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# Flotation of sphalerite and pyrite in the presence of sodium sulfite

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## Abstract

Sodium sulfite was used to improve the separation of copper-activated sphalerite from pyrite in mildly alkaline pH conditions. This improved separation was mainly the result of the much larger depression of the flotation of pyrite than sphalerite. A further improvement in this separation was obtained by conditioning the minerals with oxygen and by decreasing the time interval between sulfite and xanthate additions. The results of spectroscopic studies have shown that sodium sulfite promotes the oxidation of copper on pyrite as copper hydroxide, but has no effect on sphalerite. This increase in the amount of oxidation products on the pyrite surface and, as a result, decrease in xanthate adsorption may explain the depression of the flotation of pyrite in the presence of sodium sulfite. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Selective flotation; Sphalerite; Pyrite; Depressants

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## 1. Introduction

Pyrite is one of the major diluents of copper, lead and zinc concentrates. One explanation for the high flotation of pyrite in alkaline pH conditions is its inadvertent activation by copper either dissolved from copper minerals present in the ore or added in the zinc circuit to activate the flotation of sphalerite (Bushell and Krauss, 1962; Voigt et al., 1994). High conditioning pH values, long conditioning time and extensive surface oxidation are usually required to depress pyrite flotation (Kristall et al., 1994; Shen et al., 1998). To reduce plant-operating cost, alternative reagents could be used to provide

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mineral separations in less alkaline pH conditions. Copper selective collectors such as thionocarbamate and thiourea have produced better separations of chalcopyrite or copper-activated sphalerite from pyrite than xanthates in neutral to alkaline pH conditions (Fairthorne et al., 1997; Shen et al., 1998)

Sodium sulfite and similar sulfoxyl species such as sodium bisulfite, metabisulfite or sulfur dioxide gas have also been used as depressants of pyrite, but also of galena and sphalerite in copper circuits in neutral pH conditions (Yamamoto, 1980; Pattison, 1983; Misra et al., 1985; Grano et al., 1997a,b; Houot and Duhamet, 1992). The depressing effect of sulfites generally increases from copper sulfides to galena, pyrite and sphalerite (Peres, 1981). However, after activation with copper, sphalerite behaves more like a copper mineral in relation to depression by sulfites (Yamamoto, 1980). As for copper-activated pyrite, the effect of sodium sulfite on its flotation is not well documented in the literature and is the subject of this study together with its separation from sphalerite in mildly alkaline pH conditions. Several mechanisms have been put forward to explain the depression of the flotation of sphalerite by sulfites (Misra et al., 1985). They include: the formation of a zinc sulfite hydrophilic layer at the mineral surface; the reduction of copper-activation as a result of consumption of copper in solution as copper sulfite; the decomposition of xanthate; the decrease in xanthate adsorption or the decomposition of dioxanthogen following the Eh decrease; and the consumption of dissolved oxygen. Sulfite ions are also known to react with polysulfide or elemental sulfur and form thiosulfate ions (Li et al., 1995); a decrease in surface hydrophobicity is therefore expected from this reaction. These mechanisms should also apply to copper-activated pyrite. Several solution and surface analytical techniques will be used in this study to determine the more likely mechanism(s).

## 2. Experimental

All chemicals were of analytical grade. High purity nitrogen and oxygen gases (CIG) were scrubbed by bubbling through precipitated silica (BDH) suspension prior to use. All solutions were made with high purity water (conductivity  $\leq 0.5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ , surface tension =  $72.8 \text{ mN m}^{-1}$  at  $20^\circ\text{C}$ ) prepared by reverse osmosis followed by two stages of ion exchange and two stages of activated carbon prior to final filtration through a  $0.22 \mu\text{m}$  filter. This water was “pretreated” in  $0.001 \text{ mol dm}^{-3} \text{ KNO}_3$  by bubbling nitrogen or oxygen gas into it to remove dissolved  $\text{CO}_2$  and its pH was adjusted to 8.5.

The sphalerite and pyrite samples were purchased from Ward’s Natural Science Establishment, USA. Their chemical analysis is reported in Table 1. Potassium ethyl

Table 1  
Chemical composition of sphalerite and pyrite samples

Mineral	Element				
	Zn	S	Pb	Fe	Cu
Sphalerite, ZnS (Elmwood mine, Tennessee)	64.9	33.1	0.9	0.3	510 (ppm)
Pyrite, $\text{FeS}_2$ (Huanzala, Peru)	< 50 (ppm)	53.5	60 (ppm)	40.8	0.29

xanthate (KEX) obtained from Aldrich was further purified by dissolution in acetone and recrystallization from petroleum ether as described elsewhere (Montalti et al., 1991).

Just prior to use, the samples of sphalerite and pyrite (1.0 g each) were ground together in a small amount of “pretreated” water with a ceramic mortar and pestle. The sphalerite and pyrite samples have an average particle size of 20  $\mu\text{m}$  with a BET surface area of 0.29  $\text{m}^2/\text{g}$  for sphalerite and 0.32  $\text{m}^2/\text{g}$  for pyrite. Both minerals were then transferred into a water-jacketed, closed reaction vessel and conditioned together at  $21 \pm 0.2^\circ\text{C}$  for 20 min in 0.75  $\text{dm}^3$  of “pretreated” water in the presence of nitrogen or oxygen gas. The pH was kept at a fixed value of 8.5 by adding small quantities of a concentrated solution of nitric acid or potassium hydroxide. The redox potential of the pulp solution was measured with a platinum electrode. The minerals were conditioned for a further 10-min period in the presence of a known amount of  $\text{Cu}(\text{NO}_3)_2$  and for a further 10-min period after the addition of a concentrate solution of collector. The total mineral conditioning time before flotation was therefore 40 min, irrespective of the presence of sodium sulfite or its order of addition. The mineral dispersion was then transferred into a modified Smith and Partridge microflotation column (tube length = 86 cm; average size of  $\text{N}_2$  bubbles = 0.5 mm). The length of the flotation column insures that entrainment of particles is kept to a low level; the recovery of clean quartz particles was less than 5% after 8 min of flotation. The concentrates were collected after 1, 2, 4 and 8 min of flotation and recovered on 0.2  $\mu\text{m}$  filters. The mineral concentrate and tail fractions were dissolved in a concentrated acidic solution and the concentration of each mineral was determined by atomic absorption spectroscopy (Varian Techtron Model AA-4). The reproducibility of the flotation recoveries was better than  $\pm 2\%$ .

The concentration of the xanthate remaining in solution after the addition of 2 g of mineral was measured as a function of time by UV–visible spectroscopy using a Varian CARY 5E spectrophotometer. A molar absorptivity of 17,547  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  was used for KEX (Montalti et al., 1991). A porosity #5 sintered glass filter immersed in the solution was connected to a peristaltic pump which circulated the filtered solution from the reaction vessel to a quartz cell inside the spectrophotometer and back to the reaction vessel.

XPS measurements were obtained with a Perkin Elmer Physical Electronics Division (PHI) 5100 spectrometer using an  $\text{MgK}\alpha$  irradiation X-ray source operated at 300 W. A pass energy of 17.9 eV was used for all elemental spectral regions. The pressure in the analyser chamber was  $10^{-7}$  Pa. The energy scale was calibrated using the Fermi edge and the  $4f_{7/2}$  line (BE = 84.0 eV) for gold, whilst the retardation voltage was calibrated with the position of the  $\text{Cu}(2p_{3/2})$  peak (BE = 932.67 eV) and the  $\text{Cu}(3p_{3/2})$  peak (BE = 75.13 eV). An accelerated  $\text{Ar}^+$  ion beam at 3 kV was used to etch the mineral surface for 5 min. For the XPS analysis, the minerals were prepared in a similar way as in the flotation experiments. After decantation, the mineral slurry was washed once with “pretreated” water to remove any suspended colloidal particles and was introduced immediately into the fore-vacuum of the XPS as a slurry. The procedure used to analyse the XPS spectra of the minerals has been presented in details in a previous XPS study (Fullston et al., 1999).

Fourier Transform Infrared (FTIR) spectra were measured with a Nicolet Magna 750 spectrometer at a resolution of  $4 \text{ cm}^{-1}$  using a broad band mercury–cadmium–telluride

liquid–nitrogen-cooled detector. After conditioning and filtration, the mineral was placed in the cup of a Spectra Tech diffuse reflectance apparatus inside the spectrometer. The contribution from the mineral was subtracted in all the infrared spectra.

### 3. Results

#### 3.1. Flotation study

As the effect of sodium sulfite on pyrite flotation was very similar in the pH region from neutral to mildly alkaline, a pH value of 8.5 was chosen in this study as it corresponds to pH values generally used in the copper or lead circuits. Fig. 1 shows the effect of sodium sulfite on the flotation of copper activated-sphalerite and pyrite. In the absence of sodium sulfite, a poor separation of sphalerite from pyrite is obtained. The effect of sulfite is more important on pyrite flotation than on sphalerite flotation, hence the better separation obtained in the presence of sodium sulfite. Sphalerite flotation slightly decreases with an increase in sodium sulfite concentration with recoveries (after 8 min of flotation) of 88% in the absence and 73% in the presence of  $10^{-3}$  mol  $\text{dm}^{-3}$  sodium sulfite. The effect of sodium sulfite on pyrite flotation is more pronounced than on sphalerite flotation with flotation recoveries being reduced by half at a sodium sulfite concentration of  $2 \times 10^{-4}$  mol  $\text{dm}^{-3}$ . However, at higher sodium sulfite concentrations, pyrite recovery increases. A sodium sulfite concentration of  $2 \times 10^{-4}$  mol  $\text{dm}^{-3}$  was therefore used in this study as it provides maximum pyrite depression. Fig. 1 shows also that within experimental errors the order of addition of sodium sulfite, prior to or after

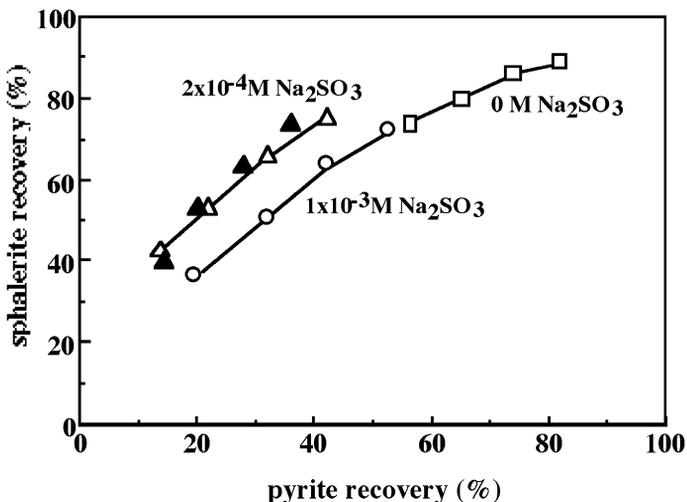


Fig. 1. Flotation recoveries of copper-activated sphalerite and pyrite at pH 8.5 as a function of sodium sulfite concentration and for sodium sulfite added before (filled symbols) and after (empty symbols) copper addition ( $\text{N}_2$  conditioning;  $[\text{Cu(II)}] = [\text{KEX}] = 2 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ).

copper ion addition, has no or little effect on the flotation of both sphalerite and pyrite; sodium sulfite was added after copper in the subsequent experiments. Fig. 2 shows the effects of conditioning gas and time interval between the additions of sulfite and xanthate (20 s or 10 min) on the separation of sphalerite from pyrite in the presence of sodium sulfite. With nitrogen as the conditioning gas, sphalerite flotation is always lower than when oxygen gas is used. The increase in the flotation of both sphalerite and pyrite with oxygen gas conditioning has previously been observed when the mineral conditioning time is relatively short (less than 20 min) and has been linked to an increase in reactivity between the collector and copper species at the mineral surface (Shen et al., 1998). More importantly, a decrease of the time interval between the additions of sulfite and xanthate from 10 min to 20 s has a beneficial effect on the separation of these minerals with either nitrogen or oxygen gas conditioning. In this study, the best separation of sphalerite from pyrite was obtained in the presence of sodium sulfite, using oxygen as the conditioning gas and with a short time interval between the additions of sulfite and xanthate.

### 3.2. UV-visible spectroscopic study

The effects of sodium sulfite on the stability of xanthate in solution and on the adsorption of xanthate on the surface of sphalerite and pyrite were investigated. The concentration of xanthate in solution at pH 8.5 with nitrogen or oxygen gas conditioning is shown in Fig. 3 as a function of time and sodium sulfite concentration. When nitrogen is used as the conditioning gas, no or little change in xanthate concentration is observed at this pH value in the absence or presence of  $3 \times 10^{-3} \text{ mol dm}^{-3}$  sodium sulfite. In the

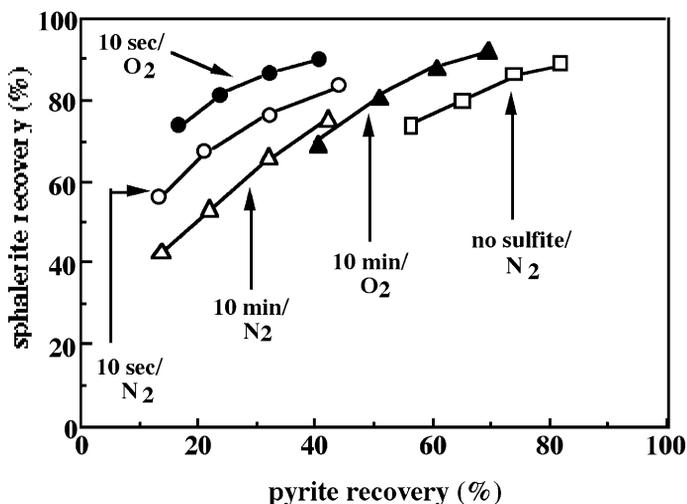


Fig. 2. Flotation recoveries of copper-activated sphalerite and pyrite at pH 8.5 as a function of the time interval (20 s or 10 min) between the additions of sodium sulfite and xanthate, and conditioning gas ( $[\text{Cu(II)}] = [\text{KEX}] = 2 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[\text{Na}_2\text{SO}_3] = 2 \times 10^{-4} \text{ mol dm}^{-3}$ ).

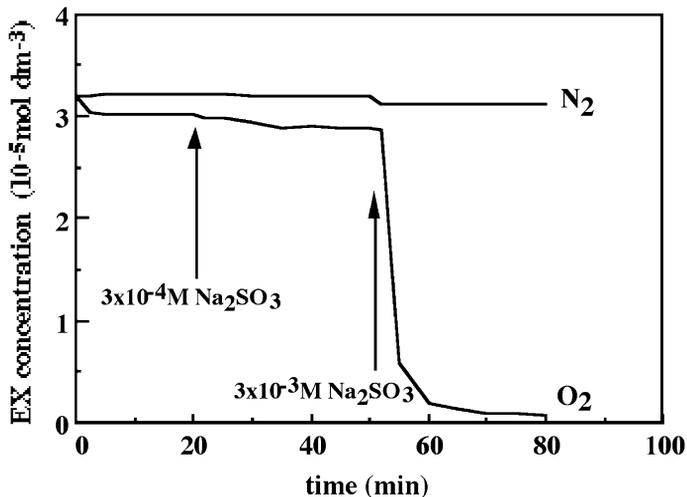


Fig. 3. Concentration of ethyl xanthate in solution at pH 8.5 as a function of time, conditioning gas and sodium sulfite concentration.

presence of oxygen, the same result is obtained at a sodium sulfite concentration of  $3 \times 10^{-4} \text{ mol dm}^{-3}$ , but after the addition of  $3 \times 10^{-3} \text{ mol dm}^{-3}$  sodium sulfite, the concentration of xanthate in solution decreases rapidly to zero. A close inspection of the visible spectrum revealed that the decrease of the xanthate absorbance peak at 301 nm is accompanied by an increase in intensity of a new peak at 348 nm that is characteristic of perxanthate, the product of xanthate decomposition (Yamamoto, 1980; Misra et al., 1985). However, the concentration of perxanthate in solution at any time was less than the concentration of xanthate that has disappeared, which implies that the decomposition of ethyl perxanthate to ethanol and carbon disulfide is fast (Montalti et al., 1991).

Fig. 4 shows the effect of sodium sulfite on the adsorption of ethyl xanthate on copper-activated pyrite conditioned with nitrogen gas at pH 8.5. The adsorption of xanthate is fast in the first 10 min, but levels off thereafter. As the decomposition of xanthate in solution is negligible at a sodium sulfite concentration of  $3 \times 10^{-4} \text{ mol dm}^{-3}$  (Fig. 3), one concludes that less xanthate is adsorbed on copper-activated pyrite in the presence of sodium sulfite. It was also found that, within experimental errors, the amount of xanthate adsorbed on copper-activated sphalerite is the same without or with sodium sulfite (results not shown).

### 3.3. Infrared spectroscopic study

Fig. 5 shows the infrared spectra of ethyl xanthate adsorbed on copper-activated sphalerite and pyrite conditioned at pH 8.5 with nitrogen or oxygen gas, and in the absence or presence of sodium sulfite. All the infrared spectra are characteristic of cuprous-ethyl xanthate (Thermes and Richardson, 1986; Leppinen, 1990). From the intensity of the peaks in each spectrum, one concludes first that, in the absence of

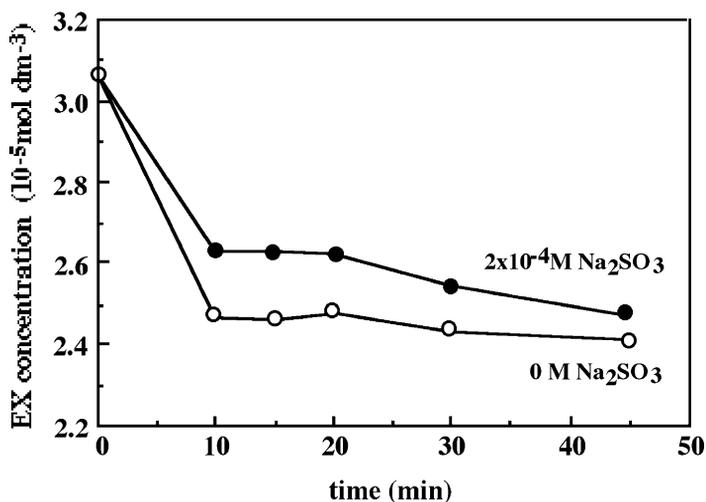


Fig. 4. Concentration of ethyl xanthate remaining in solution at pH 8.5 as a function of contact time with pyrite in the absence or presence of sodium sulfite ([pyrite] = 2.7 g dm<sup>-3</sup>; N<sub>2</sub> conditioning; [Cu(II)] = [KEX] = 3.06 × 10<sup>-5</sup> mol dm<sup>-3</sup>).

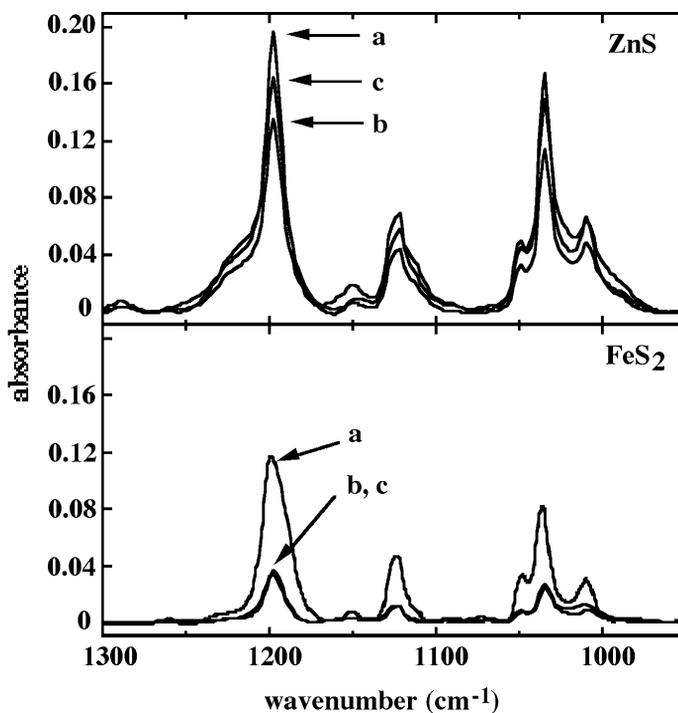


Fig. 5. Infrared spectra of ethyl xanthate adsorbed on (top) sphalerite and (bottom) pyrite conditioned at pH 8.5 with (a, b) nitrogen or (c) oxygen gas and in the (a) absence or (b, c) presence of sodium sulfite. Xanthate was added immediately after the sodium sulfite addition ([Cu(II)] = [KEX] = 2 × 10<sup>-5</sup> mol dm<sup>-3</sup>; [Na<sub>2</sub>SO<sub>3</sub>] = 2 × 10<sup>-4</sup> mol dm<sup>-3</sup>).

Table 2

Proportion (at.%) of the elements measured by XPS on the surface of sphalerite and pyrite

Mineral	Reagent addition	Element				
		O	Zn	Fe	S	Cu
ZnS	Cu(II)	24 (3)	9 (39)	0	50 (53)	17 (5)
	Cu(II) + Na <sub>2</sub> SO <sub>3</sub>	24 (3)	14 (37)	0	44 (52)	18 (8)
FeS <sub>2</sub>	Cu(II)	33	0	14	41	12
	Cu(II) + Na <sub>2</sub> SO <sub>3</sub>	37	0	10	42	11

The proportion of elements after surface etching is represented in brackets (pH = 8.5; conditioning time = 20 min in N<sub>2</sub>; [Cu(II)] =  $2 \times 10^{-5}$  mol dm<sup>-3</sup>; [Na<sub>2</sub>SO<sub>3</sub>] =  $2 \times 10^{-4}$  mol dm<sup>-3</sup>)

sodium sulfite, less cuprous-xanthate is formed on pyrite than on sphalerite. Secondly, in the presence of sodium sulfite, the amount of cuprous-xanthate formed on both minerals is reduced, but much more on pyrite than on sphalerite. Thirdly, in the presence of sodium sulfite, more cuprous-xanthate is formed on sphalerite conditioned with oxygen than with nitrogen gas, but no or little change is observed for pyrite.

### 3.4. XPS study

The surfaces of copper-activated sphalerite and pyrite were analysed by XPS before and after sodium sulfite addition (Table 2). In the absence of sulfite, copper has replaced zinc and formed cuprous sulfide on the sphalerite surface (Buckley et al., 1989; Kartio et al., 1998). This cuprous sulfide layer is rather thin as etching removes almost all of the copper. A deconvolution of the S(2p) spectrum into its individual components revealed

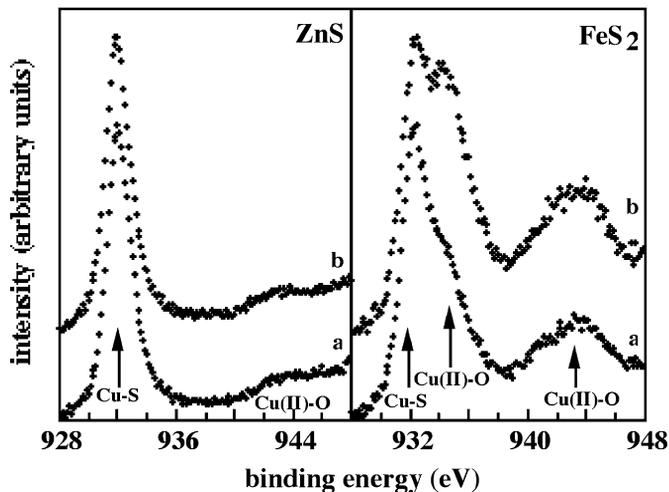


Fig. 6. Cu(2p<sub>3/2</sub>) XPS spectra of copper-activated (left) sphalerite and (right) pyrite in the (a) absence or (b) presence of sodium sulfite (20 min conditioning in N<sub>2</sub>; pH = 8.5; [Cu(II)] =  $2 \times 10^{-5}$  mol dm<sup>-3</sup>; [Na<sub>2</sub>SO<sub>3</sub>] =  $2 \times 10^{-4}$  mol dm<sup>-3</sup>).

that a small amount of metal-deficient sulfide or polysulfide is present on the surface but no sulfoxy species, e.g. sulfate, is formed (spectrum not shown). As no carbonate was observed in the C(1s) spectrum, it was concluded that the surface oxygen on sphalerite must belong to zinc as zinc hydroxide/oxide (it is not possible in the Zn(2p) spectrum to separate the contribution of ZnS from Zn(OH)<sub>2</sub>). The result of the etching experiment indicates that this hydroxide layer is thin. The proportions of the surface elements are not affected to a large extent by sodium sulfite addition, except for a small increase in zinc and decrease in sulfur (Table 2). The Cu(1s) spectra show that, before or after sodium sulfite addition, copper sulfide is the main copper species on the sphalerite surface with no or only a very small amount of copper hydroxide (Fig. 6).

The major difference between the two minerals is the larger oxidation of the pyrite surface, mainly as copper hydroxide/oxide, with consequently less copper exposed at the top surface (Table 2). After sodium sulfite addition, even more copper hydroxide is found on the pyrite surface (Fig. 6) while the proportion of iron hydroxide species remains the same (Fe(2p) spectra not shown). No carbonate and only a very small quantity of sulfate are detected on the pyrite surface (C(1s) and S(2p) spectra not shown).

#### 4. Discussion

The trends observed in this study in the spectroscopic analyses of the minerals with addition of sodium sulfite, and changes in conditioning time and type of gases are generally in agreement with the flotation results.

The results from infrared spectroscopy have shown that xanthate only interacts with copper on the surface of copper-activated sphalerite and pyrite to form cuprous xanthate. As no dixanthogen is formed in the conditions used in this study, cuprous xanthate is the only xanthate species responsible for the flotation of these minerals. In the absence of sodium sulfite, the high flotation of both minerals may be explained by the XPS results that showed a relatively low level of copper hydroxide species on both mineral surfaces, conditions which are favourable for strong collector adsorption (Fig. 4). The small difference in flotation recoveries between the two minerals may also be explained by the difference in the amount of copper hydroxide and cuprous xanthate present on the two minerals (Figs. 5 and 6). Collector adsorption is generally reduced on oxidised sulfide minerals (Shen et al., 1998). In the presence of sodium sulfite, the amount of copper hydroxide increases on the pyrite surface, but not on the sphalerite surface (Fig. 6). As a consequence, less cuprous xanthate is formed on the mineral surface after sulfite addition, and on pyrite than on sphalerite in agreement with the flotation results (Figs. 2 and 5). More importantly, this study has shown that when xanthate is added immediately after the sulfite addition, changing the conditioning gas from nitrogen to oxygen restores sphalerite recovery to the level obtained in the absence of sodium sulfite, but leaves the pyrite flotation depressed (Fig. 2). The effect of conditioning gas on mineral flotation can be explained by the amount of copper xanthate present on each mineral: the amount of copper xanthate on sphalerite increases after oxygen conditioning but remains the same on pyrite (Fig. 5).

From the results obtained in this study, several mechanisms that have been suggested in the Introduction for the depressing effect of sulfites on sphalerite and pyrite can now be discarded. No xanthate decomposition by sulfite ions was observed in solution in the conditions used in the flotation experiments and no metal sulfite or sulfoxy species were formed at the mineral surface. Also, dixanthogen decomposition did not occur as no dixanthogen was observed on the mineral surface by infrared spectroscopy in the absence of sodium sulfite. The results of surface analysis have shown that this decrease in mineral flotation after sulfite addition is rather produced by the oxidation of copper to copper hydroxide/oxide at the mineral surface, which inhibits collector adsorption. However, the 70 mV decrease in Eh value observed in solution after sodium sulfite addition may also explain this decrease in xanthate adsorption.

The following mechanism is proposed to explain the depressing effect of sodium sulfite on copper-activated pyrite,



This mechanism incorporates both the consumption of dissolved oxygen (decrease in solution Eh) and the formation of copper hydroxide in solution or at the mineral surface. Copper hydroxide/oxide is a thermodynamically stable species at pH 8.5 in the range of pulp potentials measured in this study (190 to 250 mV SHE). Copper hydroxide observed on the pyrite surface may have precipitated from solution or been the product, with cupric sulfide, of the surface reaction between cuprous sulfide and hydroxide ion (the positions of the XPS peaks for  $\text{Cu}_2\text{S}$  and  $\text{CuS}$  are identical (Fullston et al., 1999)). Galvanic interactions may also occur between the cuprous sulfide layer at the pyrite or sphalerite surface and the mineral itself. As a result of this galvanic interaction, cuprous sulfide (the less cathodic phase) is oxidised, forming cupric ions, while oxygen is reduced at the pyrite or sphalerite surface (more cathodic), forming  $\text{OH}^-$  ions (Fig. 7).

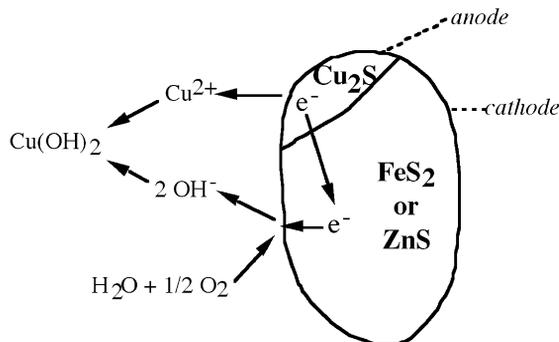


Fig. 7. Schematic representation of galvanic interactions that may occur at the copper-activated pyrite or sphalerite surface.

Sodium sulfite together with oxygen may act as catalysts in the oxidation of cuprous sulfide (Devuyt et al., 1982). The differences between the two minerals may then be explained by their different electrochemical activities, with pyrite being the most cathodic mineral (Hayes et al., 1987; Rao et al., 1992). As a result, the galvanic interaction is stronger for pyrite than for sphalerite, hence the higher proportion of copper hydroxide/oxide formed (reaction 3) on pyrite than on sphalerite. As the above reactions are time dependent, copper hydroxide is formed more rapidly on pyrite than on sphalerite and, therefore, reducing the time interval between sulfite and xanthate additions should favour the interaction of xanthate with the less oxidised mineral, sphalerite, and produce a larger separation of sphalerite from pyrite.

## 5. Conclusions

An improved separation of sphalerite from pyrite can be obtained at pH 8.5 with the use of sodium sulfite. This separation can be further improved with oxygen conditioning and when xanthate is added immediately after the sodium sulfite addition. UV–visible, infrared and XPS spectroscopic studies have shown that the selective depression of the flotation of pyrite with sodium sulfite is the result of an increased oxidation of the pyrite surface, mainly as copper hydroxide which inhibits collector adsorption.

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