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Selective Separation of Cu, Zn, and As from Solution by Flotation Techniques

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Abstract

The selective precipitation and flotation of copper, zinc, and arsenic ions from dilute aqueous solutions were investigated. Phase separation was accomplished effectively by the dissolved-air technique for the production of fine gas bubbles, and a short-chain xanthate was applied as the collector for copper ions, dialkyldithiocarbamate for zinc, and ferric sulfate for the pentavalent arsenic. The procedures followed were ion flotation for copper and zinc, and adsorbing colloid flotation for arsenic (without a surfactant).

INTRODUCTION

Dissolved-air flotation uses bubbles of air generated under controlled conditions by pressure release from a saturated solution of air in water (in higher pressure). The technique, which is established in effluent treatment, was proposed as a candidate for fines processing (*1*). Its main application, however, is in the treatment of oily contaminated waters, for example, refinery wastes. A large number of dissolved-air flotation plants are currently operating in Europe. The majority utilize a circular flotation cell, usually in conjunction with a flocculation tank.

Industries engaged in metal production operations or metal finishing use large quantities of contact process water, and the spent process streams generally contain moderate concentrations of heavy metal ions, such as Cu, Zn, and As. Heavy metals are also discharged in chemical cleaning wastes and the effluents from coal-fired power plants. Thio collectors such as *O*-alkyl dithiocarbonates (usually termed xanthates) are known to exhibit a high level of chemical reactivity for heavy metals, either in solution or at sulfide mineral surfaces (*2*). Dialkyl dithiocarbamates (DTC), which exhibit similar properties, have been used extensively in analytical chemistry, but applications as collectors are rather limited due to costs (*3*). Monolauryl DTC is a weak chelating agent for the removal of copper (*4*).

In contrast, xanthate systems have often been studied for flotation practice. Among them is copper ion removal by the so-called IPU process (*5*). Soluble copper xanthate complexes were also examined (*6*). Alternative flotation routes exist; for instance, separation as zinc hydroxide (*7*) or as sulfides of copper and zinc ions (*8*). In the later, a statistical approach to flotation was presented. Ion flotation was reviewed broadly elsewhere (*9*).

Adsorbing colloid flotation involves the removal of a solute, depending on the conditions, by adsorption on or coprecipitation with a carrier floc (for example, ferric hydroxide) which is then floated (*10*). Preliminary results on the flotation of trivalent arsenic have been published (*11*). In this case the aid of a surfactant, sodium oleate, was required.

Finally, flotation in effluent treatment is a S/L or L/L separation process, usually aimed at total or collective removal of pollutants, while froth flotation is applied in minerals processing for selective separation. The scope of this paper is to investigate the possibility of selective flotation and recycle of heavy metals from synthesized wastewaters.

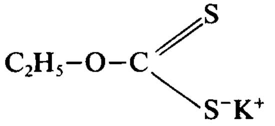
EXPERIMENTAL

A multiple dissolved-air flotation unit, manufactured by Aztec Environmental Control Ltd., was used in the batchwise experiments. It had four identical and transparent jars; these were cylindrical (9.3 cm diameter) and calibrated, and had no baffles. Synthetic mixtures (1 L) were mixed at a preset speed with a flat blade impeller (6 cm length, 2 cm width), stirred at a height of approximately 2 cm from the bottom.

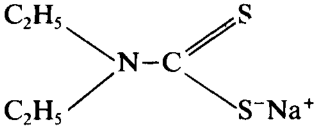
Water saturated with air under a pressure of 400–500 kN/m^2 in a large saturator was introduced to the base of each jar via a nozzle arrangement, specifically designed. With the pressure reduction, fine air bubbles of less than 120 μm were released. A 10% recycle was applied (i.e., an additional volume of 100 cm^3). Stirring was slowed down during flotation.

The pH of the solution was adjusted by nitric acid or sodium hydroxide solutions (both Merck, pro analysi), and the pH value, recorded in the jar tests, was that of precipitation, while the pH was increased after reagent addition. Solution samples were taken from a side sampling outlet for chemical analysis. Copper and zinc were analyzed by atomic absorption in the normal way with a Pye-Unicam Model 192 AA spectrophotometer. Arsenic was analyzed by the molybdenum blue method at 840 nm (*12*).

The reagents used were copper nitrate, $Cu(NO_3)_2 \cdot 3H_2O$; zinc nitrate, $Zn(NO_3)_2 \cdot 4H_2O$; and disodium hydrogen arsenate, $Na_2HAsO_4 \cdot 7H_2O$ (all Merck, pro analysi). Ferric sulfate, $Fe_2(SO_4)_3$ (BDH, technical), potassium *O*-ethyl-dithiocarbonate (denoted hereafter as KEtX) (Merck, for synthesis), and the sodium salt of diethyl-dithiocarbamate (with 3 mol H_2O) (Merck, pro analysi) were used as flotation collectors. The chemical formulas of these two thio reagents are



KEtX



(Diethyl) DTC

The xanthate was analyzed by UV at 301 nm in the normal manner (*13*). The floatability of each system was investigated separately and in mixtures of the heavy metal ions studied.

RESULTS AND DISCUSSION

Flotation from Solutions

The chemical and physical properties of thio reagents were reviewed (*2*). It is known that the reaction of certain dissolved metal ions, such as Cu^{2+}, with xanthate anions (homogeneously, heterogeneously, or electrocatalytically) gives an unstable complex which decomposes to produce dixanthogen and cuprous xanthate; both precipitate out of solution as an agglomerate.

$$4(EtX^-) + 2Cu^{2+} \rightarrow 2Cu(EtX)_2 \rightarrow 2CuEtX + (EtX)_2$$

The particle size of the precipitate obtained when KEtX is added to cupric salt solutions depends on the concentration of reagents (*6*). Since the size of a precipitate is an effective parameter in flotation, affected by pretreatment conditions, the rate of preliminary mixing of a solution containing 50 ppm copper ions and an almost equivalent, stoichiometric amount of KEtX at double the copper concentration, was initially examined for two periods of 300 and 600 s at a pH of approximately 3.0, followed by dissolved-air flotation. The results are shown in Fig. 1, where near 90% flotation recovery of copper ions was obtained at 400 rpm initial mixing for 600 s. The pH did not affect the process from a value of 2.5 to about 5.5, as presented in Fig. 2. The use of a 10% excess of xanthate appreciably improved the flotation results (>95%), as shown.

A xanthate analysis was also carried out for the remaining solution. No xanthate was found. The remaining copper in solution under optimum operating conditions was under 1 ppm, i.e., an acceptable level (as also found later for Zn and As).

The flotation time was of the order of 30 s. This constitutes a significant advantage for flotation against sedimentation; for instance, sulfides or hydroxides usually need a retention time of several hours. Therefore, a smaller treatment unit is needed, with a corresponding area economy. Also, by-products recovery may be a profitable contribution toward

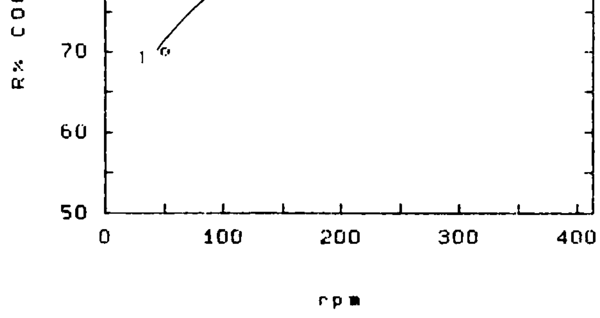


FIG. 1. Effect of mixing speed (in rpm) on copper flotation recovery (R) by xanthate at mixing times of (1) 300 s and (2) 600 s. Initially, [Cu^{2+}] = 50 ppm, pH = 3.0 ± 0.1, KEtX = 1.0 equivalent of Cu^{2+}.

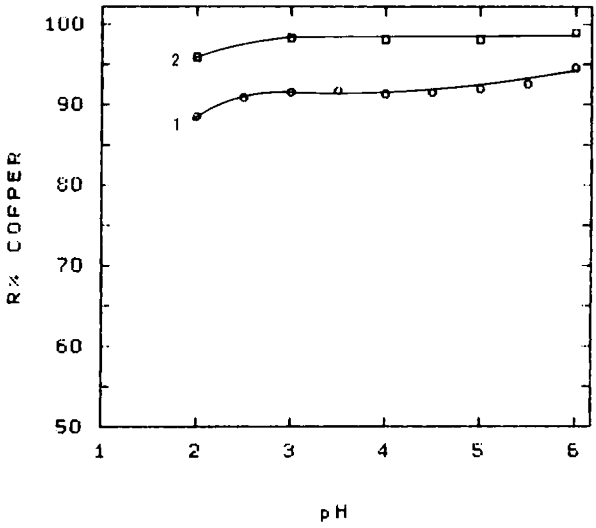


FIG. 2. Effect of pH on copper ion flotation at KEtX concentrations of (1) 1.0 equivalent of Cu^{2+} and (2) 10% excess; t_M = 600 s at 400 rpm.

the generally higher operating costs of flotation in comparison with sedimentation.

Dithiocarbamates have been applied in analytical chemistry for precipitation of metals as highly insoluble complexes (*2*). This was the reason for their selection for zinc ion flotation removal, at a pH of approximately 5.0, from an initial solution of 50 ppm zinc concentration. The results are shown in Fig. 3 for various preliminary mixing rates employing two mixing periods; an equivalent stoichiometric concentration of diethyl DTC was tried at a ratio of 2:1 and the recovery was over 95%. The rest optimum conditions were similar to the aforementioned case of copper (400 rpm for 600 s during precipitation). The pH, which ranged from approximately 3.5 to 5.7, was found to be effective, as shown in Fig. 4. IR and UV spectra of dialkyl DTC were examined with particular attention to flotation applications (*3*).

Diethyl DTC was likewise examined as a flotation collector for copper ions. Promising results were also obtained by preliminary pretreatment at 400 rpm mixing for 300 s. The influence of the pH of the solution on the process is presented in Fig. 5. Flotation recoveries of over 99% were found by adding a 10% excess of the stoichiometric amount.

The two processes examined were copper and zinc ion removal by the mechanism of ion flotation. Both of them can operate in acidic medium,

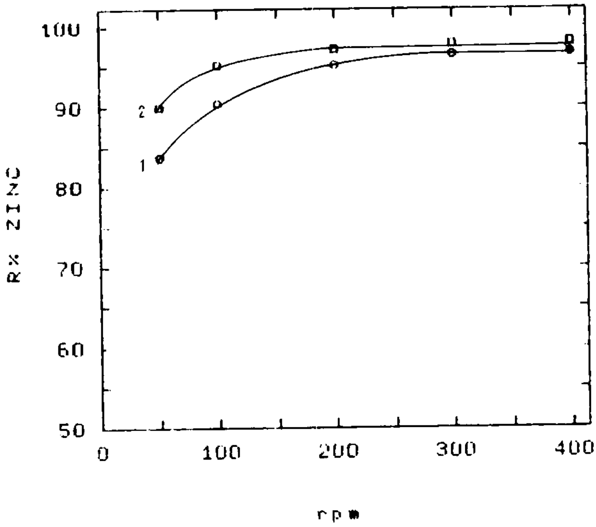


FIG. 3. Effect of mixing speed on zinc flotation by dithiocarbamate at pH = 5.0 ± 0.1: (1) 300 s and (2) 600 s; initially, [Zn^{2+}] = 50 ppm, DTC = 1.0 equivalent of Zn^{2+}.

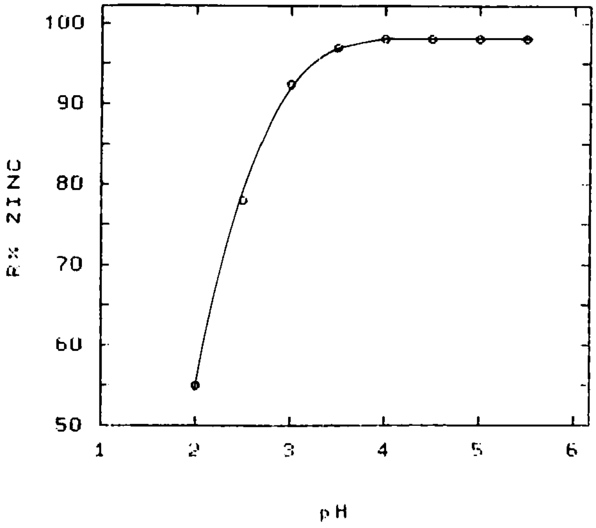


FIG. 4. Effect of pH on zinc ion flotation (of 50 ppm initially); t_M = 600 s at 400 rpm.

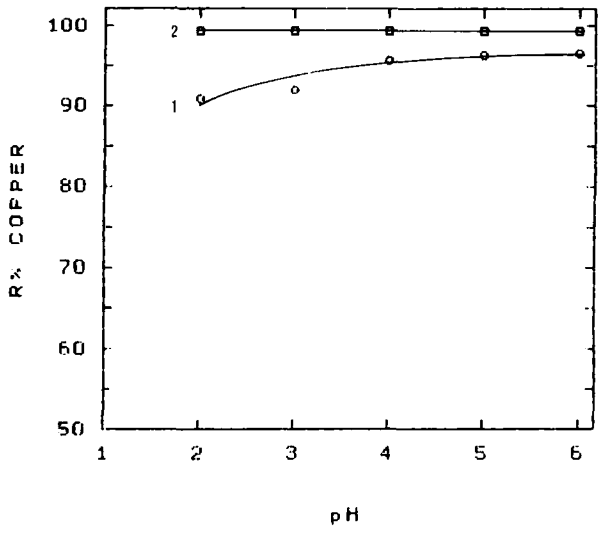


FIG. 5. Effect of pH on copper ion flotation (of 50 ppm initially) by DTC: (1) 1.0 equivalent of Cu^{2+}, (2) 10% excess; t_M = 300 s at 400 rpm.

which industrial wastes containing heavy metals usually are. The use of basic solutions for pH adjustment is therefore avoided (for example, for the precipitation as hydroxides). Also, the application of sulfides in any form for precipitation would bring undesirable pollution problems (mainly due to odors), leading to a collective coprecipitation of both ions in this pH region.

Adsorbing colloid flotation for arsenic removal was the second separation method investigated. The technique does not involve a stoichiometric reaction of the collector with the substance being transferred to the foam layer. It is known that ferric sulfate in aqueous solutions above pH values of about 2.5 hydrolyzes to produce ferric hydroxo-complexes which are positively charged at pHs lower than approximately 9.0, depending on the solution conditions (*11*). This method was expected to remove other heavy metals also (Cu^{2+}, Zn^{2+}, etc.) if applied in a mixture, as reported elsewhere (*14*).

The chemical forms of arsenic in water and its removal by adsorption were previously published (*15*). Figure 6 shows the results of this series of experiments at a pH of about 5.0, with initial solutions containing 10, 50, and 100 ppm pentavalent arsenic. Iron is insoluble at this pH. Satisfactory results were found for arsenic recovery by 400 rpm initial mixing

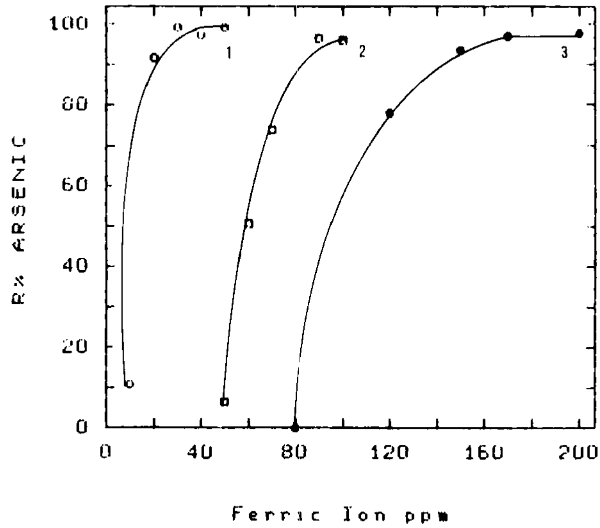


FIG. 6. Adsorbing colloid flotation of arsenic ions by ferric hydroxo complexes. Initially, (1) 10, (2) 50, and (3) 100 ppm [As^{5+}]. pH = 5.0 ± 0.1, t_M = 600 s at 400 rpm.

for 600 s, followed by dissolved-air flotation. The corresponding concentrations of Fe^{3+} required for separation are also shown in Fig. 6. As the arsenic content in solution increased, the ratio of ferric ions needed (as hydroxo-complexes) decreased from 3 to 1.5. In this case a surfactant was not necessary for flotation because the flocs were easily removed.

Adsorbing colloid flotation is successful for the simultaneous removal of germanium and arsenic (*16*). This ability to separate and concentrate from dilute aqueous solutions is one of the interesting advantages of flotation, with possible applications in the fields of waste treatment and even analytical chemistry. Flotation presents a means of reclaiming metals of value from effluent streams.

Heavy Metals Mixtures

The basic parameters affecting ion flotation are surfactant concentration, gas flow rate, bubble size, temperature, solution pH, ionic strength, and feed concentration. The applications and potential of the process have been discussed (*9*). Ion flotation was originally introduced by Sebba. According to Pinfold, the type of process applied here for copper and zinc could also be termed precipitate flotation of the "third kind," where the precipitate formed contains the surfactant or collector as a chemical constituent and float, i.e., the process is a form of ion flotation (*7*).

However, precipitate flotation is better than ion flotation, generally, because it does not need a great amount of surfactant (stoichiometric) and of other chemical reagents (as activators, complex agents, etc.) for separation. For example, the precipitate flotation of zinc ions as hydroxide, in the concentration range 10–500 ppm, was successful with an ethanolic solution of only 8×10^{-6} *M* laurylamine; gas bubbles were generated by dispersed air.

Ion flotation has the remarkable advantage, in contrast to other flotation techniques such as precipitate and adsorbing colloid flotation, of being a selective method if the proper experimental conditions are selected. It was found successful in separating germanium from arsenic ions in dilute solutions by the addition of pyrogallol as activator and laurylamine as surfactant and following a stoichiometric mechanism (*16*).

Moving to artificial mixtures of the same system, a copper–zinc solution of 500 ppm each was studied by the addition of xanthate in a pH range of 2.0–6.0. The dissolved-air flotation results are shown in Fig. 7. The use of 10% excess of KEtX (of the stoichiometric amount) produced better recoveries. It was observed that zinc remained in solution almost quantitatively. This can be explained by the solubility products of ethyl xanthate, which are 4.9×10^{-9} for zinc and only 5.2×10^{-20} for copper, according to Kakovsky (*3*). In this way, copper was selectively precipitated and then floated by fine bubbles. The initial precipitation conditions in the mixing tank, 400 rpm for 600 s, were selected in order to produce the appropriate floc size for flotation, with the latter applied as an indirect control measure.

It is noted that, according to Poling, the solubility data for heavy metal alkyl xanthates correlate with the covalent character of the metal–S bonds and with the infrared band positions for each metal xanthate (*2*). The nature of the metal appears to be more significant than the length of the hydrocarbon chain in determining their aqueous solubilities and polar/nonpolar character (for instance, the solubility product is 4.7×10^{-21} for copper butyl xanthate and 8.8×10^{-24} for the octyl).

A binary mixture of copper and arsenic ions was then floated by KEtX, keeping the same preliminary mixing conditions. The results are presented in Fig. 8, again showing a selective separation of copper in the foam layer. What is noticeable in these tests is a slight recovery reduction

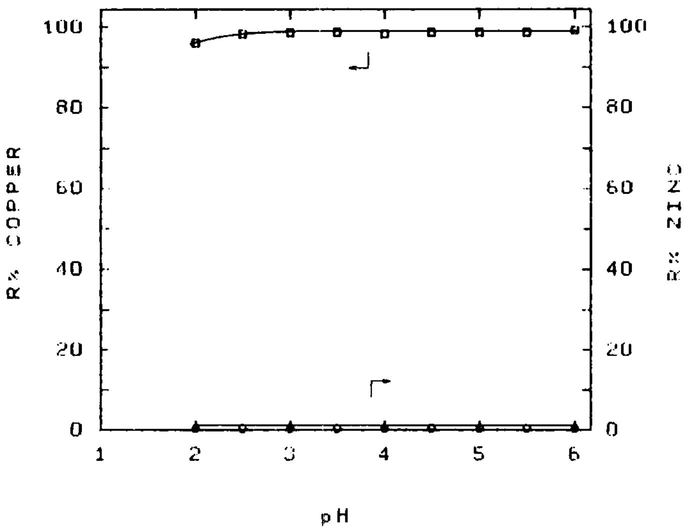


FIG. 7. Selective flotation of copper from zinc ions, both at 50 ppm initially, by KEtX at various pH solution values. KEtX = 1.10 equivalents of Cu^{2+} (initial mixing at 400 rpm for 600 s).

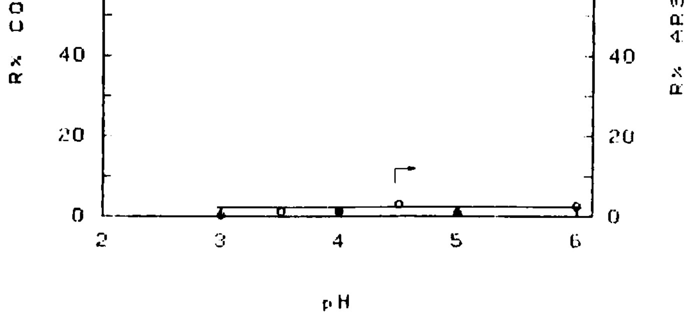


FIG. 8. Selective flotation of copper from arsenic ions by KEtX at a 10% excess of stoichiometric; concentrations of copper and arsenic, 50 ppm initially.

of copper obtained at pH values over approximately 5.0. This can be attributed to a possible reaction of copper cations with arsenic ions due to the increased presence of the $H_2AsO_4^-$ species caused by the increase in pH of the solution.

The ternary system of Cu/Zn/As ions was also examined, and the flotation recoveries by KEtX are shown in Fig. 9. Promising results were found for the selective sepration of copper ions in the pH range of approximately 2.0–4.7. At higher pH values a more pronounced coflotation of all the heavy metal ions was observed, particularly at pH 6.0, the highest value studied. In this case, in the chemical reaction with the anionic arsenic species, the zinc ions in solution also participated.

After the flotation of copper from the mixture, the selective separation of zinc ion by precipitation with dithiocarbamate and dissolved-air flotation was used as the second stage. Figure 10 shows the results obtained by processing a mixture of zinc and arsenic ions. Selective removal of zinc in the foam layer occurred, with recoveries over 95% in the pH range of 3.5–6.0. DTC acts as an anionic collector, so it was not expected to float arsenic under these conditions. Finally, as the third separation stage for pentavalent arsenic, an adsorbing colloid flotation

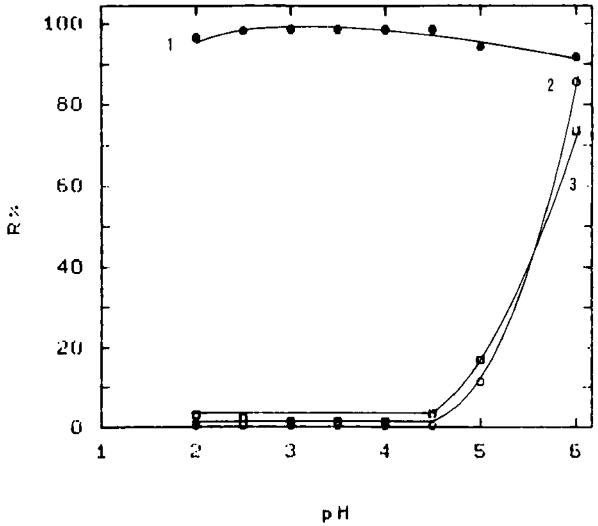


FIG. 9. Selective flotation of copper ions from zinc and arsenic by KEtX (10% excess, all ions 50 ppm initially): (1) Cu^{2+}, (2) Zn^{2+}, (3) As^{5+}.

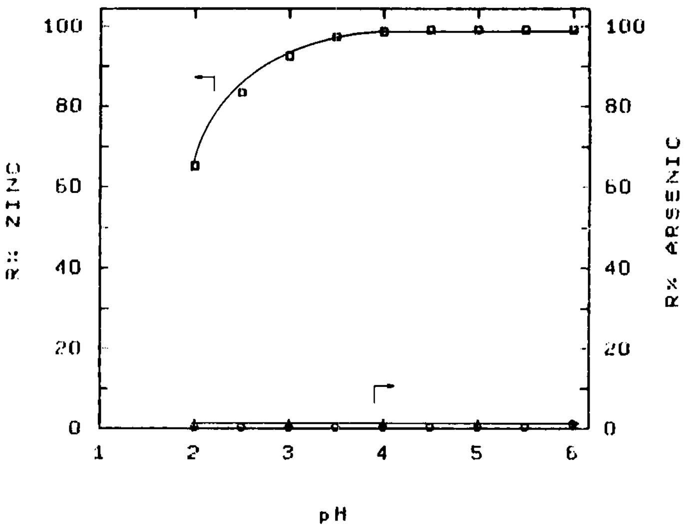


FIG. 10. Selective flotation of zinc ions from arsenic by stoichiometric DTC (50 ppm).

only by ferric hydroxo-complexes is proposed; in this case also, the bubbles were generated by dissolved air (Fig. 6).

The thio collectors used in the present work offer the further advantage that the collector and frother actions can be controlled independently (*2*). They do not adsorb actively at the air/liquid interface due mainly to their short hydrocarbon chains and to the high aqueous solubilities of their anionic forms. Lack of significant chain association also explains the inability of dissolved thio anions to form colloidal micelles that could be detrimental to flotation.

CONCLUSIONS

A selective separation was accomplished in a synthesized solution of Cu, Zn, and As ions, with recoveries over 95%. Ion flotation of copper by potassium ethyl-xanthate (in 10% excess of the stoichiometric amount and at pH 3.0–5.0) was carried out, followed by ion flotation of zinc by a stoichiometric amount of diethyl-dithiocarbamate at the same pH. In both cases an initial precipitation before flotation was conducted for 600 s at 400 rpm stirring. Arsenic was removed by adsorbing colloid flotation on hydrolyzed ferric sulfate at pH 5.0 (with greater additions of iron in relation to arsenic), but without any other anionic surfactant, i.e., sodium oleate. Air bubbles, the working tool of flotation, were generated by dissolved-air flotation, which produces fine bubbles. The technique proved effective for selective separation.

REFERENCES

1. K. A. Matis and G. P. Gallios, in *Mineral Processing at a Crossroads* (B. A. Wills and R. W. Barley, eds.), Martinus Nijhoff, Dordrecht, 1986, p. 37.

2. G. W. Poling, in *Flotation—A. M. Gaudin Memorial Volume* (M. C. Fuerstenau, ed.), SME/AIME, New York, 1976, p. 334.

3. J. Leja, *Surface Chemistry of Froth Flotation,* Plenum, New York, 1982, p. 228.

4. N. A. Mumallah and D. J. Wilson, *Sep. Sci. Technol., 16,* 213 (1981).

5. T. Nagahama, *CIM Bull.,* p. 79 (April 1974).

6. G. Sparrow, A. Pomianowski, and J. Leja, *Sep. Sci., 12,* 87 (1977).

7. A. I. Zoumboulis, K. A. Matis, and P. K. Spathis, *Tech. Chron., C7,* 5 (1987) (in Greek, with extended English summary).

8. G. A. Stalidis, K. A. Matis, and N. K. Lazaridis, *Int. J. Miner. Process.,* To Be Published.

9. A. I. Zoumboulis and K. A. Matis, *Chemosphere, 16,* 623 (1987).

10. A. N. Clarke and D. J. Wilson, *Foam Flotation,* Dekker, New York, 1983.

11. G. A. Stalidis, K. A. Matis, and A. I. Zoumboulis, *Chim. Chron. [N.S.], 15,* 133 (1986).

12. ASTM, *Chemical Analysis of Metals and Metal Bearing Ores,* Part 12, Philadelphia, 1982, p. 326.

13. M. H. Jones and J. T. Woodcock, *Ultraviolet Spectrometry of Flotation Reagents with Special Reference to the Determination of Xanthate in Flotation Liquors,* IMM, London, 1973, 25 pp.

14. S. Mukai, T. Wakamatsu and Y. Nakahire, *Recent Dev. Sep. Sci., 5,* 67 (1979).

15. J. F. Ferguson and M. A. Anderson, in *Chemistry of Water Supply Treatment and Distribution* (A. J. Rubin, ed.), Ann Arbor Science, Ann Arbor, Michigan, 1974, p. 137.

16. K. A. Matis, I. N. Papadoyannis and A. I. Zoumboulis, *Int. J. Miner. Process., 21,* 83 (1987).

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