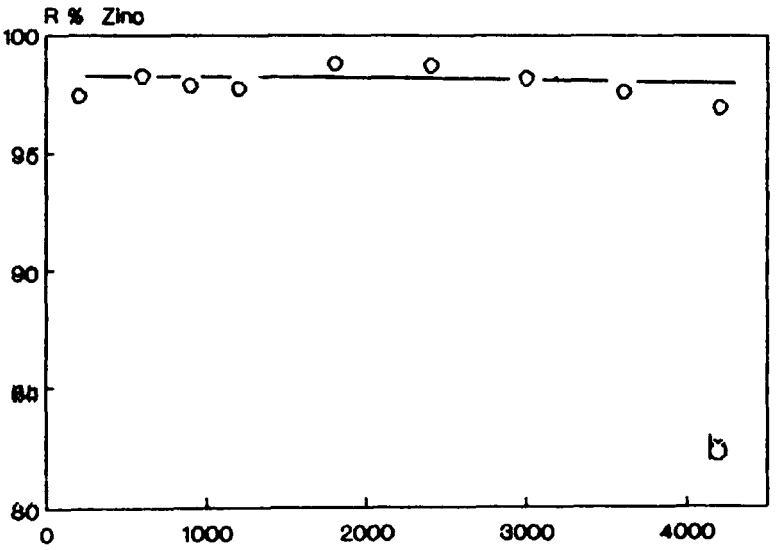


FIG. 7. Flotation of 50 ppm Zn^{2+} in the presence of 5 ppm Cu^{2+}; $\{R-NH_2\}$ = 5 ppm in 0.1% ethanolic solution, $\{CPCl\}$ = 5 ppm, t_M = 600 s at: (a) 50 and (b) 150 rpm (Na_2S for both Cu and Zn in excess as in Figs. 5 and 6).





recycle. Selectivity can be accomplished by the careful selection of conditions (pH, etc.).

In the present study the ratio of collector (laurylamine)—usually in a 0.1% ethanolic solution—to colligend was equal to 0.1 up to 0.2, being higher in the case of 50 ppm initially. A small amount (5 ppm) of cetylpyridinium chloride was also necessary for better foam. A maximum liquid residence time of 20 min was found to establish a steady state at an air flow rate of the order of 2-3 cm^3/s through the porous diffuser. The preliminary mixing of feed for the precipitation-coagulation stage was also critical, with mixing time and impeller speed being important variables.

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