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K. A. Kydros[a]; G. P. Gallios[a]; K. A. Matis[a]
[a] LABORATORY OF GENERAL AND INORGANIC CHEMICAL TECHNOLOGY DEPARTMENT OF CHEMISTRY, ARISTOTLE UNIVERSITY, THESSALONIKI, GREECE

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Modification of Pyrite and Sphalerite Flotation by Dextrin

K. A. KYDROS, G. P. GALLIOS,* and K. A. MATIS
LABORATORY OF GENERAL AND INORGANIC CHEMICAL TECHNOLOGY
DEPARTMENT OF CHEMISTRY
ARISTOTLE UNIVERSITY
GR-540 06 THESSALONIKI, GREECE

ABSTRACT

The role of dextrin in the xanthate flotation of pyrite and sphalerite was examined by means of flotation tests and microelectrophoretic measurements. Floatability and ζ-potential of both minerals were found to be depressed in a suitable pH range due to the formation of their respective superficial metal hydroxide layers. The influences of surface oxidation and flocculation of mineral particles were also discussed. The selective flotation of sphalerite from pyrite in an acidic medium in the presence of copper sulfate was found to be possible, as shown by artificial mixture separation studies. In this way, the possible exclusion of cyanides (for environmental reasons) may be advanced.

INTRODUCTION

The common depression requirement in the selective flotation of minerals is that of gangue iron sulfides, like pyrite and pyrrhotite. Generally, copper and lead sulfides can be bulk floated from zinc and iron sulfides in the presence of such reagents as cyanides, thio or zinc salts, and lime. Some of these, and also copper salts, are necessary for the subsequent separation of zinc from iron sulfides. Cyanides, however, are hazardous, and their use has been gradually restricted by increasing environmental concern. Therefore, the exclusion of cyanides in mineral processing is of particular interest.

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* To whom correspondence should be addressed.

Organic polymeric depressants (such as starches, dextrins, and related products) have long been used in the beneficiation of salt-type minerals (1, 2). Recent studies concerning their potential application in sulfides flotation have shown that they enhance the depression of pyrites during flotation of copper sulfides as well as the depression of galena during flotation of chalcopyrite from copper–lead bulk concentrates (3–5). The depressing effect of dextrin (denoted hereafter as DEX) in inherently hydrophobic minerals like molybdenite and coal was reported (6).

Electrokinetic studies on pyrite were recently published (7). Finch and coworkers (8), among others, reported on the effects of oxygen-limited flotation of sphalerite. The role of copper sulfate in pyrite flotation was studied by O'Connor et al. (9) in a number of plants; the survey showed that this modifier was able to increase both grades and recoveries when used in correct dosages. Copper sulfate is the most commonly added activator to float sphalerite (in the presence of cyanides).

Dextrin in Minerals Flotation

Starches consist of macromolecules in which carbohydrate units (dextrose molecules) are regularly repeated and linked through 1–4 (straight chains) or 1–6 (branched chains) glycosidic linkages. Such products contain trace amounts of phosphorous and silica. They are used either unmodified or partially hydrolyzed in the more soluble form of dextrins. During the acid hydrolysis process, the starch chain is broken and the structural units are recombined in a new, highly branched polymer.

The adsorption of dextrin onto mineral surfaces is not yet clearly understood. Hydrophobic and chemical interactions were both reported to participate or predominate in the mechanism of this process (6). Laskowski and his group (4) examined the interactions between dextrin molecules and metallic species. They found that dextrin–metal (i.e., Fe, Pb, Cu) complexes are formed by the interaction of dextrin with a metal hydroxide. No dextrin abstraction or coprecipitation was observed in the pH range of metal cation predominance.

These researchers extended their work with studies of dextrin adsorption on lead-coated quartz (10) and on chalcopyrite and galena surfaces (11); a selective separation of the aforementioned sulfides was also achieved (5, 11, 12). In all cases, dextrin adsorption reached a maximum in the pH region around the isoelectric point (IEP) of the respective hydroxides. This led to the conclusion that chemical interactions constitute the primary mechanism involved with dextrin adsorption in the presence of hydrolyzed, metallic surface species, although hydrophobic interactions were also detected.

EXPERIMENTAL

Hand picked-up, comparatively pure pyrite and sphalerite crystals, coming from the Stratoni mines in Chalkidiki (Greece) and identified by x-ray analysis, were used throughout this work. Pyrite samples were found by chemical analysis to assay about 41% Fe and 5% insoluble matter; sphalerite assayed 43.5% Zn, 5% Fe, and 7% insolubles. The minerals used in the floatability experiments were dry crushed and pulverized in the laboratory (in a disk mill). The $-75+45$ μm size range was separated by wet screening and used in the experiments after drying at ambient conditions. A modified Hallimond tube was used in this work to apply the standard conditions given elsewhere (13). Caution is needed for observations coming from monomineral tests. The flotation time was kept constant at 10 minutes.

In the electrokinetic investigation, the minerals were ground by means of an agate mortar just before each measurement for freshly ground studies or after a 2-week aging period at ambient conditions in tests involving oxidized minerals. A Rank Brothers (UK) microelectrophoretic apparatus was used, equipped with a flat cell (7).

Analytical grade white (according to the company) dextrin, copper sulfate pentahydrate, and potassium ethyl xanthate (denoted KEX) were used as purchased from Merck (Germany). The necessary amounts of dextrin were dissolved by the appropriate volume addition of hot, deionized water. Weighed amounts of the prepared mineral samples were pulped in deionized water (1% solids in the flotation and 0.1% in the ζ-potential measurements); the pH was adjusted to the desired value and was controlled during the conditioning stage by sodium hydroxide and sulfuric acid additions. The order of reagent additions (10 minutes conditioning for each) is important and was as follows: $CuSO_4$, DEX, and KEX—unless otherwise stated.

RESULTS AND DISCUSSION

Adsorption of Dextrin

It is generally accepted that sulfide minerals undergo superficial oxidation when they are ground in aqueous media unless strict precautions are taken. A hydroxide coating over a sulfur-rich inner layer is finally developed (14). The surface properties of the minerals change; this phenomenon has been examined by electrokinetic studies (7).

In Fig. 1 the ζ-potentials of freshly ground and oxidized pyrite and sphalerite as a function of the solution pH are presented. The ζ-potentials of both minerals are shifted toward less negative (or even positive) values

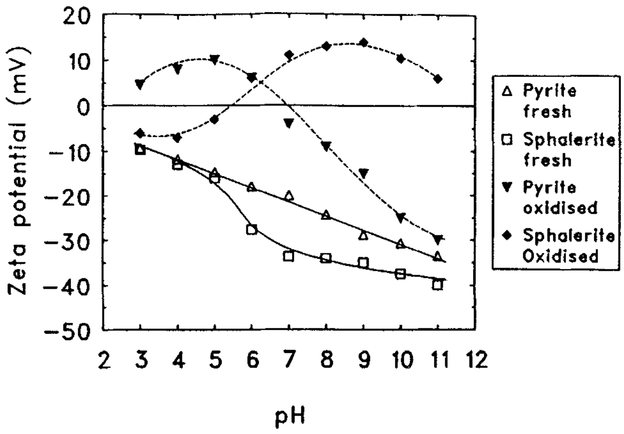


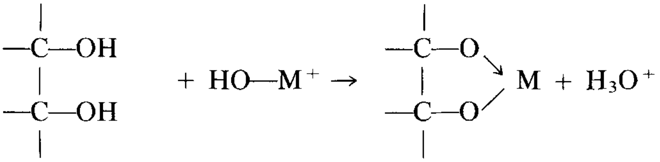
FIG. 1 Electrokinetic features of freshly ground and aged pyrite and sphalerite samples; ζ-potential vs pH.

over the whole pH range studied (3.0–11.0). These changes are attributed to the development of the aforementioned adsorbed metal hydroxide layer. The positive charge originates from the formation of a partially hydrolyzed cationic species, and it is eliminated in the pH range of complete hydrolysis (7, 15).

In mineral processing research and practice, sulfide surfaces are usually oxidized to some extent, as was commented on recently (16). Electrokinetic testing with oxidized samples, therefore, may lead to conclusions closer to reality.

In Fig. 2 the ζ-potential of dextrin dispersion as a function of solution pH in the presence and the absence of metallic species is given. Dextrin appeared to be negatively charged over the entire pH range studied. In the presence of copper or iron species, however, the negative charge was eliminated in the pH range of the respective hydroxide formation. This can be attributed to the formation of a neutral surface complex.

The aforementioned behavior corresponds to the mechanism proposed by Laskowski et al. (11) concerning dextrin adsorption on metallic surfaces:



$$\begin{array}{l} \;| \\ -C-OH \\ \;| \\ -C-OH \\ \;| \end{array} + HO-M^{+} \rightarrow \begin{array}{l} \;| \\ -C-O \searrow \\ \;| \qquad\quad M + H_3O^{+} \\ -C-O \nearrow \\ \;| \end{array}$$

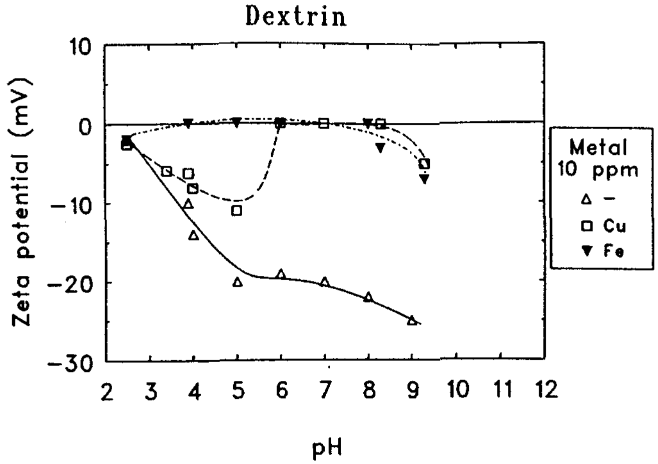


FIG. 2 Electrokinetic features of dextrin (1000 ppm) in the presence and absence of metallic species (10 ppm).

The elimination of the negative charge of dextrin was followed by a destabilization of the dispersion, with the particles flocculated to a great extent. The application of starches as flocculants was also reviewed by Krishanan and Attia (17). Recently, adsorption and electrokinetic studies were reported on the interactions of dextrin with some sulfide minerals (i.e., Heazlewoodite and chalcocite) (18).

Monominerals Floatability

The effect of dextrin on pyrite floatability is shown in Fig. 3. The addition of dextrin (at concentrations of 5, 10, and 50 ppm) depressed pyrite over the whole pH range studied. At a pH value of around 7, where the formation of iron hydroxide has been completed, the floatability approached zero. Around this pH value, the IEP of the ferric hydroxide formed was also noted (19). On the other hand, a depression of the surface charge was observed (see Fig. 4) and the pyrite was flocculated at pH values of less than 10.

This minimization of ζ-potential values in the presence of dextrin is in agreement with the literature (12). From Figs. 2 and 4 it is apparent that the surface of a dextrin-treated pyrite behaves similarly to a iron-treated dextrin surface.

The depressing effect of dextrin was found to be independent of the xanthate concentration (up to 30 ppm), as shown in Fig. 5. Dextrin was

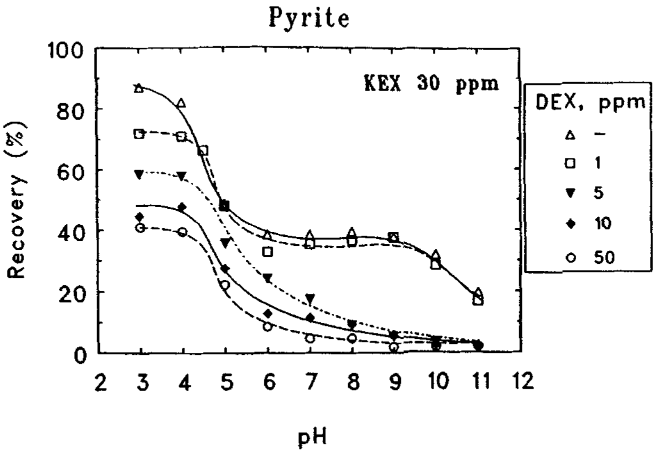


FIG. 3 Floatability of pyrite in the presence of various additions of dextrin; effect of dispersion pH on recovery (KEX 30 ppm).

also found to depress pyrite effectively over the entire pH range studied, even after copper activation (see Fig. 6).

The ζ-potential of copper-activated pyrite in the presence and the absence of dextrin is shown in Fig. 7. This time the ζ-potential of pyrite (in the absence of dextrin) reverses sign at a pH value of around 8.5, where the formation of copper hydroxide is complete. The adsorption of dextrin on the iron- and copper-hydroxide-coated surface of pyrite again leads to

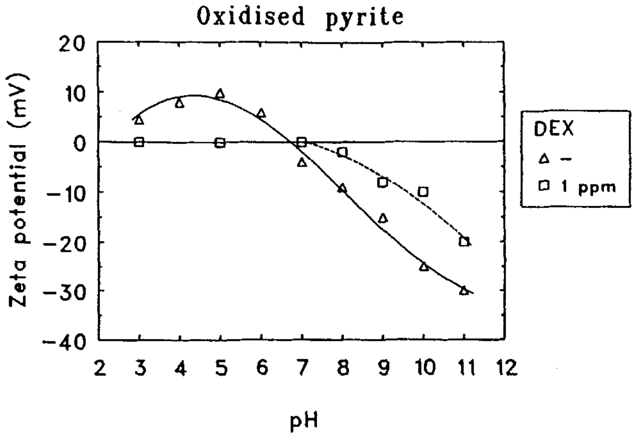


FIG. 4 Electrokinetic features of oxidized pyrite in the presence and absence of dextrin.

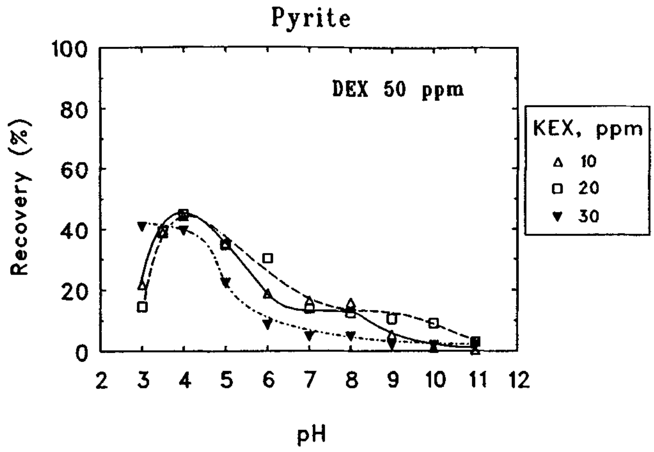


FIG. 5 Floatability of pyrite as a function of pH in the presence of dextrin; effect of xanthate concentration (DEX 50 ppm).

elimination of the ζ-potential at pH values of 3.0 to 7.0. The mineral is flocculated and also hydrophilic over the entire pH range (Fig. 6).

In Fig. 8 the effect of dextrin on the floatability of pure and copper-activated sphalerite is presented. Under these conditions and in contrast to pyrite, Cu-activated sphalerite sustains its floatability even after the addition of dextrin at pH values of 3.0 to 5.0. Indeed, the ζ-potential

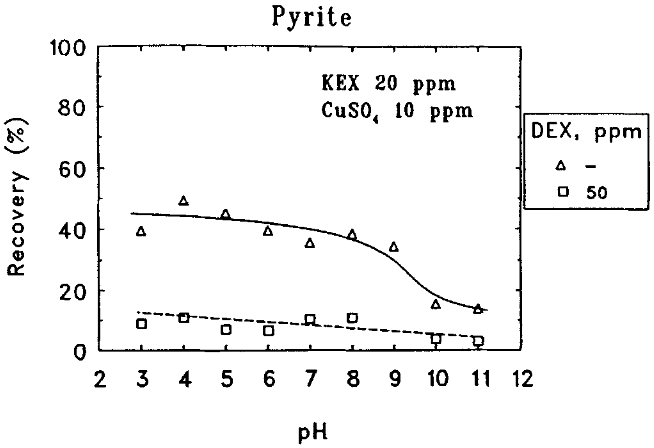


FIG. 6 Floatability of copper-activated pyrite as a function of pH in the presence and absence of dextrin (copper sulfate 10 ppm).

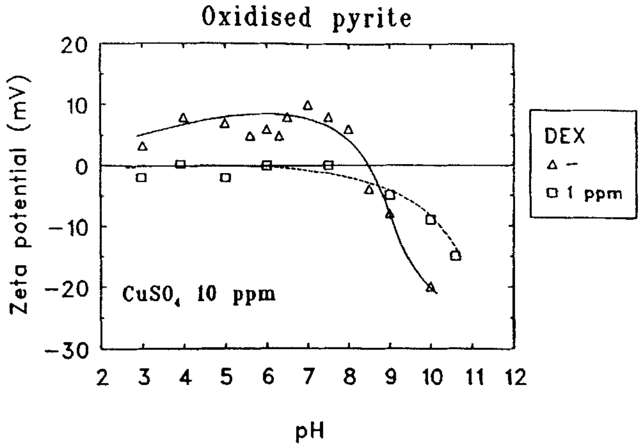


FIG. 7 Electrokinetic features of copper-treated, oxidized pyrite in the presence and absence of dextrin (copper sulfate 2 ppm).

depression, indicating dextrin species–mineral surface interactions, was observed this time at pH values greater than 6, where hydrolysis of copper and zinc is possible and the mineral acquires a positive charge (see Fig. 9). Similar electrokinetic features were also observed in the case of copper-treated dextrin (see also Fig. 2).

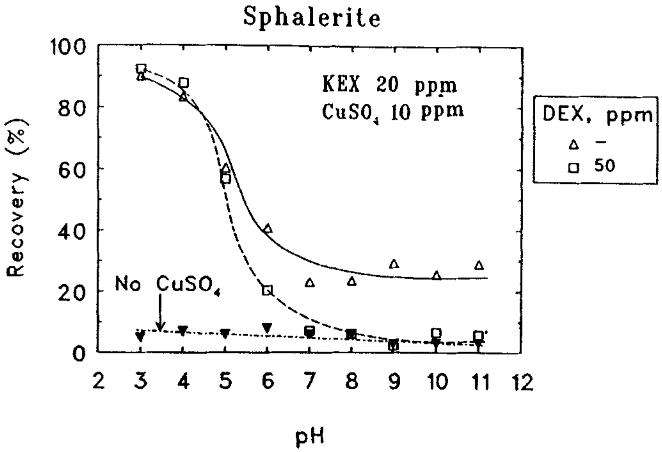


FIG. 8 Floatability of sphalerite as a function of pH in the presence of dextrin (copper sulfate 10 ppm, KEX 20 ppm).

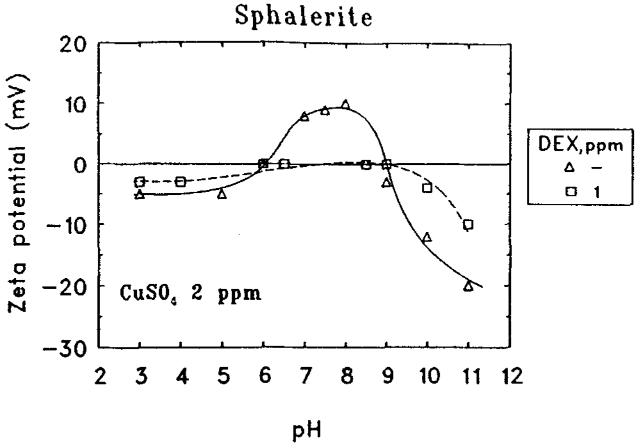


FIG. 9 Electrokinetic features of copper-treated, oxidized sphalerite in the presence and absence of dextrin (copper sulfate 2 ppm).

The aforementioned results are summarized in Fig. 10. The left ordinate represents flotation recoveries, while the right ordinate represents the ζ-potential values of the two minerals. The flotation experiments were conducted with 10 ppm copper sulfate, 50 ppm dextrin, and 30 ppm collector (KEX), while in the ζ-potential measurements only 10 ppm copper sulfate was added.

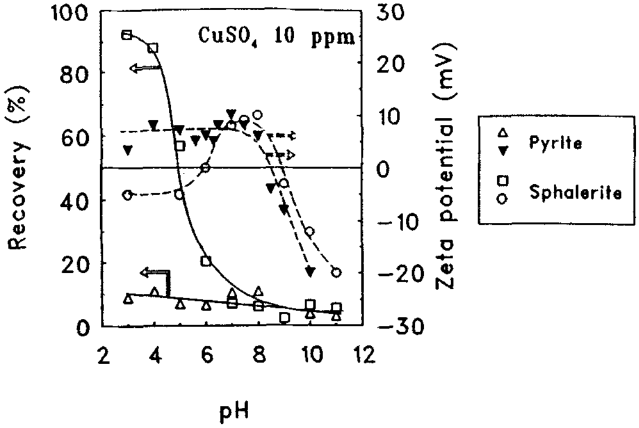


FIG. 10 Floatability of copper-activated pyrite and sphalerite in the presence of dextrin (copper sulfate 10 ppm, DEX 50 ppm, KEX 20 ppm); comparison with their electrokinetic features (in the presence of 10 ppm copper sulfate) before dextrin addition.

It seems possible that the depressing effect of dextrin is apparent only at pH values where the formation of hydroxide coatings takes place, which could be recognized by the subsequent ζ-potential reversal of mineral surfaces.

Artificial Mixtures

Sulfide minerals may also be oxidized because of galvanic interactions, i.e., charge transfer reactions occurring between conductive solids with different electrochemical activities (20). Taking into consideration that pyrite is the most cathodic sulfide mineral, its presence is expected to enhance the oxidation of more anodic minerals like sphalerite and galena. Thus, the flotation behavior of minerals in a mixture may differ significantly from their behavior in monomineral systems. We decided that the conclusions obtained from preliminary flotation tests should be checked with artificial mixtures studies.

Figure 11 presents the results obtained with an artificial pyrite–sphalerite mixture made from pure minerals. The solid lines represent recoveries and refer to the left ordinate, while the dashed lines represent grades and refer to the right ordinate. The feed grade (13.4% Zn) is represented by the horizontal dashed line.

The reagents were 50 ppm dextrin, 10 ppm copper sulfate, and 20 ppm collector (KEX). The reagents were added in the order given above, and a 10-minute conditioning period followed each addition. From the point

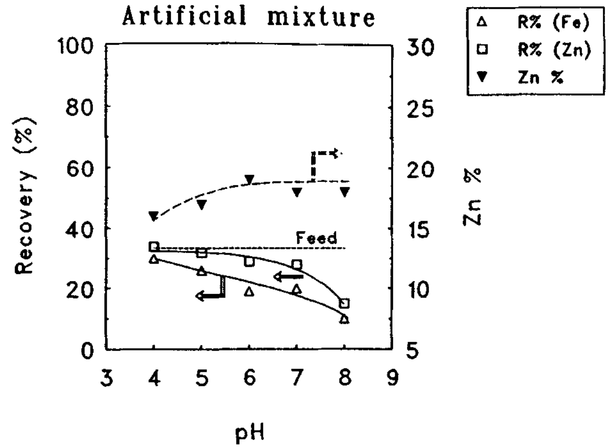


FIG. 11 Separation studies of artificial mixtures. Order of reagents addition: DEX (50 ppm), copper sulfate (10 ppm), and KEX (20 ppm).

of view of grades and recoveries, quite poor results were obtained. The sole action of dextrin in this case was a serious depression of the floatability of both minerals.

When copper sulfate was added prior to dextrin (10 ppm copper sulfate, 50 ppm dextrin, and 20 ppm KEX), much better results were achieved (see Fig. 12). Sphalerite was found to be selectively floated in the slightly acidic pH region. The floated fraction contained 28% Zn, with a zinc recovery value of around 75% at pH 4.0.

The considerable influence of the order of reagent addition may be attributed to the discrimination of copper adsorption in dextrin-treated sphalerite surfaces. The copper hydroxide which precipitates on the sphalerite surface may serve as a "pool" to supply copper abstracted from the solution to the mineral lattice where copper sulfide is formed (21). In the presence of the polymeric depressant, competition between dextrin and the copper species for surface-active sites is possible, leading to the elimination of copper activation. Such a competition was also observed in the case of sodium oleate adsorption onto lead-coated quartz in the presence of dextrin (9).

CONCLUDING REMARKS

1. The depressing effect of dextrin reaches a maximum in the pH range of complete hydrolysis of the respective metal cations.

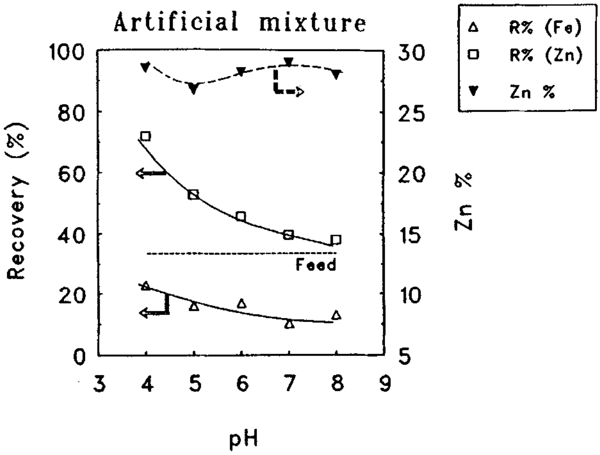


FIG. 12 Artificial mixture separation studies. Order of reagents addition: copper sulfate (10 ppm), DEX (50 ppm), and KEX (20 ppm).

2. Superficial oxidation, caused mainly by grinding conditions, governs the depression process. The oxidation state should be examined (possibly electrokinetically) in each ore in order to define the dextrin depression characteristics.

3. The adsorption of dextrin leads to elimination of the surface charge and causes flocculation of the particles.

4. Sphalerite may be selectively floated from pyrite in the presence of dextrin with a xanthate collector at slightly acidic pH values.

5. Dextrin-treated sphalerite is not easily activated by copper sulfate. The activation process should be carried out prior to dextrin adsorption.

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