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Adsorbing Flotation of Copper Hydroxo Precipitates by Pyrite Fines

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Abstract

The removal of copper ions from dilute aqueous solutions by the addition of mineral (pyrite) fine particles was undertaken by following an adsorbing (scavenging) flotation mechanism. Pyrite generally constitutes a residual or a solid industrial waste by-product in mixed sulfides processing plants. This paper suggests a further utilization for pyrite. The dissolved-air method was applied for solid/liquid separation when the mineral particles were in the fine (subsieve) size range. Various unconventional collectors for pyrite flotation were also examined.

INTRODUCTION

Copper is a common toxic metal encountered in many dilute leach solutions, spent process streams, and liquid effluents in industry (*1*). Different separation methods have already been studied for copper ion removal, and various flotation techniques among them were recently reviewed (*2*). Other articles involve copper ion and precipitate flotation, the former as copper xanthate and the latter as sulfide (*3*, *4*); another alternative technique is adsorbing colloid flotation (*5*).

A possible utilization of an industrial by-product, such as iron sulfide pyrite, may be as an adsorbent/solid substrate material. A further aim of this paper is the transfer of mineral processing know-how to environmental technology (and vice versa). It is also worth pointing out that a classical example of froth flotation application is the beneficiation of sulfide minerals (*6*).

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Mineral Processing

Pyrite is associated with most sulfide ores and with coal. It is separated from them by flotation, usually during the last beneficiation stage. According to present practice, pyrite concentrates are stockpiled in the mine area, perhaps creating a pollution hazard unless they contain uranium or gold, in which case they are generally recovered by applying posttreatment processes. In this direction, a flotation process has been investigated for the selective separation of auriferous arsenopyrite by modifiers (*7*).

The chemistry of pyrite flotation is rather well known; see Reference *8*. Common collectors for pyrite are the thio reagents such as xanthates, dithiophosphates, dithiocarbamates, etc.

On the other hand, the problem of mineral fines in flotation processing has been emphasized (*9*). Ideally, fine mineral particles should be produced only for the purpose for the liberation of valuable materials (like lead, zinc and copper sulfides) from gangue minerals (as calcite, quartz, etc.). However, the fine size ranges are suitable for processes like adsorption, where the increased surface area generally improves the process efficiency. The removal of fatty acids from wastewaters after adsorption on fines (magnesite and dolomite) has already been reported (*10*). The removal of mercury from wastewaters by applying iron sulfide minerals has also been studied (*11*).

EXPERIMENTAL

Pyrite (FeS_2) of about 95% purity and containing some silicates and calcite came from Stratoni, Chalkidiki (Greece). The samples were hand-collected, crushed, and pulverized in the laboratory. The −45-μm size range was taken by wet sieving and used in the experiments as a 0.5 g/L concentration dispersion in pyrite, unless otherwise stated. Cu(II) (50 mg/L) was the solution under investigation; copper was added as the hydrous sulfate salt.

The ionic equilibria diagram constructed by means of a specific computer program is presented as Fig. 1 (*12*). A total copper concentration of 0.8 m*M* (equal to about 50 mg/L) was considered. For the construction of this diagram, thermodynamic equilibrium data from the literature were used (*13*).

The laboratory flotation experiments were carried out in a dissolved-air flotation (DAF) apparatus, described elsewhere (*3*). Sodium dodecyl sulfate (SDS) and cetyl trimethyl-ammonium bromide (CTMA-Br) were tried, i.e., an anionic and a cationic, respectively, as surfactants (when used). Copper adsorption and surfactant conditioning were 600 s each at a stirring speed of 200 rpm, while the pH was continuously controlled during ad-

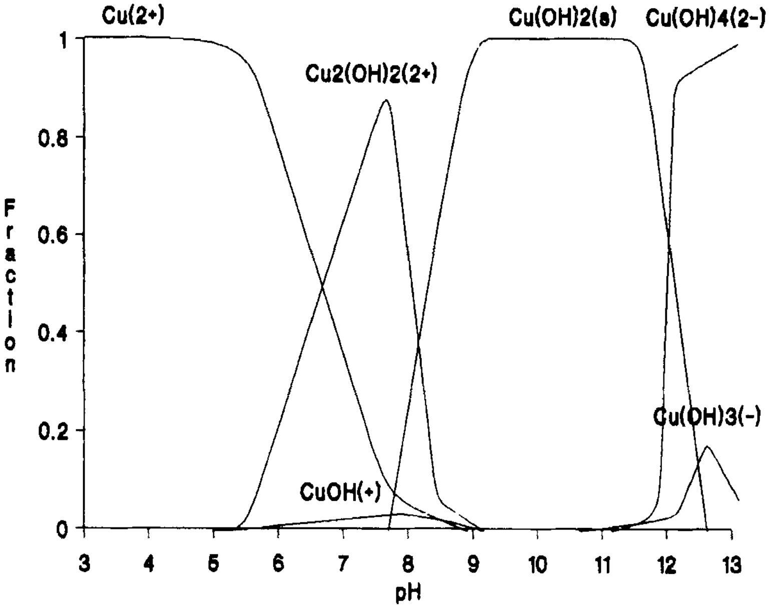

FIG. 1. Copper ionic equilibria diagram for an initial concentration of 0.8 m*M*.

sorption. Sulfuric acid and sodium hydroxide solutions were used for pH modification (lime is known to depress pyrite flotation), and deionized water was used in most experiments, unless otherwise stated.

After the adsorption step, both filtration and centrifugation were tried as solid/liquid separation methods, and both gave similar results (Fig. 2). The recovered solid containing the adsorbed copper was used in a similar way for the desorption experiments, and its stability was examined in the full pH range. Copper analysis was undertaken using AAS (Perkin-Elmer model 2380), and copper removals have been calculated as usual.

The electrokinetic investigation of purite suspensions was carried out by using a microelectrophoretic apparatus (Rank Brothers, Mark II) and applying the flat cell. The measured electophoretic mobilities were converted to ζ-potential by means of the Smoluchowski equation.

Preliminary results have already been presented, but by using a xanthate salt as a collector during dissolved-air flotation, the size distribution of copper precipitates with solution pH was also examined (*14*). It has been suggested that by creating fine gas bubbles, such flotation techniques are suitable for fines flotation (*9*).

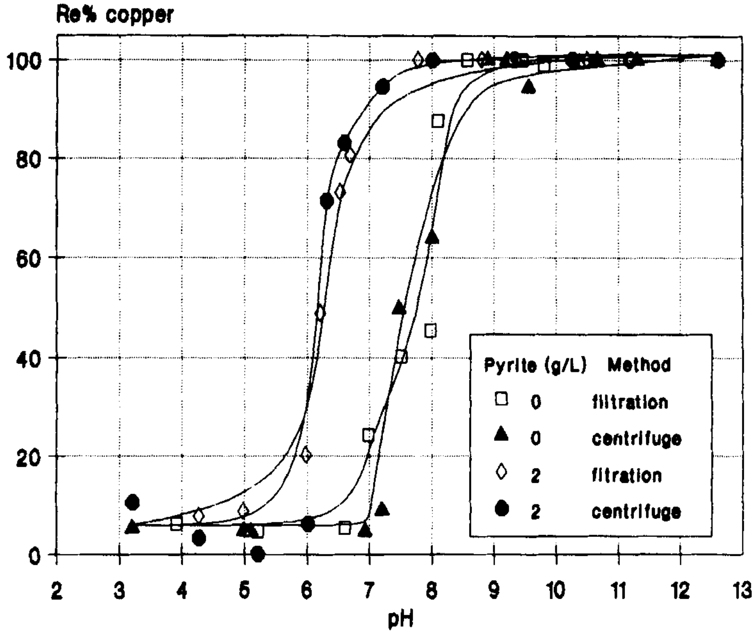

FIG. 2. Influence of solution pH on copper removal by pyrite fines; comparison of filtration and centifugation.

RESULTS AND DISCUSSION

Dissolved copper is a common component in sulfide mineral slurries. One of the most important characteristics of sulfide minerals is their instability in atmospheric conditions; they are slowly transformed into stable oxidized minerals (e.g., $PbSO_4$, $ZnSO_4$, etc.) (*15*). Considerable changes on the particle surface occur during this oxidation, which is represented for a sulfide, denoted as MeS, by the simple reaction

$$MeS \longrightarrow Me^{2+} + S + 2e^-$$

In this way, copper ions always exist in solution with ground copper ores (as chalcocite, covellite, chalcopyrite, bornite), and hence, in the circulating water in mixed sulfides flotation plants (*16*). It has also been reported that copper sulfate is added to the pulp of many South African pyrite flotation plants (*17*). It should be also noted that copper sulfate is the unique activator added for sphalerite flotation in beneficiation plants. Its action was explained by chemisorption, and the following equation was proposed (*18*):

$$ZnS(s) + Cu^{2+}(aq) = CuS(s) + Zn^{2+}(aq), \qquad K = 9 \times 10^{10}$$

So, considerable interactions between copper ion and sulfide surfaces were expected. Another incentive came from the so-called carrier flotation (ultraflotation or "piggyback" flotation), which uses an auxiliary mineral (for instance, calcite) for the flotation of fine particles; in this way, anatase was separated from kaolin (*19*).

Adsorption Studies

Among a number of theories that have been proposed in order to explain the role of copper sulfate in pyrite flotation, the most possible suggests that copper ions are adsorbed onto pyrite, thus modifying the surface of its particles (*17*).

Pyrite fines were applied in the present work as adsorbents (scavengers) for the removal of copper from solutions. The effect of copper concentration (up to 500 mg/L) was initially examined at pH 8, and it showed no significance; adsorption removal of copper on pyrite in the whole range was of the order of 100%. Copper is expected to be hydrolyzed completely in alkaline pH values, about 8.5. The influence of the solution pH on copper adsorption/removal in the presence (or not) of pyrite is also studied in Fig. 2. It was observed that the addition of 2 g/L pyrite to the system shifted the removal curves to approximately pH 6.5 where copper hydrolysis is in its very early stages (Fig. 1).

The effect of added pyrite concentration in the full pH range is presented in Fig. 3. The results obtained, i.e., increasing the pyrite concentration leads to a shift of the adsorption curves to lower pH values, are an indication of interfacial precipitation of the metal hydroxide which may occur at a pH lower than that required for precipitation in the absence of pyrite. The adsorption of some divalent cations (Ca, Mn, etc., but not Cu) onto the pyrite surface has also been reported; it has been suggested that a surface-induced hydrolysis reaction mechanism (i.e., the interfacial precipitation), which was also observed in our results, is the most realistic possibility for these systems (*20*).

The electrokinetic investigation favors this point of view. The ζ-potential of pyrite in dilute suspensions (0.1 g/L) as a function of pH in the presence of increasing amounts of copper ions is shown in Fig. 4. A reversal of ζ-potential can be observed around the neutral and slightly alkaline pH range.

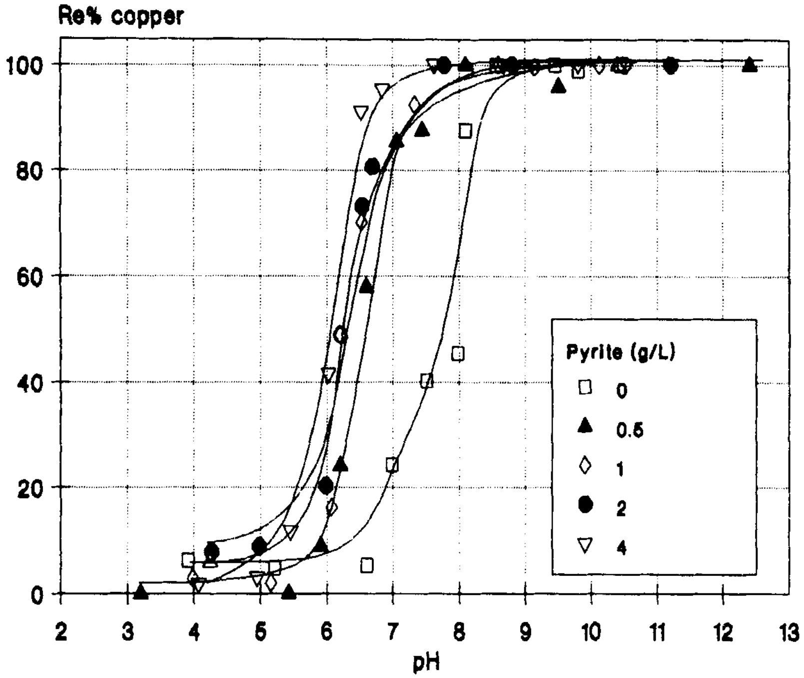

FIG. 3. Effect of pyrite concentration on copper removal ([Cu]: 50 mg/L); pH influence.

Similar reversals in the ζ-potential of sphalerite and quartz in the presence of copper have already been reported and discussed (*21*). It seems that this reversal is due to pyrite surface coverage by hydrolyzed copper cationic species (see also Fig. 1).

According to a detailed analysis by Hunder in relation to the interfacial precipitation model (*22*), the point of ζ-potential reversal (pzr) at pH 2.5 is actually the zero point charge (zpc) of the underlying mineral (i.e., pyrite), while the pzr at pH 6–7 corresponds to the surface precipitation of the copper hydroxide. Depending on the ion concentration in the solution, this layer may be incomplete, and the more complete it is, the earlier pzr occurs and the more positive becomes the pyrite surface. The final reversal (around pH 8.2) is shifted at higher pH values (by increasing the ion concentration), having as a limit the zpc of the bulk metallic hydroxide. The zpc of copper hydroxide was reported to be 7.6 and 9.4 after precipitation from chloride and nitrate media, respectively (*23*).

A series of experiments using tap water of relatively high hardness (equivalent to around 260 mg/L $CaCO_3$), shown as Fig. 5, gave no appre-

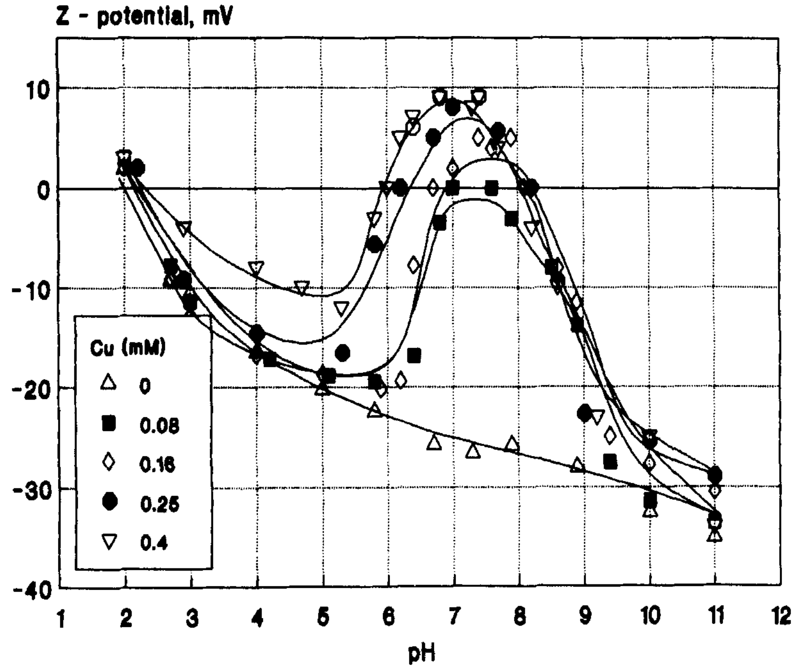

FIG. 4. Zeta potential measurements of pyrite in the presence of copper ions.

ciable difference, showing that this process could be carried out in hard water.

The irreversibility of the adsorption process was also checked (Fig. 6). The desorption of copper from the pyrite surface seems possible in the acidic pH region where copper is redissolved. However, over pH 7, the system copper/pyrite is quite stable. This phenomenon may permit its safe disposal in alkaline (e.g., dolomitic) soils. In conclusion, copper did adsorb specifically onto pyrite surface.

Flotation Studies

After the adsorption of copper ions, the separation was accomplished by flotation, following what might be termed as an adsorbing flotation technique; the dissolved-air method for bubble generation was applied.

The first problem to be solved was the removal of the added pyrite particles (as the copper carrier) by the process. Figure 7 presents the results when two different flotation surfactants were tried at pH 8. It is apparent that addition of a cationic surfactant does not favor the separation of the

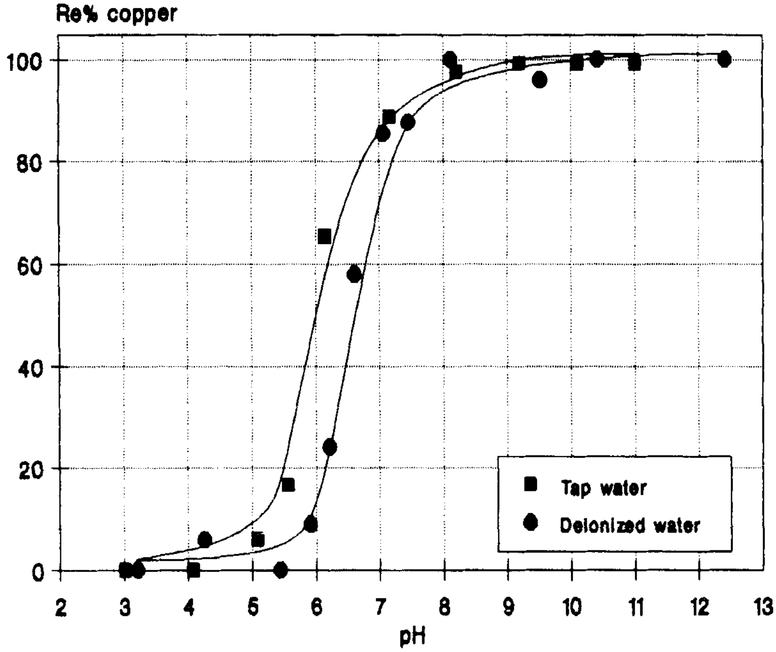

FIG. 5. Effect of water hardness on copper removal; comparison between tap and deionized water.

copper/pyrite system. This fact coincides with the ζ-potential results because pyrite was slightly positively charged at pH 8.

The effect of solution pH on pyrite removals loaded with copper is presented as Fig. 8. It is interesting that a collectorless process can effectively separate the pyrite. Another observation of these experimental series was the role of fines in stabilizing the froth layer, thus assisting copper removals. Collectorless flotation in the processing of complex sulfide ores has already been reported (*24*).

On the other hand, Fig. 9 presents the results of copper removal when CTMA-Br is applied. The flotation curves in the presence and absence of pyrite in the process are similar to the adsorption curves; pyrite slightly improves the maximum copper removal by around 10%, and the maximum removal is also shifted to more acidic pH values.

The influence of surfactant concentration at pH 9 is given in Fig. 10. The addition of 10 mg/L CTMA-Br gives similar results for copper removal with and without pyrite. In contrast to xanthates, both present surfactants are not expected to form special compounds with copper precipitates. The

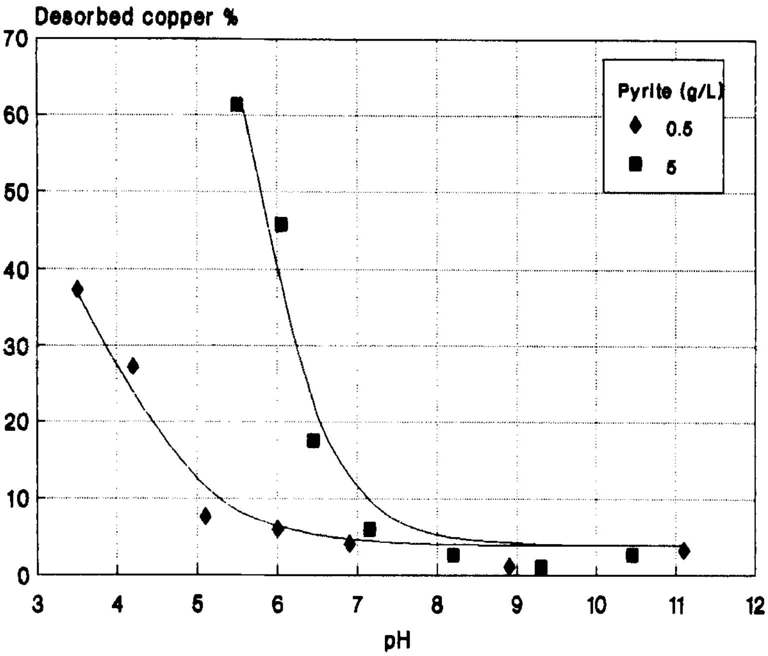

FIG. 6. Desorption of copper from pyrite; pH influence.

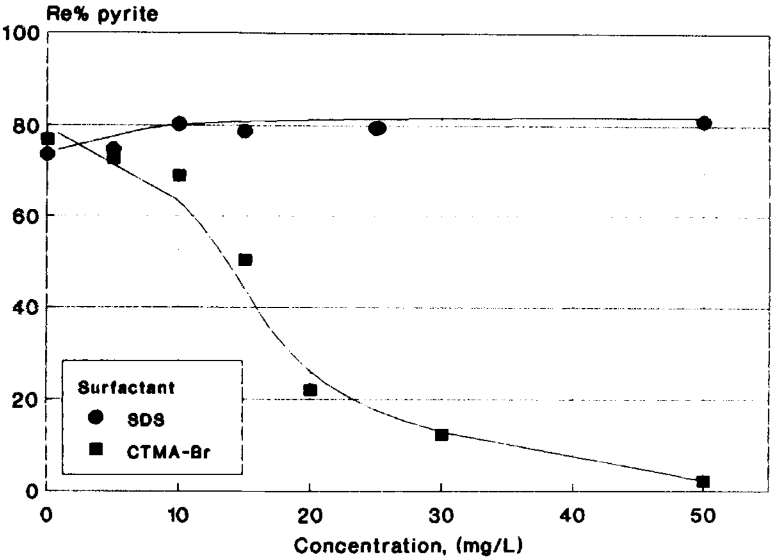

FIG. 7. DAF pyrite flotation after adsorption of 50 mg/L copper; effect of different surfactant concentrations (SDS and CTMA-Br).

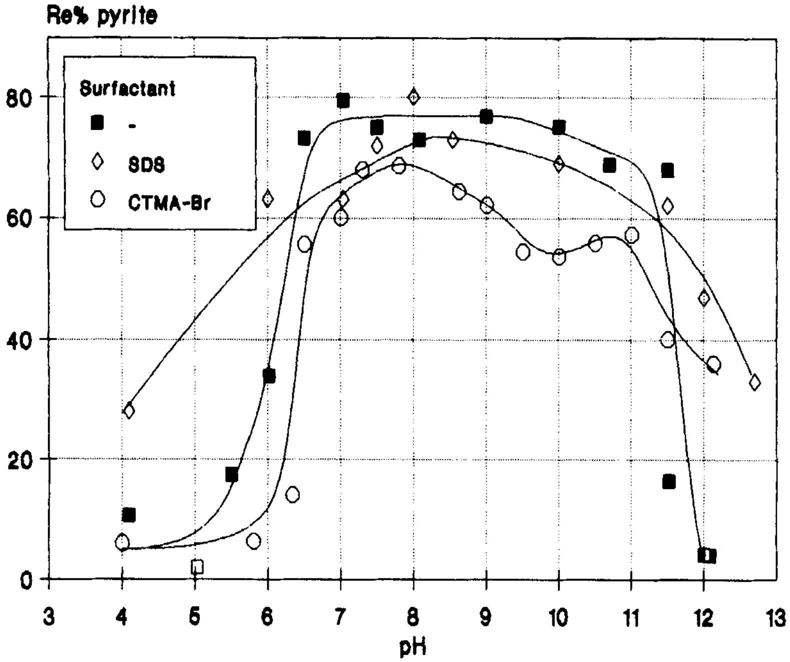

FIG. 8. Effect of pH on pyrite flotation in the presence (10 mg/L) and absence of surfactants.

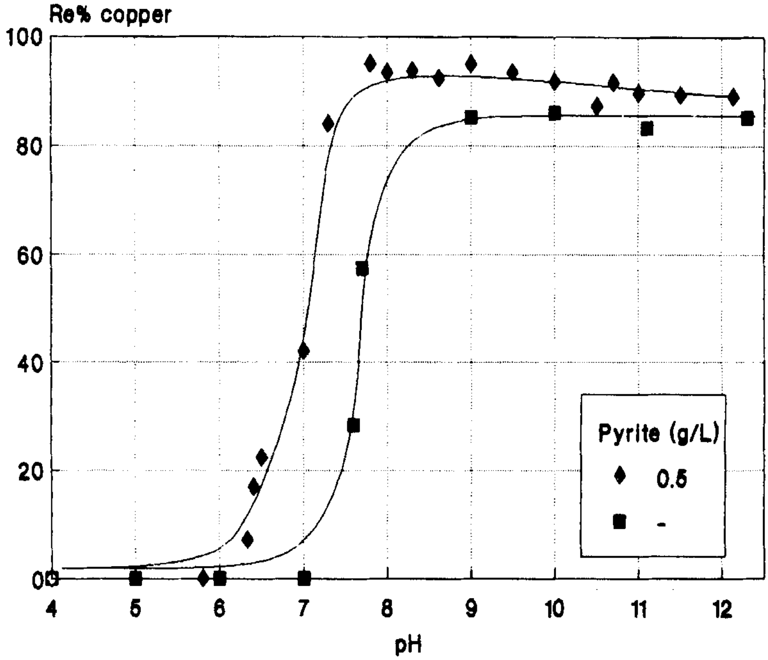

FIG. 9. DAF copper removal by CTMA-Br (10 mg/L); pH influence.

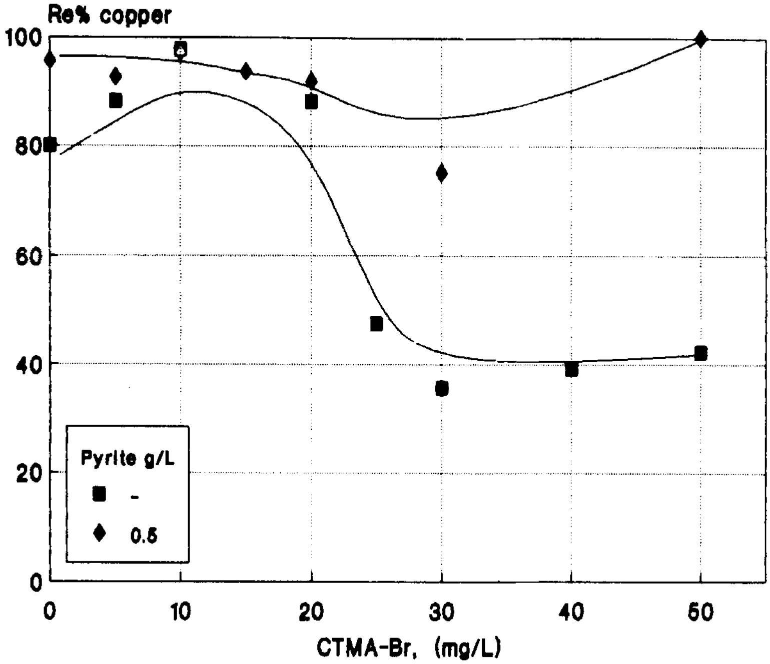

FIG. 10. Varying CTMA-Br concentration in copper flotation (pH 9).

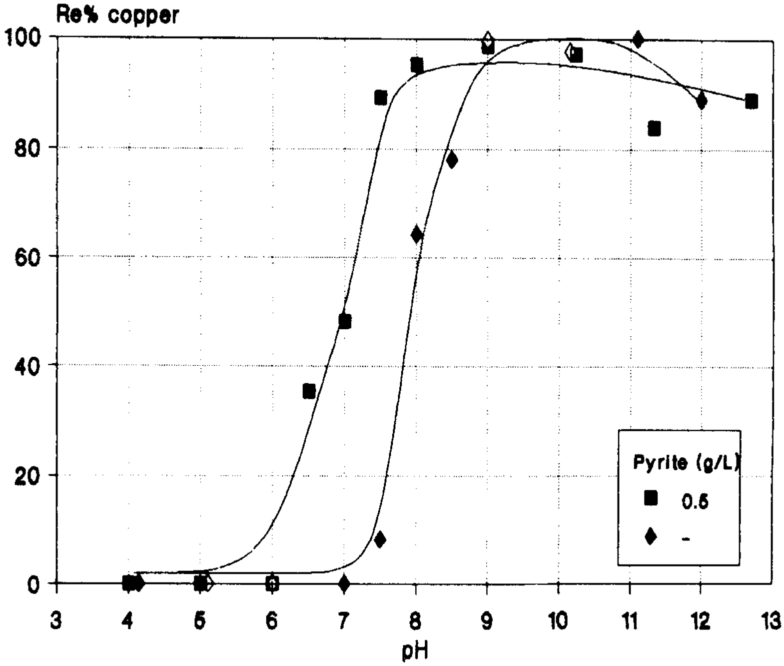

FIG. 11. Influence of pH on copper flotation by SDS (10 mg/L).

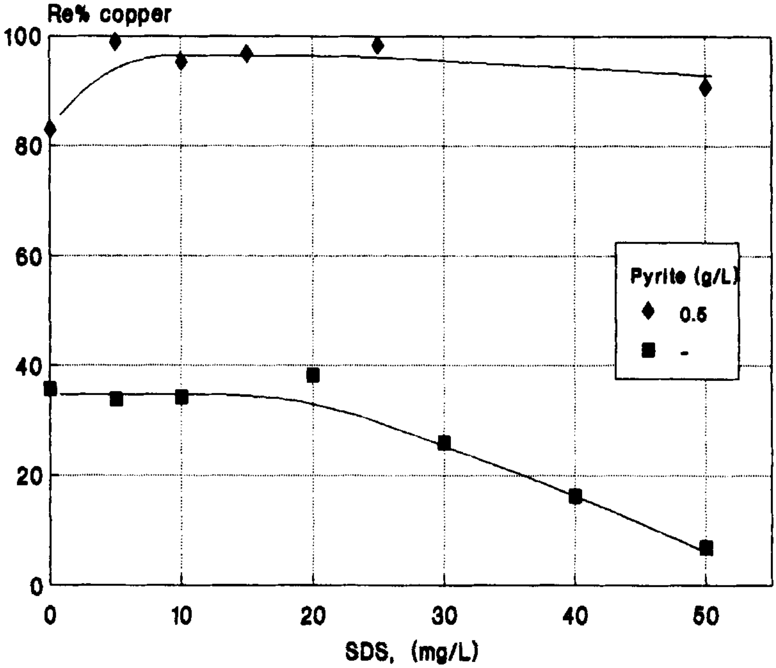

FIG. 12. Varying SDS concentration in copper flotation (pH 8).

reaction of dissolved copper ions with xanthate anions is known to give dixanthogen and cuprous xanthate precipitates (*3*).

The pH influence on the results for copper removal when applying SDS are shown in Fig. 11. They are similar to these observed when CTMA-Br was used (Fig. 8). The effect of varying surfactant concentrations at pH 8 is presented in Fig. 12; this time it lies on the boundary area. The presence of pyrite is crucial; it increases copper removal by about 50%. The addition of 10 mg/L SDS also improved the results for copper, reaching almost complete separation.

In conclusion, the adsorbing flotation technique for copper removal of copper on pyrite mineral fines is an effective process. The system may be generally promising for the separation of toxic metals from solutions by the application of a suitable industrial by-product (flotation concentrate or even a solid waste).

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