Pyrite Flotation With Xanthate Under Alkaline Conditions — Application to Environmental Desulfurisation

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ABSTRACT

The extensive literature on sulfide flotation indicates that pyrite poorly floats under alkaline condition. Xanthate concentration has a positive effect on pyrite flotation, but above a pH of 11, pyrite seems to be strongly depressed, independently of the concentration in xanthate. In this investigation, aeration and xanthate concentration effects were studied for pyrite flotation conditioned at pH 11 with lime. Results presented in this paper include surface infrared analyses and pulp chemistry measurements which have showed that aeration had a dual effect on pyrite flotation. It induced pyrite surface activation by oxygen, and oxidation of ferrous iron to ferric hydroxides or oxyhydroxides species. It also favoured dissolution of CO\textsubscript{2}, leading to calcium carbonate precipitation and adsorption onto pyrite surface. Both CO\textsubscript{2} dissolution and ferrous oxidation generated protons and decreased pulp pH. Pyrite flotation was observed to be effective with a statistical monolayer of xanthate that could be adsorbed as mixture of dioxanthogen and metal-xanthate complex. Non-floated fractions showed high amounts of carbonate, and presence of hydroxyl iron sulfate (Fe\textsubscript{3}O(OH)\textsubscript{4}(SO\textsubscript{4})\textsubscript{p,x} H\textsubscript{2}O) which have inhibited the hydrophobicity effect of adsorbed xanthate. Environmental desulfurisation could be improved by aeration control causing pyrite oxidation and pH decrease to reach optimal flotation condition with a relatively low xanthate concentration.

INTRODUCTION

Pyrite is the most common sulfide mineral. Pyrite is often associated with other base-metal sulfide minerals and coal. It is generally considered as a barren mineral and concentrated in the mine tailings produced at the mill. However, pyrite is strongly oxidative and generates acid mine drainage and soluble iron by weathering in mine tailings storage areas (eg Ritcey, 1989; Aubertin, Bussière and Bernier, 2002). To limit acid mine drainage generation, mining companies must apply control strategies that aim at preventing oxidation of pyrite, by reducing the presence of oxygen and/or water. A tailings management solution called desulfurisation has been also recently proposed to limit production of AMD from pyritic tailings. It consists in applying the mineral processing technique of froth flotation to the tailings and to manage separately the two fractions produced (Leppinen and Palosaari, 1995; Benzaazoua et al, 2000; Bassière et al, 2004). Desulfurisation has been recently demonstrated as an economically and environmentally effective technique to decrease acid generation potential of mine tailings (Bois et al, 2004).

The desulfurisation technique involves different specific mineral processing challenges. The most critical relates to the difficulty in floating tailings pyrite resulting from a base-metal flotation circuit where pyrite is already depressed. Current mineral processing treatments consist in grinding sulfur-rich ore at a high pH (above pH 10), using lime (CaO) or caustic soda (NaOH). Under such alkaline condition, it is widely accepted that exposed pyrite surfaces are mainly covered by iron oxides and iron hydroxides: Fe(OH)\textsubscript{3}, Fe(OH)\textsubscript{4}, or α-FeOOH (Janetski, Woodburn and Woods, 1977; Hamilton and Woods, 1981; Fuerstenau, 1984; Buckley and Woods, 1987; Wang, 1989; Ahlberg, Forsberg and Wang, 1990; Chander, 1991; Fornasiero and Ralston, 1992; Cases et al, 1993; Chander, Briceno and Pang, 1993; Woods, 1994; Kelsall et al, 1999). However, it has also been demonstrated that sulfates are non-negligible surface species under alkaline conditions, with Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} or Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{3}H\textsubscript{2}O and Fe\textsubscript{2}SO\textsubscript{4} or Fe\textsubscript{3}SO\textsubscript{4}H\textsubscript{2}O often found on pyrite surfaces (Buckley and Woods, 1987; Cases et al, 1990; Cases et al, 1993; de Donato et al, 1993; Godociová et al, 2002; Monte et al, 2002). Lime (CaO) is a widely used pyrite depressant for flotation under alkaline conditions. For decades, calcium adsorption has been clearly identified (Gaudin and Charles, 1953), but no clear identification of calcium species has been published to date (Persson, 1992; Abraitis et al, 2000). Nevertheless, some Ca-bearing species have been postulated: Ca(OH)\textsubscript{2} (Buckley and Woods, 1987), CaSO\textsubscript{4} (Cases et al, 1993), CaO (Xiaojun and Kelebek, 2000), CaCO\textsubscript{3} (Caldeira et al, 2003).

De Donato and coworkers have investigated the spatial distribution of oxidised surface species on pyrite surfaces after dry grinding (de Donato et al, 1993). Surface species are distributed as a pillar of iron sulfates associated with a skeleton of iron hydroxides and hydrated iron oxides. The pillar shows a base made of polysulfide (S\textsubscript{5}S\textsubscript{2}\textsuperscript{-}) and elemental sulfur (S\textsubscript{8}), with a predominance of hydrated ferrous sulfate at the bottom and ferric sulfate dominance at the top (de Donato et al, 1998). Many AFM and STM observations on different oxidised pyrite surfaces have illustrated pillar growth of surface species located at specific zones of oxidation (Eggleson and Hochella, 1990; Eggleson, Ehhrhardt and Stumm, 1996; Abraitis et al, 2000; Miller et al, 2002; Smart et al, 2003).

All these oxidation species adsorbed on pyrite surfaces explain its flotation behaviour, depending on pH and Eh conditions. Pyrite flotation is usually enhanced by addition of organic collectors. Among these, xanthates are the most widely used (Wang and Forsberg, 1991; Wills, 1997). For decades, the three main surface xanthate compounds, xanthate ion, iron-xanthate complex and dixanthogen, have been considered to improve pyrite flotation mechanisms. A combination of surface xanthate species seems to be involved in the pyrite-xanthate interaction at near-neutral pH as synthesised by Wang (1995). First, negatively charged xanthate ions are preferentially attracted to positively charged pyrite surfaces. At pH below 6, the zeta potential studies of Fornasiero and Ralston (1992) showed a positively charged pyrite surface. Then, a metal-xanthate complex forms on the pyrite surface by an ion-exchange reaction; the ensuing ferric dihydroxoy xanthate complex is thermodynamically stable (Wang, Forsberg and Bolin, 1989; Wang and Forsberg, 1991; Fornasiero and Ralston, 1992). Finally, if the redox potential is sufficient, the xanthate ion or iron-xanthate complex could oxidise on pyrite surfaces leading to dixanthogen precipitation which is then physically adsorbed onto the previous iron-xanthate complex layer (Wang and Forsberg, 1991; Cases et al, 1993). Dixanthogen formation depends on equilibrium conditions....
potential ($E_{w}$) of the couple dixanthogen/xanthate ($X_2/X^-$): $E_{eq} = E_0 - 0.059[X]$, according to the Nessut equation and with a standard redox potential ($E_0$) of -0.158 V SHE for amylxanthate (Winter and Woods, 1973; Miller et al., 2002). The stabilisation zone for dixanthogen ($i.e.$ $E_{w}>E_{eq}$) is larger with high concentration of xanthate. Cases and coworkers (1993) have clearly demonstrated that the ferrous-xanthate complex oxidises faster to dixanthogen than the ferric-xanthate complex. The dixanthogen precipitation leads to three-dimensional layers, explaining the large flotation zone between pH 2 and 10 at high collector concentration (de Donato, Cases and Kongolo, 1989; Cases et al., 1989; Cases et al., 1990; Kongolo, 1991; Cases et al., 1993). Dixanthogen formation is critical for pyrite flotation because it is a highly hydrophobic compound, whereas iron-xanthate complex shows low hydrophobic properties (Wang and Forssberg, 1991; Pang and Chander, 1993; Chander and Khan, 2000). For redox potential below the equilibrium potential of the couple $X_2/X^-$, xanthate ion could adsorb onto metal-xanthate complexes and increase hydrophobicity of pyrite surface (Trahar, 1984).

The authors have investigated more specifically the effect of aeration prior to and during pyrite flotation. Infrared spectroscopic surface analyses of floated and non-floated pyrite were used to assess new flotation mechanisms. Pyrite oxidation species and carbonate precipitation in alkaline pH have been identified, suggesting new process conditions for environmental desulphurisation of pyritic mine tailings.

MATERIALS AND METHODS

Materials

The pyrite used for this study came from a hydrothermal deposit in Peru. The chemical and mineralogical analyses showed a high purity for the pyrite sample (Table 1). The analyses were done respectively by x-ray diffraction (Bruker D8 advanced) and by electron probe microanalysis (Cameca SX100). The pyrite sample was grounded with a titanium carbide vibratory disc (Retsch model Mill RS 100) under a dry state and sieved to obtain a fraction between 32 and 63 µm. Particle size distribution within this fraction was controlled by laser diffraction (Malvern Mastersizer S). A specific surface area of 0.12 m²/g was determined by the BET method using nitrogen adsorption for the 32 - 63 µm fraction.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>DRX analysis (wt %)</th>
<th>Chemical composition of pyrite grains (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>99.3 ± 0.2</td>
<td>Fe 47.2 ± 0.5</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>0.4 ± 0.2</td>
<td>S 52.7 ± 0.7</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.3 ± 0.2</td>
<td>Co 0.0250 ± 0.0050</td>
</tr>
</tbody>
</table>

Analytical conditions:

Rietveld quantification method associated with TOPAS software system

Voltage: 20 kV; Counting time: 60 s

Current: 200 mA (Fe and S) and 20 mA (Co)

The reagents used as pH modifier were chemically pure sodium hydroxide and sulfuric acid (Aldrich Chemicals). Lime (CaO) was provided by a base-metal mine; chemical analyses have shown a purity of 90 wt per cent with water and calcium carbonate as impurities. The collector was potassium isoamylxanthate, having an approximate technical purity of 60 - 70 wt per cent (Cytec Chemicals). All xanthate concentrations presented in this paper were adjusted according to the purity of the real xanthate concentration based on analyses performed with UV-visible spectrophotometry (Kongolo et al., 2004).

Experimental and analytical methods

Pyrite flotation tests were made with a small Denver cell of 150 ml, 1000 rpm agitation and natural aeration. No control or measurements of temperature or aeration gas composition were performed during the flotation experiment. An amount of pyrite of 47 g was conditioned with 140 ml of de-ionised water (per cent solid = 25 wt per cent). For each experiment, pyrite was depressed before any other conditioning step: the pH was fixed at 11 with CaO and the pulp was agitated in the flotation cell without aeration during 30 minutes. Two types of experiments were then conducted.

Experiment 1: Pyrite flotation without aeration

In the first experiment, the pH of the pulp was reduced with sulfuric acid, from 11 to the targeted pH. The pulp was agitated in the flotation cell without aeration at the targeted pH during 30 minutes. The pulp was then conditioned with potassium isoamylxanthate during ten minutes. Flotation was pursued during another five minutes. There was no frother addition in these experiments.

Experiment 2: Pyrite flotation with aeration

In the second experiment, pulp aeration was performed during five minutes, right after 30-minute pulp conditioning at pH 11. The pH of the pulp was then adjusted with sulfuric acid or lime to reach the targeted pH. Following this, the pulp was immediately conditioned with potassium isoamylxanthate for ten minutes. Flotation was continued for another five minutes. No frother was added in the Denver cell.

Analytical methods

For all experiments, infrared analyses were performed by diffuse reflectance infrared Fourier transform spectroscopy (Bruker IFS 55 equipped with a Harrick Corporation diffused reflectance apparatus). Flotation products were filtered and air dried on a filter paper under ambient atmosphere for few minutes prior to infrared analyses. The infrared reference was a KBr powder and each sample was diluted at 15 wt per cent with KBr. Pyrite spectra were numerically corrected for atmospheric H₂O and CO₂ pollution by subtracting pure atmospheric H₂O and CO₂ spectra.

Statistical surface coverage of xanthate was estimated by two methods. A theoretical value was calculated according to the formula used by Kongolo and coworkers (2004) based on UV-visible analyses of xanthate concentration at equilibrium. Another value was estimated by observation of the alkyl zone absorption of the infrared spectra (3000 - 2800 cm⁻¹). A calculation of the statistical surface coverage was possible using the absorption area of the alkyl zone and calibration curves established during previous projects (Cases et al., 1989, Mermillod-Blondin et al., in prep a). The notion of statistical surface coverage is calculated with the total surface area of the particle (N₂ adsorption and BET surface). Since xanthate adsorption is limited to oxidised zone; the statistical surface coverage is a comparison parameter and not an absolute value of the collector coverage (Cases et al., 1990).

Mineralogical (DRX) and chemical (EPMA) analysis of the pyrite sample from Peru.

Table 1
The chemistry of the solution was analysed for pH and for redox potential using a platinum electrode with calomel electrolyte ($E_0$ Hg/Hg$_2$Cl$_2$ = 241.5 mV). Redox potential values presented here have been converted to the standard hydrogen reference (SHE).

**RESULTS**

**Experiment 1: Pyrite flotation without aeration**

**Effect of pH**

The preliminary flotation tests were performed with relatively low concentrations of K$_2$AX ($5 \times 10^{-4}$ mol/L) to confirm the flotation behaviour of pyrite, for different pH (Figure 1). Flotation was high at pH 6 and dropped rapidly at a pH above 6 to approach the entrainment recovery value (around ten wt per cent). These results confirm the well-known flotation behaviour (Fuerstenau, Khun and Elgillani, 1968; Fuerstenau, 1980; Jiang et al., 1998; Bulut, Arslan and Atak, 2004), with pyrite flotation being more effective for a pH below 6.

**Effect of xanthate concentration at pH 11**

At pH 11 and $5 \times 10^{-4}$ mol/L of xanthate, flotation recovery was very low; the floated fraction represented only ten wt per cent (Figure 2a). The surface observation showed presence of organic compound but the infrared absorption profile of the alkyl zone did not correspond to amylxanthate carbon chain (Figure 3a-2). No xanthate was observed onto non-floated pyrite (Figure 3a-4). This suggests very weak interactions between xanthate and pyrite under these conditions.

At $1.1 \times 10^{-3}$ mol/L of xanthate, flotation recovery increased to 90 wt per cent (Figure 2b). The surface of the floated fraction showed amounts of xanthate (Figure 3a-3); dixanthogen was identified from the 1266 cm$^{-1}$ vibration band (Figure 3b-3). Iron-xanthate complexes could be suspected but it was not clearly identified. Characterisation band of iron-xanthate complex at 1245 cm$^{-1}$ was overlapped by sulfate species vibration. Cases and coworkers (1989) showed that such adsorption corresponds to one or two layers of xanthate onto the pyrite surface. A small amount of carbonate was also visible on the floated fraction (Figure 3b-3). The infrared spectrum of the non-floated fraction was also indicative of an amount of adsorbed dixanthogen (Figure 3b-5). A large amount of calcium carbonate (band at 1460 cm$^{-1}$) was equally observed (Figure 3b-5). The sulfate vibration band showed an increase in the low vibration at 1020 cm$^{-1}$ characteristic of hydroxyl iron sulfates ($Fe_x(OH)_{y}(SO_4)_{z} \cdot xH_2O$).

**Experiment 2: Pyrite flotation with aeration**

**Effect of aeration time**

Pulp aeration prior to xanthate conditioning induced two major effects. First, physicochemical parameters changed strongly. In the first instant of aeration the redox potential increased by almost 100 mV, then the increase continued slowly adding 100 mV more. At the same time, the pH decreased slowly from 11 to around 9 after five minutes of aeration, when there was no lime addition (Figure 4). The redox potential evolution was correlated with the $O_2/H_2O$ redox couple (Chander, 2003) using the following equation.

$$\frac{1}{2}O_2 + 2H^+ + 2e^- = H_2O$$  

The equilibrium potential is calculated from the Nernst equation:

$$E = E_0 + 0.012 \log(P_{O_2}) - 0.059 \, \text{pH}$$

This equation clearly showed that the redox potential increases when the oxygen partial pressure increases and also when the pH decreases.
Secondly, the pulp aeration increased the amount of superficial carbonate, observed as a vibration band at 1460 cm$^{-1}$ (Figure 5). The carbonate was identified as CaCO$_3$ by the vibration band at 876 cm$^{-1}$ when the carbonate amount was high (van der Marel, 1976). A slight change in the hydroxyl group region suggested the increase of the hydroxides and oxyhydroxides species on the pyrite surface (large band centred on 3300 cm$^{-1}$, not showed in the spectra). Five minutes of aeration did not produce any change in the superficial sulfate species onto pyrite (Figure 5: massive band in the region 1300 - 900 cm$^{-1}$).

**Effect of xanthate concentration at pH 11**

The three flotation experiments led to high recovery of pyrite with pulp aeration: mass recoveries are 90, 94 and 96 wt per cent for 5 × 10$^{-4}$, 7 × 10$^{-4}$ and 1.1 × 10$^{-3}$ mol/L of xanthate concentration respectively (Figure 6). Surface observations showed similar amounts of collector onto floated fractions (Figure 7a-2-3-4).
Differentiation between dixanthogen and metal-xanthate complex was not very precise because of the poor resolution of the 1266 - 1245 cm⁻¹ vibration bands (Figure 7b-2-3-4). Moreover, the sulfate vibration band could overlap xanthate species vibrations. Nevertheless, infrared profile in the range 1300 - 1200 cm⁻¹, appears more characteristic of iron xanthate complex (band at 1245 cm⁻¹). The shoulder at 1266 cm⁻¹, characteristic of dixanthogen, did not appear clearly. Statistical surface coverage was estimated from the alkyl chain absorption of the adsorbed xanthate. These calculations have resulted in one to two layers of xanthate adsorbed onto floated fractions (Figure 8), which have confirmed the good recovery and have suggested the adsorption of the collector as a mixture of iron-xanthate complex and dixanthogen. However, the adsorption was too weak to identify clearly xanthate species as explained elsewhere (Mermillod-Blondin et al, in prep a). All floated fractions showed a relatively important amount of calcium carbonate (Figure 7b-2-3-4). The non-floated fractions showed higher amounts of xanthate than the floated fraction (Figure 7a-5-6-7). These amounts of xanthate corresponded to high statistical surface coverage of three to seven layers (Figure 8). The profiles of the vibration bands 1266 - 1245 cm⁻¹ provided good resolution to identify the two bands characteristic of dixanthogen (band at 1266 and 1025 cm⁻¹) and iron-xanthate complex (band at 1245 cm⁻¹). The increase in xanthate concentration led to an increase in dixanthogen adsorption onto non-floated pyrite surface (Figure 7b-5-6-7; band at 1266 cm⁻¹). The amount of calcium carbonate observed onto non-floated fractions is also higher than on the floated fractions. Carbonates could depress pyrite flotation even if xanthate adsorption was high, confirming the observations of the spectra in Figure 3. Moreover, the presence of hydroxyl ferric sulfate (band at 1020 cm⁻¹) could also increase hydrophilic properties of the pyrite surfaces. The vibration band at 1020 - 1025 cm⁻¹ was too high to contain only dixanthogen component. The dixanthogen bands at 1266 and 1020 cm⁻¹ show usually similar relative absorbance (Kongolo, 1991).

The chemical characteristics of the flotation fractions have changed during aeration. A significant decrease in the pulp pH was observed (Table 2b). Floated fractions showed a pH closer to 11 than non-floated fractions. The aeration duration of the floated fractions was shorter because of concentrate extraction, confirming the pulp aeration observations on aeration effects mentioned above.

All the flotation spectra show the disappearance of the vibration band at 1160 cm⁻¹ observed during lime conditioning. This band could correspond to Fe₂(SO₄)₃.9H₂O (Farmer, 1974; Baláz, 2000; Centenary of Flotation Symposium Brisbane, QLD, 6 - 9 June 2005 687
Godocíková et al, 2002) or hydroxyl iron sulfates (van der Marel and Beutelspacher, 1976). No change in the sulfate state was observed by simple aeration, as shown in Figure 5. The xanthate-pyrite interaction could be responsible for the desorption of Fe$_2$(SO$_4$)$_3$.9H$_2$O and hydroxyl iron sulfates after flotation.

**DISCUSSION**

Following the results presented above, various points are discussed, including: the production mechanisms and the depressant role of calcium carbonate; the pyrite-oxygen interaction during pulp aeration resulting in the production of reactive sites onto pyrite surface; and the nature of the adsorbed layers produced by xanthate adsorption. An illustrative model of xanthate adsorption onto pyrite surface is suggested. Application to desulfurisation ends the discussion.

**Role of carbonates: formation and depression effect**

The presence of calcium carbonate on the pyrite surface and the decrease of pH with aeration demonstrated that aeration had an important effect on the pulp chemistry by means of gas interaction with the solution (Evangelou and Huang, 1994; Caldeira et al, 2003). Precipitation of CaCO$_3$ confirmed the aqueous formation of CO$_3^{2-}$ from CO$_2$ of the aeration gas, which rapidly precipitates as CaCO$_3$ due to the high amount of Ca$^{2+}$ provided by CaO (Equations 3 and 4). These equations also show that H$^+$ was produced and that dissolution of CO$_2$ implied a pH decrease confirmed by the graph presented in Figure 4.

\[
\text{CO}_2(g) + \text{H}_2\text{O} = \text{CO}_3^{2-}_{(aq)} + 2\text{H}^+_{(aq)} \tag{3}
\]

\[
\text{CO}_3^{2-}_{(aq)} + \text{Ca}^{2+}_{(aq)} = \text{CaCO}_3(s) \tag{4}
\]
PYRITE FLOTATION WITH XANTHATE UNDER ALKALINE CONDITIONS

Non-floated fractions conditioned with aeration showed a high amount of xanthate on pyrite surfaces. The authors have suggested that the hydrophobicity induced by adsorbed xanthate was balanced by calcium carbonate precipitation. Under these conditions, calcium carbonate would play the role of depressant for pyrite flotation despite the high amount of collector. This phenomenon is linked to the amount of carbonate present in the system. In the floated fractions, the hydrophobicity from xanthate adsorption was still predominant and favoured pyrite flotation. Pyrite was extracted from the system, showing a sufficient amount of xanthate at the surface (one or two layers) and a limited amount of carbonate. With aeration time, carbonate precipitation and/or adsorption increased as shown in Figure 5. The increased concentration of hydroxides and oxyhydroxides species with aeration time emphasised the role of oxygen in pyrite surface oxidation. Dissolved oxygen interacts with surface species of pyrite through oxidation of superficial ferrous iron rather than production of sulfate (Lowson, 1982; Moses et al., 1987; Guevremont et al., 1998; Rimstidt and Vaughan, 2003; Borda, Strongin and Schoonen, 2004). The sulfate formation requires a longer oxidation time. This explains why there was no change observed on the sulfate vibration band (Figure 5: region 1300 - 900 cm\(^{-1}\)). Moreover, under alkaline conditions, the oxidation process is controlled by ferric hydroxides or oxyhydroxides stability (Bonnissel-Gissinger et al., 1998; Todd, Sherman and Purton, 2003; Abraitis et al., 2000). Equations 5 and 6 show that acidity is also produced by this process.

\[
\text{FeS}_2 - \text{Fe}^{2+} (\text{surf}) + \frac{4}{3} \text{O}_2 (\text{aq}) + 2\text{H}_2\text{O} = \text{FeS}_2 - \text{Fe(OH)}_3 (\text{surf}) + 2\text{H}^+ (\text{aq}) \tag{5}
\]

\[
\text{FeS}_2 - \text{Fe}^{2+} (\text{surf}) + \frac{1}{3} \text{O}_2 (\text{aq}) + \frac{1}{3} \text{H}_2\text{O} = \text{FeS}_2 - \text{FeOOH} (\text{surf}) + 2\text{H}^+ (\text{aq}) \tag{6}
\]

At the same time, oxidation of sulfur site could lead to the formation of polysulfide or elemental sulfur. Only this last species would increase hydrophobicity of the pyrite surfaces. However, confirmation was not possible because the sulfur vibration bands did not appear in the infrared spectra.
Xanthate adsorption: nature of the adsorbed layers

The calculation of the equilibrium half-cell potential for the $X_2/X^-$ couple at different initial xanthate concentration (Table 3) showed that the redox potential was sufficient for dixanthogen formation at any time during flotation step.

**Table 3**

<table>
<thead>
<tr>
<th>Initial xanthate concentration (mol/L)</th>
<th>Equilibrium half-cell potential for the $X_2/X^-$ couple (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-4}$</td>
<td>37</td>
</tr>
<tr>
<td>$7 \times 10^{-4}$</td>
<td>28</td>
</tr>
<tr>
<td>$1.1 \times 10^{-3}$</td>
<td>17</td>
</tr>
</tbody>
</table>

The infrared spectra of the floated fractions with aeration (Figure 7) did not provide an identification of the nature of the xanthate species responsible for pyrite flotation. The statistical surface coverage was below the xanthate species detection and the xanthate-mineral vibration band was strongly overlapped by the sulfate vibration bands induced by lime depression (Kongolo et al., 2004; Mermillod-Blondin et al., in prep a). However, a mixture of iron-xanthate complexes and dixanthogen could be suggested, based on the IR profile of the non-floated fraction where iron-xanthate complexes (band at 1245 cm$^{-1}$) and dixanthogen (band at 1266 cm$^{-1}$) were observed. Moreover, the xanthate statistical surface coverage of the floated fraction was slightly superior to the monolayer, which is judged to be sufficient for flotation according to the conclusions drawn by Cases and coworkers (1993); these authors have suggested that theoretically, iron-xanthate complexes formed onto pyrite surfaces is limited to a monolayer. Moreover, a slight amount of iron-xanthate complexes and dixanthogen were involved with pyrite flotation under alkaline conditions (Mermillod-Blondin et al., in prep b).

**Xanthate adsorption model**

Conscious of the difficulties in proposing a model for the complex surface phenomena, the authors have suggested an illustrative model to have a global view of pyrite surface state modifications at pH 11 and xanthate adsorption (Figure 9). This illustrative model was based on the spatial distribution of pyrite oxidised species as described by de Donato and coworkers (1993). The location of the xanthate complexation with superficial ferric iron tends to indicate that aeration has directly increased superficial ferric sites as iron hydroxides and oxyhydroxides. No sensible increase of the sulfate vibration band has been noted. The aeration has led to a growth of the pillar structure limited to the iron hydroxide oxyhydroxide skeleton (Figure 9). Therefore, sulfates did not seem to be essential for site reactivity and xanthate interaction onto pyrite surface. This could also indicate that only a limited part of such mixed sulfates forming the pillar structure was involved in the metal-xanthate complexation. However, numerous studies have emphasised the increase of sulfate in solution after xanthate adsorption. Figure 7 shows the decrease of $Fe_2(SO_4)_{3.9}H_2O$ and hydroxyl iron sulfate from the spectrum of the pyrite conditioned at pH 11, floated fraction with aeration. These species were located at the top of the pillar structure of oxidation species on the surface of pyrite. The authors have suggested that the formation of xanthate...
complexes with ferric iron could also be associated with a degradation of a complete pillar as described in the literature (de Donato et al., 1993, Miller et al., 2002). The interaction would be located essentially close to the top of the pillar and would lead to the liberation of the underlying reactive ferric sites (Figure 9). Some carbonate could be fixed close to the pillar structure due to reaction with the adsorbed calcium ions. The amounts of iron-xanthate complexes and dixanthogen moderated by the amounts of carbonates and hydroxyl iron sulfates would control the floatability of the pyrite particle.

Application to environmental desulphurisation

The statistical surface coverage calculations of Figure 8 show that high collector concentrations were not very efficient because only a monolayer of xanthate is sufficient for flotation. The remaining xanthate was oxidised to dixanthate at the surface of the non-floated pyrite. According to Figure 8, around 5 × 10⁻³ mol/L of xanthate would be the optimal concentration, as floated and non-floated fractions showed the same statistical surface coverage of xanthate. Taking into account the amount of pyrite used for the flotation tests, the optimal xanthate concentration would approach 100 g/t for a tailing containing 30 wt per cent pyrite.

CONCLUSIONS

Results from the flotation tests of pyrite conditioned at pH 11 with lime have led to the following conclusions.

- Solubilisation of O₂ and CO₂ during flotation aeration had an antagonistic effect on pyrite flotation. The gases have activated pyrite surface by increasing ferrous iron oxidation to superficial ferric hydroxides and oxyhydroxides and by decreasing the pulp pH. On the other hand, CO₂ has precipitated the hydrophilic calcium carbonate which adsorbed onto pyrite surfaces.
- Pyrite flotation was efficient with a statistical monolayer of xanthate. Xanthate species responsible for pyrite flotation in alkaline pH would be a mixture of iron-xanthate complexes overlaid by dixanthogen.
- Hydrophobic properties of the pyrite surface with xanthate adsorption were balanced by carbonates and dixanthogen. A threshold ratio (iron-xanthate complex + dixanthogen)/(carbonates + hydroxyl iron sulfates) could control the flotation fractioning between floated and non-floated parts.
- Environmental desulphurisation of pyrite-rich tailing could be pursued by controlling aeration, which involves pyrite surface oxidation and pH decrease. A relatively low xanthate concentration would be efficient taking into account the high pyrite composition of some tailings.

ACKNOWLEDGEMENTS

The authors would like to acknowledge funding obtained from the NSERC Polytechnique-UQAT Industrial Chair. The authors would like to express their deepest gratitude to the referees for the pertinent suggestions.

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