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Published in:
Minerals Engineering

DOI:
10.1016/j.mineng.2021.106985

Published: 01/08/2021

Document Version
Publisher's PDF, also known as Version of record

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The effect of sodium isobutyl xanthate on galena and chalcopyrite flotation in the presence of dithionite ions

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ARTICLE INFO

Keywords:
Galena
Chalcopyrite
Surface oxidation
FTIR Analysis
XPS Analysis
Xanthate decomposition

ABSTRACT

Sulphoxy anions in recycled flotation process waters possess the potential to reduce the flotation efficacy of flotation reagents. In this study, dithionite ions and their interaction with thiol collectors in solution and the surface modifications of galena and chalcopyrite surfaces in the presence of dithionite ions were investigated. Microflotation tests, zeta potential tests, electrochemistry studies, solution xanthate degradation kinetics and surface analyses were carried out. Microflotation results showed a reduction in chalcopyrite and galena recoveries in dithionite solutions even in the presence of xanthate. Zeta potential and rest potential measurements showed that the potential determining effect of dithionites on the sulphide mineral surfaces (zeta potentials) and the solution (pulp potential), inherently decrease collector-mineral interactions. Xanthate degradation tests showed that more than half of the collector in solution was consumed in 10 min of reacting 20 mg/L of xanthate with 500 mg/L of dithionites. Surface analyses results also revealed that dithionites strongly influenced the chemical state of the sulphide minerals under investigation by producing oxidised sulphur species in the form of sulphites on the galena surface and oxidised iron species in the form of oxides and hydroxides on chalcopyrite. The current study presents a complete view of dithionite behaviours in plant waters by considering the dithionite-mineral surface interactions and dithionite-collector interactions in addition to the traditionally agreed on pulp potential alterations.

1. Introduction

Short circuit recycling of flotation process waters entails the reintroduction of water from units such as thickeners and filters into the flotation circuit, bypassing tailings ponds. It results in process water return streams loaded with multiple metastable sulphoxy intermediates (thiosalts) which are not fully oxidised to the thermodynamically stable sulphate species (Negeri et al., 1999). Owing to the complex chemistry of the multiple sulphoxy species, multiple oxidation-reduction couples are present in the system making it difficult to study the kinetics and speciation under various conditions (Miranda-Trevino et al., 2013; Negeri et al., 1999). Some of these sulphoxy species present in flotation solutions are often overlooked owing to their short residence time before decomposition and difficulty in identification using conventional analytical techniques. One such species is the dithionite ions (S2O4 2-), which are an intermediate product in the oxidation of tetrathionate to higher oxidation state sulphoxy compounds (Chander and Briceno, 1987; Peres, 1979). At neutral to slightly alkaline pH, the dithionite ions are a precursor to the formation of trithionates (S3O6 2-) and metabisulphite (HSO3 -) ions, products of the oxidation and rearrangement of tetrathionate (S4O6 2-) ions (Munchow and Steudel, 1994; Peres, 1979). Dithionites easily react with water, but they are constituents of the suite of sulphoxy compounds in flotation process waters, and ought to be investigated as water recycling will lead to future increases of their concentrations in plant water.

In plant practice, dithionites have also been used as pulp potential (Eh) modifiers and as depressants in the flotation of lead bearing ores (Prestidge et al., 1993). Existing research recognizes the critical role played by dithionites in controlling the Eh in the flotation of galena from pyrite and sphalerites. Sulphide mineral depression is achieved through electrochemical alteration of the pulp and reducing the dissolved oxygen (DO) content thereby retarding (i) collector adsorption and (ii) mineral oxidation (Guy and Trahar, 1984; Heyes and Trahar, 1979; Kydros et al., 1993). Literature is scarce on the action of dithionites at the solid-liquid
interface of sulphide minerals. However, it has been established that dithionites in solution reduce the dissolution of galena and inherent release of Pb\(^{2+}\) into solution, effectively limiting sphalerite activation and flotation (Sui et al., 2000).

Research to date is yet to holistically view the possible side reactions between dithionite and collectors occurring in solution, the dithionite–mineral surface interactions, and the traditionally agreed on Eh alterations and their effect on flotation performance. Therefore, the objective of the current study is to holistically address the possible sources of poor galena and chalcopyrite flotation in the presence of dithionite ions. Xanthate solution decomposition kinetics will be evaluated under different conditions of pH and gas. Fourier Transform Infrared Spectroscopy (FTIR) studies which have previously been widely used to identify xanthate species on sulphide minerals will be presented in this paper. X-ray Photoelectron Spectroscopy (XPS) will provide a quantitative and qualitative view of the state of mineral oxidation and elemental composition on the sulphide minerals after exposure to dithionite ions. The findings from these studies should make an important contribution to the field of water chemistry in the flotation of sulphide minerals, a topic of interest to mineral processing professionals.

2. Experimental

2.1. Materials

2.1.1. Mineral sample preparation

Galena and chalcopyrite samples from Ward’s Natural Science Establishment, (Rochester, NY, USA) were crushed followed by pulverization using a laboratory disk mill (Siebtechnik) and screening to obtain 4 size fractions (25–28 μm; 25–38 μm; 38–108 μm and 108–125 μm). The samples were split into representative 2 g samples and packed in bottles purged with nitrogen. The sample bottles were stored in the freezer at –17 °C, and they were only removed just before use in an experiment. XRD analysis of the mineral samples showed that the minerals were of high purity as summarized in Table 1. Galena was 98.2% pure with 1.8% of impurities. Chalcopyrite was 94.3% pure with chloride and magnetite as the major impurities.

2.1.2. Reagents

Analytical grade sodium dithionate, (Na\(_2\)S\(_2\)O\(_4\)) (Sigma Aldrich) was used throughout this study except for when deionised water was utilised. When required sodium tetraborate decahydrate, (Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O) (Sigma Aldrich) was used as a buffer for pH stability. Sodium isobutyl xanthate (SIBX) from Senmin, South Africa was used as a collector in all tests. A fresh 1% w/v SIBX stock solution was prepared before any experiments were conducted. NaOH from Merck (Darmstadt, Germany) and HCl (37%) obtained from VWR Chemicals (Darmstadt, Germany) were prepared as required and used as pH modifiers in all the tests.

2.2. SIBX decomposition in dithionites solutions.

Decomposition studies were conducted in 500 mg/L, 250 mg/L and 100 mg/L dithionite solutions. The wide range of concentrations used in this study was tailored for ease of analysis. The reactions were initiated by adding 50 μL of a 1% w/v stock solution of SIBX to the dithionite solution. The reaction was monitored for 1 h. At selected times, aliquots of the solution were drawn and the residual xanthate in solution was measured using the HACH DR6000 UV/Vis spectrophotometer (Hach Lange GmbH, Düsseldorf, Germany) at a wavelength of 301 nm. To study the effect of gas purging on the decomposition kinetics of SIBX in dithionite solutions, the solutions were purged with oxygen gas and nitrogen gas for 1 h before adding SIBX to the dithionite solution. Gas purging was also maintained throughout the adsorption reaction. Nonlinear regression and Excel’s Solver function were employed in evaluating the decomposition kinetics at all conditions.

2.3. Zeta potential studies

Zeta potentials measurements were conducted using a Malvern Zetasizer (Malvern, United Kingdom). The equipment tracks the electrophoretic mobility of particles in a dilute solution in which an electric field is applied, converting the electrophoretic mobilities into zeta potentials using the Smoluchowski equation (Fuerstentau and Pradip, 2005). The zeta potentials of fine mineral particles in a dilute solution, of deionised water or dithionite were measured utilizing a 633 nm laser beam. The equipment operation and data capturing were performed using the built-in Malvern Software v.7.11. Before analysis, 80 mg of finely ground ~5 μm fraction of mineral particles was conditioned in deionised water and dithionite solutions respectively. Conditioning of the minerals in solution was carried out for 20 min. 0.001 M KNO\(_3\) was utilised as an indifferent electrolyte in all measurements. After conditioning, the mixtures settled for 5 mins before aliquots of the supernatant were drawn and transferred to a Malvern dip cell for analysis. The zeta potentials were evaluated at pH values between pH 3 and pH 11.

2.4. Rest potential measurements

Rest potential data were collected under three experimental conditions: in the presence of xanthate and tetraborate buffer (pH 9); in the presence of a tetraborate buffer + xanthate + 500 mg/L dithionite ions and the presence of a tetraborate buffer + xanthate + 2000 mg/L dithionite ions. Galena and chalcopyrite electrodes were used as test minerals. The electrode construction is well explained in Tadie et al. (2015). A three-electrode electrochemical cell was arranged with potentials measured relative to the Ag/AgCl and reported against a platinum standard hydrogen electrode (SHE). Before rest potential measurements, the mineral was polished using a 600-grit silicon carbide paper, followed by finer polishing with alumina powders from IMP Spectrum (FTIR-ATR) spectrometer (Perkin Elmer Inc, Waltham, MA, USA) and Gamry Framework computer software (version 7). The rest potentials were measured in the absence of reagents for 600 s and 1500 s for galena and chalcopyrite, respectively, allowing the surface to equilibrate, followed by SIBX addition at 2.4 × 10\(^{-4}\) M.

2.5. FTIR measurements

FTIR measurements were carried out using a Perkin Elmer-Two Spectrum (FTIR-ATR) spectrometer (Perkin Elmer Inc, Waltham, MA, USA). The equipment is fitted with a LiI\(_2\)O\(_2\) (lithium tantalate) detector and KBr detection windows for data collection from 350 cm\(^{-1}\) to 8000 cm\(^{-1}\). Infrared (IR) readings of species on the mineral surface were collected after 32 scans. Before IR readings were recorded, 1 g of mineral sample was conditioned in a solution of deionised water with 5 × 10\(^{-4}\) M SIBX or a dithionite solution with 5 × 10\(^{-4}\) M SIBX at the desired pH. The mixture was conditioned for 30 min. After conditioning, the mineral sample was filtered with an MN615 grade cellulose filter paper (Macherey-Nagel- Duren, Germany) of 0.16 mm thickness and pore size of 4–12 μm. A final wash with deionised water and acetone was applied.
to remove excess xanthate solution. The mineral sample was directly placed on the ATR crystal and pressed down for IR readings.

2.6. XPS measurements

XPS analyses were performed using an AXIS Ultra (Kratos Analytical) applying monochromatic Al Kα irradiation at 100 W. Samples were attached to the sample holder with an ultra-high vacuum compatible carbon tape, and pre-evacuated overnight before the measurement. An initial survey of the sulphide mineral surface was carried out to identify the major elements. Wide energy range survey spectra were recorded using 80 eV and 1 eV step, and the high-resolution elemental regions were measured using a 20 eV pass energy and 0.1 eV steps. Each sample was measured from 2 to 4 different locations. Atomic concentrations were measured from the relative peak areas of the spectra and recorded as percentages of all the scanned elements. Data from the in-situ Aalto reference sample of 100% ash-free cellulose was recorded with every sample batch, to evaluate vacuum conditions. The CasaXPS software v 2.0 was used in the analysis, and all the spectra were charge corrected using the high-resolution C 1 s main component (carbon without oxygen neighbours) at 285 eV as the reference. Before XPS analyses, mineral samples were conditioned in the same way as the FTIR samples.

2.7. Microflotation studies

Microflotation studies were performed using the University of Cape Town microflotation rig. The rig design is described in a previous publication (Bradhaw and Conner, 1996). Two grams of mineral sample, 38–108 μm, was sonicated with a WVR Ultrasonic cleaner at power rating 9, for 5 min before conditioning. Sonication was applied to deagglomerate the mineral sample. The sonicated sample was then conditioned for 30 min at pH 8.5 in either deionised water or a dithionite solution of the desired concentration. SIBX was added to the mineral slurry mixture during the conditioning and conditioning in the presence of SIBX was carried out for 3 min. SIBX was added to achieve a 50% pseudo-monolayer coverage as calculated from the active collector content and Brunauer–Emmett–Teller (BET) surface areas of the minerals under investigation. Table 2 summarises the BET surface areas of galena and chalcopyrite.

The conditioned mixture was transferred to the microflotation cell. Air was introduced at 8 L/min using a needle connected to a peristaltic pump. The hydrophobic sample was collected in the concentrate launder. The concentrates were collected after 2, 6, 12 and 20 min of flotation and filtered using an MN615 grade cellulose filter paper. The filtrate was oven-dried at 70 °C before final weighing and mineral recovery calculations.

3. Results and discussion

3.1. SIBX and dithionite interaction in solution

3.1.1. Effect of pH on the decomposition kinetics of SIBX

The residual concentration of xanthate in solution was normalized using the original xanthate concentration in solution at time t = 0 min. As can be seen in Fig. 1, SIBX degradation over 1 h shows that more than 50% of the SIBX is decomposed in the first 10 min of reacting 20 mg/L with a 500 mg/L solution of dithionite ions. Previous studies have shown that no significant xanthate decomposition occurs in deionised water at neutral to alkaline pH i.e., in the absence of sulphox compounds. Decomposition is most significant at highly acidic conditions and high temperatures (Mhonde et al., 2020; Shen et al., 2016).

At pH 5 and 7 there is an appreciable drop in pH indicative of the release of H+ ions into solution during the reaction. A mechanism to support this observation is discussed in Section 3.1.4. Rate constants were calculated using nonlinear least-squares regression analysis. To support the nonlinear least-squares fitting, linear least-squares regression was also applied applying Equation (1) and Equation (2).

\[
\frac{C_t}{C_0} - \left( \frac{C_t}{C_0} \right)_\infty = \left( \frac{C_t}{C_0} \right)_{\text{initial}} - \left( \frac{C_t}{C_0} \right)_{\text{baseline}} \cdot e^{-kt} \quad (1)
\]

\[
\ln \left( \frac{C_t}{C_0} - \left( \frac{C_t}{C_0} \right)_{\infty} \right) = \ln \left( \frac{C_t}{C_0} \right)_{\text{initial}} - \ln \left( \frac{C_t}{C_0} \right)_{\text{baseline}} \cdot -kt \quad (2)
\]

The reaction is first order with respect to the SIBX in solution. The logarithm of the normalized residual concentration versus time as shown in Fig. 2 shows a linear relationship that is expected of first-order reactions. The rate constants (from nonlinear least-squares regression) summarized in column 2 of Table 3 show that the fastest decomposition was observed at pH 3 as expected because xanthates are unstable in acidic conditions (Shen et al., 2016; Yamamoto, 1981). However, in the operating pH conditions usually expected for galena and chalcopyrite flotation (pH 7–10), the fastest decomposition was observed at pH 7. Grano et al. (1997a) suggest that the observed fast decomposition around pH 7 is indicative of the presence of HSO3⁻ in solution, which catalyses SIBX decomposition.

As the SIBX decomposed, an intermediate by-product formed with an absorption peak at 346–350 nm. This peak has been identified as perxanthate in previous studies on sulphite ions evaluated in the literature (Grano et al., 1997c; Misra et al., 1985; Yamamoto, 1981). Monitoring the perxanthate in solution showed that the intermediate gradually disappears with reaction progress as presented by absorbance values in

### Table 2

<table>
<thead>
<tr>
<th>Mineral</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galena</td>
<td>0.0688</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>0.2327</td>
</tr>
</tbody>
</table>

![Fig. 1. Normalised residual xanthate concentration in solution after decomposition in 500 mg/L dithionite solution at pH 3, 5, 7, 9, 11. ΔpH was monitored at pH 5 and 7, where there was a significant change in pH. Starting SIBX solution = 20 mg/L.](image1)

![Fig. 2. Natural logarithm of the residual xanthate concentration after reacting SIBX with dithionite ions.](image2)
Fig. 3 and Fig. 4. The fastest increase in absorbance (concentration) and decrease in absorbance values of perxanthate is observed at pH 7 followed by pH 9. At other pH values tested (pH 3, 5 and 11) the reaction is either too fast or too slow resulting in no peaks at 346 nm. There was no evidence of the formation of xanthyl thiosulphate which is usually associated with a shift in the xanthate UV peak from 301 nm towards 290 nm. Xanthyl thiosulphate has been previously observed in past studies which investigated the interaction of sulphoxy compounds e.g. sulphites, thiosulphates and tetrathionates with xanthates in flotation liquors (Jones and Woodcock, 1981; Yamamoto, 1981).

3.1.2. Effect of dithionite concentration on SIBX decomposition in solution

Fig. 5 shows the overall decomposition of SIBX in the absence and presence of three starting concentrations of dithionite ions at pH 5, 7, 9 and 11. Reducing the concentration of dithionites in solution resulted in a decline in the overall SIBX decomposition and reaction kinetics. In these experiments, a concentration of 500 mg/L dithionites almost degraded all the SIBX in 1 h. The lowest decomposition kinetics and overall xanthate removal from solution is exhibited at pH 11. From this observation, it can be said that at pH 11, the extent of interaction between dithionite ions and xanthate decreases, however, some xanthate degradation is still present in the solution. Dithionites are stable compounds above pH 6. Munchow and Steudel, (1994) showed that dithionites in aqueous solutions exhibited little decomposition in 120 min in neutral to alkaline conditions. In high alkaline conditions (ca. pH 13), the dithionite stability lasted for more than 4 days.

3.1.3. Effect of gas purging on SIBX decomposition in dithionite solution

Purging the SIBX + dithionite solutions with oxygen and nitrogen was aimed at assessing the significance of the processing gas on the SIBX + dithionite reaction. In Fig. 6, the non-linearised decomposition kinetics of SIBX in oxygen (a) and nitrogen (b) are illustrated. As seen in Fig. 6(a) in presence of oxygen, the decline in normalized residual xanthate concentrations is greater at pH 7. At pH 9, a delay (induction period) exists before the concentration declines, and interestingly, at pH 11 decomposition was absent. The induction period is consistent with findings by Yamamoto, (1981) and Shen et al. (2001). Both authors observed induction periods in the decomposition of xanthates by sulphite ions in the presence of oxygen. Shen (2001) also observed that SIBX decomposition by sulphite ions in oxygen-enriched solutions only occurred when the concentration was increased tenfold, although no plausible explanation for this occurrence was provided. In nitrogen purged solutions, the decomposition rates of SIBX are significantly retarded as seen in Fig. 6(b). This was attributed to the removal of oxygen from the system rendering the kinetics slow (see Table 3). From Fig. 6 it can be inferred that the decomposition reaction is dependent on the dissolved oxygen in solution in agreement with studies by Misra et al. (1985) on SO2 decomposition of xanthates. These results indicate similarities in reaction mechanisms for sulphur dioxide interactions with xanthate and dithionite interactions with xanthates. A discussion of the mechanism is presented in the following section.

3.1.4. Mechanisms of SIBX decomposition in the presence of dithionite ions

The current investigation on solution interactions of dithionites and xanthate has revealed a xanthate decomposition behaviour consistent with that observed when sulphite ions or sulphur dioxide interact with xanthate ions. It can be inferred that the products from the decomposition of dithionites according to Equation (3) characterize the behaviour of dithionites ions in xanthate solutions. Dithionites have been noted to decompose in water to produce bisulphite ions (HSO3-) and thiosulphate ions (Lister and Garvie, 1959; Munchow and Steudel, 1994).

\[
2S_2O_4^{2-} + H_2O = 2HSO_3^- + S_2O_3^{2-}
\]  

(3)

Table 3
Rate constants (k) for the degradation of 20 mg/L of SIBX in 500 mg/L dithionite solution in a standing solution, oxygen bubbled solution and nitrogen bubble solution.

<table>
<thead>
<tr>
<th>pH</th>
<th>Rate Constants (k)/ min^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S2O4 Solution</td>
</tr>
<tr>
<td>3</td>
<td>0.254</td>
</tr>
<tr>
<td>5</td>
<td>0.116</td>
</tr>
<tr>
<td>7</td>
<td>0.162</td>
</tr>
<tr>
<td>9</td>
<td>0.150</td>
</tr>
<tr>
<td>11</td>
<td>0.114</td>
</tr>
</tbody>
</table>

Fig. 4. Monitoring perxanthate formation at pH 7 (a) and pH 9 (b) in the reaction between 20 mg/L SIBX and 500 mg/L dithionite solutions.
The bisulphite is a key reactant in the decomposition of xanthate in solution. Jones and Woodcock (1988), reported that the bisulphite ion is a precursor to the formation of the peroxymonosulphate ion. The latter reacts with xanthate ions to form perxanthate ions as in Equation (4) and Equation (5). The reaction consumes oxygen concomitantly releasing $\text{H}^+$ into the solution. Misra et al. (1985) and Yamamoto (1981) also reported a decrease in pH around neutral conditions alluding to the release of $\text{H}^+$ ions in solution. The perxanthate is simultaneously consumed according to Equation (6) forming alcohol, thiosalts and carbon dioxide.

$$\text{HSO}_3^- + \text{O}_2 \rightarrow \text{SO}_3^{2-} + \text{H}^+ \quad (4)$$

$$\text{ROCSS}^- + \text{SO}_3^{2-} \rightarrow \text{ROCSSO}^- + \text{SO}_4^{2-} \quad (5)$$

$$\text{ROCSSO}^- + 3\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{ROH} + 3\text{SO}_4^{2-} + \text{H}^+ + \text{CO}_2 \quad (6)$$

On investigating the decomposition of xanthate by SO$_2$, Misra et al. (1985) proposed a mechanism where peroxide is a prerequisite for the decomposition to occur corroborating suggestions by Yamamoto (1981). Misra et al. (1985) further postulated intermediate steps entailing the formation of peroxide and perxanthate ions. In summary, the bisulphite ion produced upon SO$_2$ decomposition and dithionite decomposition is unstable and it decomposes to sulphite ions, Equation (7). The sulphite ion in turn consumes oxygen in solution to form the peroxymonosulphate ion, Equation (8). In contact with water, the peroxymonosulphate ion also reacts to form peroxide, Equation (9). The final stages of decomposition entail the xanthate ion reacting with hydrogen peroxide, forming an intermediate perxanthate ion which further reacts with the hydrogen peroxide to form bisulphite ions, alcohol and carbon dioxide, Equation (10) and Equation (11).

$$\text{HSO}_3^- + \text{O}_2 \rightarrow \text{SO}_3^{2-} + \text{H}^+ \quad (7)$$

$$\text{SO}_3^- + \text{O}_2 \text{SO}_3^{2-} \quad (8)$$

$$\text{SO}_3^{2-} + \text{H}_2\text{O} \text{H}_2\text{O}_2 + \text{SO}_4^{2-} \quad (9)$$

$$\text{ROCSS}^- + \text{H}_2\text{O}_2 \rightarrow \text{ROCSSO}^- + \text{H}_2\text{O} \quad (10)$$

$$\text{ROCSS}^- + \text{H}_2\text{O}_2 + 4\text{O}_2 \rightarrow \text{4HSO}_3^- + 2\text{ROH} + \text{CO}_2 + 2\text{H}^+ \quad (11)$$

The mechanisms differ slightly; however, they agree on the formation of perxanthate and release of $\text{H}^+$ ions in solution. The changes in pH in Fig. 1 and the presence of perxanthate as shown in Fig. 3 support these equations. The current study highlights that once dithionite ions are generated through oxidation of tetrathionates or when added as reagents to flotation waters, their immediate decomposition products consume xanthate. The solution interaction of SIBX and dithionites ought to be considered when discussing depression mechanisms of dithionites in process plant waters together with the more commonly discussed electrochemical modification to the pulp.

### 3.2. Zeta potential measurements of galena and chalcopyrite in dithionite solutions

To investigate the potential determining effect of dithionites at the solid-liquid interface of sulphide minerals, zeta potential tests were...
conducted. Fig. 7 illustrates the zeta potential of galena and chalcopyrite after conditioning in deionised water and two concentration levels of dithionite solutions. In Fig. 7(a), galena is negatively charged at all pH values in all conditions tested. As seen in Fig. 7(b), the zeta potential of chalcopyrite is affected by pH. An isoelectronic point is observed between pH 5 and pH 6 in support of observations by Mitchell et al. (2005).

It must be noted that the value for the isoelectronic point of chalcopyrite varies in the literature. The sulphide surface-solution interface is affected by the oxidation state of the mineral surface, mineral purity, pre-conditioning and pretreatment. As a result, the same sulphide minerals can have variable isoelectronic points (Ralston, 1991; Reyes-Bozo et al., 2015). As the concentration of dithionites in the solution increases, the zeta potential of the sulphide minerals is more negative. This decline in zeta potential is indicative of specific adsorption of dithionites and their decomposition species on the sulphide minerals (Miller, 1970). The sulphite and thiosulphate ions formed in the solution can react with galena to form lead sulphite on galena and copper thiosulphate complexes on chalcopyrite (Eliseev and Kirsitova, 1984; Shimoiizaka et al., 1976; Sui et al., 2006). These species have been reported to passivate the mineral surface through competitive adsorption or ion exchange with previously adsorbed xanthate (Shimoizaka et al., 1976).

3.3. Rest potential measurements

3.3.1. Rest potential measurements on galena in the presence of dithionites

To assess the extent of collector-mineral interactions in an electrochemically altered solution, rest potential measurements were applied on galena. Fig. 8 illustrates the rest potential of galena under different solution conditions. The extent of the drop in mixed potential and the associated gradient after collector addition is indicative of the degree of collector-mineral interaction (Tadie et al., 2015), with a higher drop in potential and steeper gradient alluding to greater interaction. In the absence of dithionites, the potential dropped from 130 mV to 60 mV when SIBX is used as a collector. As shown in Fig. 8, in the presence and absence of dithionite ions, the rest potential of galena after collector addition is negative with respect to the dixanthogen couple (108 mV). In agreement with the literature, PbX₂ is the expected species inducing hydrophobicity as confirmed in FTIR studies (Allison et al., 1972; Woods, 1976).

Interestingly the addition of collector in the presence of dithionites did not result in a potential drop but instead, there was an observed increase in potential. An explanation for this observation is attributed to the collector adsorption mechanism on the galena surface. The adsorption of xanthate ions to form metal thiolate on the galena surface involves an ion-exchange mechanism where sulphoxy species e.g. PbSO₄ and PbS₂O₃ are removed from the surface in exchange for metal xanthate (PbX₂) (Ikumapayi et al., 2012; Ralston, 1994; Wells and Van Cleave, 1975). During ion exchange between sulphoxy species and xanthate ions, the desorption of potential determining metal sulphoxy species such as PbS₂O₃ increases the potential on the galena surface (Wells and Van Cleave, 1975). This could explain the increase in rest potential at 600 s followed by the decrease in potential which may indicate the chemisorption of xanthate which itself, is a weak reducing agent. However, the effective chemisorption of xanthate following the desorption of sulphoxy species may be minimal owing to the strongly reducing environment which consumes oxygen and limits electron transfer necessary for collector adsorption. The question as to why a similar trend is not observed in the absence of dithionite ions is because the potentials are high enough such that the removal of sulphoxy species from the galena surface does not result in an appreciable rise in potential. Regardless of the exact mechanism occurring at the galena surface, what is clear is that the change in potential after SIBX addition in the presence and absence of dithionite ions results in an interaction between collector and mineral surface. However as confirmed by FTIR studies in Section 3.4, the effective adsorption of xanthate species is strongly diminished in dithionite solutions at high concentrations.
3.3.2. Rest potential measurements on chalcopyrite in the presence of dithionites

The rest potentials of chalcopyrite in dithionite solutions of different concentrations were investigated and presented in Fig. 9. A sharp drop in rest potential from 220 mV to 150 mV after the addition of SIBX (collector) is indicative of strong collector mineral interactions as seen in the absence of dithionites. In the presence of 500 mg/L and 2000 mg/L of dithionites, there is no change in potential after collector addition at 1500 s. It is thus inferred that the lack of potential drop is a result of poor/no collector mineral interactions at the reducing potentials of –350 to –450 mV. In the presence of dithionites, 500 mg/L solution was enough to render the mineral hydrophobic. For chalcopyrite, the collector was only added after 1500 s as this point showed a stable potential on the mineral surface in comparison to galena which obtained a stable surface potential after 600 s.

Pulp potential has always been used as a means of controlling the electrochemical environment in flotation processes (Ralston, 1991). Through changing pulp potentials some minerals are rendered hydrophobic in strongly reducing environments and collector addition does not improve mineral floatability. In the absence of dithionites, the rest potential was positive with respect to the dixanthogen couple (X/X2) alluding to the presence of dixanthogen on chalcopyrite in the absence of dithionites. Rest potentials in the presence of dithionites are strongly reducing and negative with respect to the dixanthogen couple. The species present on the mineral surface is a metal thiolate (Allison et al., 1972). However, the presence of metal thiolate is in doubt as has been established by FTIR studies. The lack of hydrophobicity inducing species on the mineral surface and the low potentials which may render natural flotation impossible result in poor flotation performance as reported in Section 3.6.

3.4. FTIR measurements

3.4.1. FTIR measurements of galena conditioned in dithionite solutions

The FTIR measurements of galena after conditioning in different solution conditions are shown in Fig. 10. Fig. 10 (a) shows that the galena sample conditioned in deionised water was peroxidised. FTIR spectrum, bands at 837 cm\(^{-1}\) and 1390 cm\(^{-1}\) are associated with PbCO\(_3\) whilst the bands appearing at 965 cm\(^{-1}\) and 1165 cm\(^{-1}\) originate from the presence of PbSO\(_4\) (Cases and De Donato, 1991; De Donato et al., 1990; Persson et al., 1991).

The addition of SIBX into different solutions introduced extra peaks in the range between 1000 cm\(^{-1}\) and 1300 cm\(^{-1}\). As depicted in Fig. 10 (b), spectrum (i) exhibits peaks at 1210 cm\(^{-1}\), 1189 cm\(^{-1}\), 1138 cm\(^{-1}\) and 1027 cm\(^{-1}\). The peaks at 1210 cm\(^{-1}\) and 1189 cm\(^{-1}\) are associated with C–O–C and S–C–S asymmetric stretching. The band at 1027 cm\(^{-1}\) is attributed to band vibrations of the S–C–S group shifting from 1022 cm\(^{-1}\) to 1027 cm\(^{-1}\). The vibrational bands are characteristic of the monocoordinated form of lead butyl xanthate and multiple layers of surface precipitated lead butyl xanthate (Cases and De Donato, 1991; De Donato et al., 1990). A weak peak at 1260 cm\(^{-1}\) characteristic of (BX)\(_2\) appears on the spectra. The xanthate adsorption mechanism involves ion exchange from the galena surface which leads to free Pb\(^{2+}\) ions in the solution formed from the dissolution of lead carbonate and sulphate (Persson and Persson, 1991). These Pb\(^{2+}\) ions interact with xanthate ions to form lead xanthate and lead sulphite in the presence of dithionites. Precipitation of solid lead alkyl xanthate also contributes to the buildup of adsorbed xanthate on galena surfaces (Ralston, 1994; Wells and Van Cleave, 1975). The intensity of the bands decreases as the concentration for dithionites is increased as seen in Fig. 10(b). At the highest concentration tested, all the peaks associated with lead xanthate do not appear as seen in the spectrum (iii). This is indicative of a lack of xanthate adsorption on the galena surface or the removal of previously adsorbed xanthate.

3.4.2. FTIR measurements of chalcopyrite in dithionite solutions

Fig. 11 depicts the baseline corrected FTIR spectra of chalcopyrite after conditioning in different solution conditions. Fig. 11 (a) shows that chalcopyrite conditioned in deionised water is characterized by a straight-line spectrum. No peaks associated with mineral pre-oxidation are visible in this spectrum (Zhang et al., 2013). Conditioning of chalcopyrite in deionised water and SIBX for 30 min resulted in the formation of multiple peaks in the range of 1000 cm\(^{-1}\) to 1300 cm\(^{-1}\) as presented in Fig. 11 (b), spectrum (i).

The intense peaks appearing at 1257 cm\(^{-1}\) and 1023 cm\(^{-1}\) are attributed to C–O symmetric stretching vibrations and C–S symmetric stretching vibrations respectively. These peaks are associated with butyl dixanthogen (BX\(_2\)) forming on the chalcopyrite surface (Leppinen, 1990; Zhang et al., 2013). The strength of these peaks suggests that butyl dixanthogen primarily induced hydrophobicity on the chalcopyrite matching findings by Li et al. (2019) and the rest potential measurements in Section 3.3.2. Minor peaks at 1160 cm\(^{-1}\), 1146 cm\(^{-1}\), 1124 cm\(^{-1}\) and 1046 cm\(^{-1}\) are characteristic of C–O–C symmetric vibrations indicative of (BX)\(_2\), C–O–C symmetric vibrations of cuprous(I) butyl xanthate and C–S stretching vibrations of CuBX (Li et al., 2019; Mielczarski et al., 1998; Peng et al., 2017). Conditioning chalcopyrite in SIBX and dithionite solutions resulted in spectra (ii) and (iii) illustrated in Fig. 11(b). At both dithionite concentrations, the peaks associated with adsorbed collector species are not present on the spectra suggesting removal of the species or lack of adsorption onto the mineral surface. The peaks associated with CuBX were completely removed whilst the peaks associated with (BX)\(_2\) were still visible as broad weak peaks around 1023 cm\(^{-1}\). This is indicative of the stability of dixanthogen over metal thiolates on the chalcopyrite surface.

3.5. X-ray photoelectron Spectroscopy (XPS) studies

3.5.1. XPS measurements on galena conditioned in dithionite solutions

XPS spectra of galena generated after conditioning in the presence and absence of dithionites for 30 min at pH 9 are presented in Fig. 12. The binding energies from these spectra were compared against the binding energies recorded in the literature (Fornasiero et al., 1994; Moulder et al., 1992; Nowak and Laajalehto, 2000; Pillai et al., 1983). The corresponding surface atomic concentration of galena determined in the different conditioning environments are shown in Table 3. According to the survey spectra, the most abundant elements of the galena surface Pb, S, C and O. These elements were further analysed in the high-resolution spectra.

For both test conditions, Cls peaks appeared at 285 eV, 286.4 eV, 288.1 eV and 290 eV. The first three peaks are attributed to C–C, C–O, O–C–O species on the galena surface (Ikumapayi et al., 2012; Moulder et al., 1992). The presence of these Cls peaks is indicative of adventitious
carbon species on the galena surface (Grano et al., 1997b; Li et al., 2019). The peak at 290 eV is attributed to the O—C—O as PbCO$_3$ which could also be a result of CO$_2$ adsorbing on the mineral surface (Nowak and Laajalehto, 2000).

The Pb$_{4f}$ peaks with binding energies 137.2 eV and 142.4 eV are associated with the PbS. These peaks are close in resemblance to those observed on unoxidized galena. However, there are peaks at 138.7 eV and 143.5 eV associated with the oxidised species such as sulphates...
The peaks broaden at higher binding energies indicating the presence of Pb(OH)2 and PbCO3 (Grano et al., 1997b). In the presence of dithionites, the broadening is reduced suggesting less oxidized species are present in the reducing environment. The reduction in the intensity of peaks associated with Pb (OH)3 on the galena surface conditioned in the dithionite solution suggests that oxidative dissolution of lead is depressed in the reducing environment.

Interpretation of the sulphur peaks is challenging owing to the presence of a broad Pb-4f energy loss spectrum in the regions of 163 eV and 167 eV (Buckley and Woods, 1984). However, S2p peaks located around 160 eV and 162 eV are assigned to sulphide (S2-) from the PbS. No clear peaks associated with sulphoxy compounds (sulphate, thiosulphate of sulphite) at higher binding energies are observed in the absence of dithionite ions. However, in the presence of dithionite ions, a peak starting at 166–168 eV appears and it is assigned to sulphite on the galena surface (Moulder et al., 1992; Sui et al., 2000). The decrease in total sulphur atomic concentration on the galena surface in the presence of dithionites is attributed to the removal of sulphide and elemental sulphur containing species on the galena surface. The oxygen, O1s spectrum is probably a contribution of oxygen containing species such as PbO and Pb(OH)2 to the peak at 531.3 eV. From Table 4, the atomic concentration of oxygen decreases in the presence of dithionite ions, which is indicative of the reducing environment limiting further oxidation of the galena surface.

3.5.2. XPS measurements on chalcopyrite conditioned in dithionite solutions

The survey spectra of chalcopyrite under different conditioning environments is presented in Fig. 13(a). The main elements identified are Cu, S, Fe, O and C. Fig. 13(b) presents the high-resolution spectra of the main elements of interest.

The Cu2p peaks in the spectra in both tests are associated with adventitious carbon species, a result of chalcopyrite oxidation. Cu2p peaks at binding energies 285 eV, 286.4 eV, 288.1 eV and 290 eV are assigned to C–C, C–O, O–C–O and O–C=O species on the chalcopyrite surface (Ikumapayi and Rao, 2015; Li et al., 2019; Moulder et al., 1992).

Copper (Cu 2p) spectra show two major peaks centred at 932 eV and 952 eV. These peaks are attributed to Cu 2p1/2 and Cu 2p3/2 respectively. The assignments in this study are in agreement with the binding energies reported by Nakai et al. (1978). The authors suggested binding energies of 932.4 eV and 952.1 eV for Cu 2p1/2 and Cu 2p3/2 respectively. The absence of satellite peaks at 943 eV suggests that the chalcopyrite is made up of monovalent Cu (I) and no Cu (II) is present. Previous studies also identified monovalent copper as the major copper species on untreated chalcopyrite (Ghahremaninezhad et al., 2013; Grano et al., 1997c; Li et al., 2019; Nakai et al., 1978). CuO and Cu2O species are excluded owing to the absence of extra peaks in addition to the Cu2p and Cu Auger spectral peaks (568 eV) associated with chalcopyrite (Grano et al., 1997c; Mieleczarski et al., 1996). At the tested conditions, no significant peak difference is observed between the copper treated in deionised water and that treated in a dithionite solution.

Assignment of the sulphur peaks is challenging owing to the multiple solutions possible in sulphur fittings. The broadening of the sulphur peaks is attributed to the changing chemical environment of sulphur at the chalcopyrite surface (Mieleczarski et al., 1996). What is more evident is the two major peaks at around 161 eV and 163 eV. The peak at 161 eV is assigned to iron bonded sulphur in chalcopyrite whilst the peak at 163 eV is characteristic of iron-deficient (sulphur enriched) chalcopyrite. Relative to the sulphur peak associated with iron bonded sulphur, the intensity of the peaks at 163 eV associated with metal deficient chalcopyrite decreases. This suggests conditioning in dithionite exposed more of the sulphur associated with chalcopyrite relative to sulphur in metals deficient chalcopyrite without a significant change in the sulphur chemical environment as there was minimal change in the concentration of copper and sulphur before and after treatment with dithionite solution. Sulphite and sulphate were not detected at pH 9 in the presence of dithionites. Sulphite interaction with chalcopyrite in the tested conditions did not result in the attachment of sulphite on the mineral surface. These results match findings made by Grano et al. (1997c) and Miki et al. (2018) who observed a low contribution from sulphite and sulphate ions at pH 6 and 8 respectively. However, Miki et al. (2018) suggest that sulphate formation occurs at high alkaline pH 10.8 and pH 11 indicative of oxidation occurring at high pH values.

O1s spectra exhibit two major peaks at 530 eV, characteristic of oxide and at approximately 531–532 eV attributed to hydroxide and chemisorbed oxygen species (Acres et al., 2010; Li et al., 2019). Since copper oxides are assumed not present, Fe species are the main source of oxides and hydroxides on untreated chalcopyrite. From the increase in the atomic concentration of oxygen in Table 5, it can be inferred that the presence of dithionite decomposition products increases the concentration of iron hydroxide species on the chalcopyrite surface and to a less extent there are contributions to the total oxygen by oxidized sulphur species on the chalcopyrite surface. The presence of these hydroxides can render the mineral hydrophilic, inducing poor mineral floatability.

3.6. Microflotation studies

Single mineral microflotation tests were conducted using galena and chalcopyrite. Although not representative of real ore behaviour, these tests make a sound base for fundamental studies. The flotation efficacy of galena and chalcopyrite in the presence and absence of dithionite ions is presented in Fig. 14. Moderate collectorless flotation was observed for both galena and chalcopyrite. Some authors report that the hydrophobicity induced in sulphide minerals is a result of mild oxidation of the sulphide minerals (Buckley et al., 1985; Hu et al., 2009). The mild oxidation produces elemental sulphur or metal deficient (sulphur rich) entities which promote the natural floatability of the sulphides. It is also noted that at the employed airflow rate, particle entrainment may contribute to mineral recoveries.

The addition of SIBX improved the flotation recovery of both minerals although chalcopyrite already exhibited strong natural floatability even in the absence of SIBX. Galena and chalcopyrite recoveries declined significantly in the presence of dithionite ions. This result corroborates the electrochemical studies and FTIR studies which show less collector interaction in the presence of dithionites. Moreover, the surface alteration of the sulphide minerals by thiosulphate or sulphite also contributes to the poor mineral recoveries of sulphide minerals (Sui et al., 2000). Given that galena was conditioned in a strongly reducing environment, starting potential –310 mV, this solution potential could limit the electrochemical reaction necessary for xanthate adsorption on sulphide. A range of flotation tests on galena bearing minerals documented by Ralston, (1994) showed that the galena was highly sensitive to Eh conditions. Furthermore, the addition of the collector may only slightly improve performance, and poor flotation characteristics are exhibited at
Eh values between −200 mV and −400 mV (Grano et al., 1990).

4. Conclusions

The flotation of sulphide minerals in the presence of dithionite ions was investigated. In this study, it was shown that in addition to pulp potential alterations mostly discussed in the literature, solution interactions between dithionites and xanthates and mineral surface modification of sulphides by dithionite oxidation derivatives affect flotation performance. In neutral to slightly alkaline pH range, more than half the xanthate in the solution degraded in 10 min of conditioning. The importance of oxygen aeration was more significant at neutral pH where oxygen presence markedly increased xanthate degradation. Since plant practice is to apply xanthate as a collector in neutral to slightly alkaline condition for the flotation of galena and chalcopyrite, the solution effects cannot be ignored. The accumulation of sulphite ions on the galena surface and oxidation of chalcopyrite through the build-up of metal hydroxides and sulphoxy compounds on chalcopyrite also contributes to the low flotation performance of the sulphide minerals. This was confirmed through XPS studies on the sulphide minerals.

The proposed effect of dithionites therefore entails xanthate decomposition through the formation of HSO₃⁻ and SO₃²⁻ which consume xanthate. Moreover, free Pb²⁺ ions react with sulphite ions leading to the formation of lead sulphite. For chalcopyrite, sulphite ions do not directly adsorb on the mineral surface but the solution environment encouraged the formation of hydrophilic species as evidenced by the overall increase in the concentration of atomic oxygen on the chalcopyrite as noted in XPS analyses.

The results from this are relevant as they set the discussion on the significance of previously ignored thiosalt compounds on flotation performance. In the processing of massive sulphide ores where recycled plant water is laden with the thiosalt compounds in varying

Table 5
Atomic concentrations and XPS binding energies on chalcopyrite in the absence and presence of dithionites.

<table>
<thead>
<tr>
<th>Element</th>
<th>Species</th>
<th>Binding energy (eV)</th>
<th>Atomic Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DIW</td>
<td>S₂O₃²⁻ Solution</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu(II)</td>
<td>932 &amp; 952</td>
<td>10.3</td>
</tr>
<tr>
<td>Sulphur</td>
<td>S²⁻</td>
<td>161 &amp; 163</td>
<td>34.4</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Oxide /Hydroxide</td>
<td>530 &amp; 531-532</td>
<td>21.2</td>
</tr>
<tr>
<td>Carbon</td>
<td>C=O, C=O, O=C=O</td>
<td>285; 286.4; 288.1; 290</td>
<td>27.9</td>
</tr>
</tbody>
</table>

Fig. 13. (a) Survey spectra of chalcopyrite treated in deionised water and 500 mg/L dithionite solution, pH 9 (b) High resolution spectra of species on the chalcopyrite surface in deionised water and 500 mg/L dithionite solution, pH 9.

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concentrations, processing decisions ought to be implemented with multiple water quality parameters in mind.

CRediT authorship contribution statement

Ngoni Mhonde: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization, Writing - review & editing. Leena-Sisko Johansson: Investigation, Writing - original draft. Kirsten Corin: Conceptualization, Resources, Validation, Writing - review & editing, Supervision, Visualization, Project administration. Nora Schreithofer: Conceptualization, Resources, Validation, Writing - review & editing, Supervision, Visualization, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research has received funding from the European Union H2020 program under grant agreement no 730480, ITERAMS project. The authors would like to thank Dr. Joel Campbell for assistance with XPS analyses.

References


Kirsten Corin: Conceptualization. Leena-Sisko Johansson: Conceptualization.


