Flotation Chemistry of Complex Sulphide Ores

Recycling of Process Water and Flotation Selectivity

Fatai Kolawole Ikumapayi
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Synopsis

Recycling of flotation effluents through the ore processing plant is one of the ways of reducing both plant-operating costs and industrial impact onto the local ecosystem. Such waters named acid mine drainage (AMD), if discharged from sulphide flotation are gypsum (CaSO₄·H₂O) saturated and have a high salinity (on the order of 1000 ppm). As minor species, they commonly contain reduced sulphur compounds (RSC) (sulfoxianions with sulphur in the oxidation state below (VI) such as SO₃²⁻, S₂O₃²⁻, S₂O₅²⁻, and S₄O₆²⁻), cations of ferrous and non-ferrous metals, frothing molecules, residual chemical reagents and products of their degradation. Tailing ponds also host communities of chemolithotrophic and heterotrophic microorganisms which play an important role in dictating their aqueous and solid phase chemical speciation. Consequently, the key step towards developing scientific approaches of recycling of the tailing waters is elucidation of how, in what extent, and why the tailing water components, taken singly or jointly influence flotation of sulphides.

In this work, the influence of main process water components of calcium and sulphate on chalcopyrite, galena, sphalerite and pyrite flotation has been investigated through Hallimond flotation, zeta-potential and diffuse reflectance FTIR spectroscopy measurements using pure mineral samples as well as bench scale flotation tests using complex sulphide ore. The significance of process water species in flotation has been assessed using deionised water, process water and simulated water containing calcium and sulphate ions in experiments. In addition, the effect of temperature in bench scale flotation tests has also been examined.

Hallimond flotation indicated depression of chalcopyrite, galena and sphalerite and activation of pyrite in the presence of calcium and sulphate ions with potassium amyl xanthate as collector. Calcium ions have significant influence on zeta-potential characteristics and xanthate adsorption behaviour of chalcopyrite, galena, sphalerite and pyrite compared to sulphate ions. FTIR studies revealed the presence of surface oxidised sulfoxo species and surface iron and calcium carbonates on chalcopyrite in the presence of process water and water containing calcium ions, surface oxidised sulfoxo and carbonate species on galena in the presence of deionised water, process water and water containing calcium ions, hydrated surface oxidised species and surface iron and calcium carbonates on pyrite in the presence of process water and water containing calcium ions all at pH 10.5 in which the surface species influenced xanthate adsorption. The presence of surface oxidised sulfoxo and carbonate species on sphalerite were also revealed at pH 11.5 in the presence of deionised water, process water and water containing calcium and sulphate ions in which surface species does not influence xanthate adsorption.

Bench scale flotation using two different complex sulphide ores showed that chalcopyrite recovery is better in process water than tap water and general depression of chalcopyrite at temperatures lower than 22°C in either tap water or process water, activation of chalcopyrite at all temperatures in process water and depression of chalcopyrite when tap water containing calcium and sulphate ions was used at 22°C. It also showed that galena recovery is better in tap water than process water and depression of galena at temperatures lower than 22°C in either tap water or process water. It also showed that sphalerite recovery is better in process water than in tap water better recovery of sphalerite at temperatures lower than 22°C in either tap water or process water.
Acknowledgement

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Fatai Ikumapayi
List of articles

Papers included in the thesis


Published papers presented at national and international conferences (not included)


Contents

Synopsis ..................................................................................................................................... 3
Acknowledgement...................................................................................................................... 5
List of articles............................................................................................................................. 7
Contents...................................................................................................................................... 9
INTRODUCTION.................................................................................................................... 11
  Description of Boliden concentrator .................................................................................... 13
EXPERIMENTAL ................................................................................................................... 14
  Materials and reagents.......................................................................................................... 14
  Hallimond flotation tests ...................................................................................................... 14
  Zeta-potential measurements.............................................................................................. 15
  Diffuse reflectance FTIR spectroscopy measurements........................................................ 15
  Bench-scale flotation tests.................................................................................................... 16
RESULTS AND DISCUSSION .............................................................................................. 17
  Hallimond flotation studies .................................................................................................. 17
  Zeta-potential studies ........................................................................................................... 24
  Diffuse reflectance FTIR studies.......................................................................................... 27
  Bench-scale flotation studies................................................................................................ 47
  Balance of calcium and sulphate species in pulp solution ................................................... 48
CONCLUSIONS...................................................................................................................... 52
  Future work .............................................................................................................................. 54
References................................................................................................................................ 55
INTRODUCTION

Froth flotation method is used annually to concentrate more than one billion tons of global sulphide ores (Fuerstenau et al., 2007). This concentration method requires billions of gallons of water in the process. In addition a number of chemicals; flotation collectors, depressants, activators, regulators etc are used in froth flotation. It is however pertinent to recycle a greater percentage of the used process water within the flotation cycle due to different reasons which includes scarcity of fresh water resources as well as to minimize the discharge of the contaminated water to the environment (Broman, 1980; Liu et al., 1993; Rao and Finch, 1989). However the chemistry of the recycled water is different from that of fresh water because a number of chemical and other components such as rest flotation reagents, suspended solid/colloid particle, cations of metals, anions of organic and inorganic pollutants are now present in it. Since the chemistry of pulp water is very crucial to the effectiveness of the flotation, there is a great concern about possible impact of the recycled water on the efficiency of flotation.

Identifying specific effects of recycled water on quality of flotation has been a difficult task as there is no common agreement on its impact on flotation, it appears to be detrimental in some studies where accumulation of species such as calcium, sulphate, carbonate, rest reagents and their oxidation products, thiosalts and other metal ions leads to reduced flotation grade and recoveries (Basilio et al., 1996; Broman, 1980; Haran et al., 1996; Levay et al., 2001; Rao and Finch, 1989), while in other studies they appear to be beneficial to the flotation process (Basilio et al., 1996; Chen et al., 2009; Liu et al., 1993).

Generally the presence of flotation effluents in process water has been implicated to degrade flotation process however no explicit experimental evidence for this assertion is yet available. Most previous studies dealt with the effect of sulphate and calcium ions on adsorption of environmentally important organic and inorganic anions and metal cations on wide band-gap metal hydroxides (Stumm, 1987). The results have been interpreted in terms of competitive (LeFèvre and Féдоров, 2006; Wu et al., 2002), promotive (Jia and Demopoulos, 2005; Ostergren et al., 2000; Swedlund and Webster, 2001); or indifferent (LeFèvre and Féдоров, 2006) adsorption, depending on speciation of the adsorbed anion and the formation of calcium-bearing surface co-precipitates. However little is generally known about effects of concentrated sulphate and calcium solutions on adsorption-reaction of collectors on semiconducting sulphides in terms of kinetics of the reagent adsorption, adsorption isotherms, kinetic of the formation of dithiophosphatogen and dixanthogen (the species required for flotation), flotation kinetics and grade, as well as about the salinity and redox control of flocculation in such systems. Another prominent obstacle to utilizing tailing waters is the presence of the reduced sulphur compounds (RSC) contaminations (such as \(SO_3^{2-}\), \(S_2O_5^{2-}\), and \(S_4O_6^{2-}\)), which arise due to the use of NaHSO_3 as a flotation depressant (Eric Forssberg et al., 1993; Gul, 2007) for pyrite; and abiotic and biotic (Johnson, 2001) oxidation of sulphides.

The depressing effect of sulphite generally increases from copper sulphides to galena, pyrite and sphalerite (Peres, 1981). However, there is no common agreement about the mechanisms. In particular i) stripping /decomposition of xanthate (Yamamoto, 1980), ii) reaction with the pyrite surface to form hydrophilic iron oxides (Khmeleva et al., 2003) and iii) a decrease of redox potential of the pulp below a level at which binding/oxidation of a collector (electron donor) becomes energetically unfavourable (Forssberg, 1991) effects were proposed for depression of pyrite flotation by \(SO_3^{2-}\) species.
In the presence of copper, sulphite was shown (Shen et al., 2001) to promote the oxidation of copper on the pyrite surface, preventing the adsorption of xanthate and thus leading to the mineral depression, but has no effect on the sphalerite. At the same time, in the case of chalcopyrite, it was postulated (Grano et al., 1997a; Grano et al., 1997b) that sulphite removes the iron oxyhydroxide phase from the surface, leaving a sulphur-rich sulphide layer, which in turn promotes collector adsorption. It was also found (Houot and Duhamet, 1993) that the depressing effect of sulphite on chalcopyrite flotation depends on the presence of Fe$^{2+}$ ions released from grinding media.

Apart from the decomposition of xanthate/dixanthogen and the decrease in xanthate adsorption following a decrease of the redox potential of the pulp, several additional mechanisms have been put forward to explain the depression of the flotation of sphalerite (Misra et al., 1985). They include: the formation of a zinc sulphite hydrophilic layer at the mineral surface; the reduction of copper activation as a result of consumption of copper in solution as copper sulphite; and the consumption of dissolved oxygen. Sulphite ions are also known to react with polysulphide or elemental sulphur and form thiosulphate ions (Li et al., 1995) and therefore a decrease in surface hydrophobicity is expected from this reaction.

Finally, compared to sulphate, these reduced sulfoxyanions have upon catalytic oxidation of sulphite species will much more strongly be bound to the sulphide surface compared with the sulphate anions that are directly adsorbed through ion exchange/outer-sphere complexation, thus competing more efficiently with collectors for the adsorption sites on sulphides, which may strengthen the depressing effect of sulphite. This effect, if properly understood, can open a new cost-effective approach to selectively regulate surface properties of sulphides.

Previous attempts on reuse of process water were reported in a number of sulphide ore concentrators: In Sweden the use of recycled water from settling pond in Kristineberg concentrator gave rise to significant problems during pumping of the froth which is considered to be as a result of insufficient destruction of frothers and collectors in the tailings pond (Forsberg et al., 1995). In addition water reuse in grinding and flotation circuits at Kristineberg and Stekenjokk concentrators indicated no disturbance in grinding and pyrite flotation but selectivity against zinc is adversely affected in flotation of copper and zinc when sulphate ions concentrations in the water is more than 100 mg/l. In Laisvall concentrator deterioration of lead flotation and over frothing was experienced due to precipitation of calcium carbonate in pipes and spray nozzles, the carbonate came from the mine water. Reuse of water in Zinkgruvan concentrator was stopped due to reduction in lead recovery and increase of zinc concentration in lead concentrate, the sulphate ions concentration in the recycled process water was between 180 and 330 mg/l. Reuse in Falun concentrator was limited to 25% due to blockage of pipes by gypsum precipitate which results from saturation of calcium sulphate solution in the tailings pond water, the sulphate ions concentration in the tailings pond water was 1580 mg/l (Broman, 1980).

In Australia, batch flotation study conducted on copper tailings from Benambra mines in Victoria indicated lower recovery, grade and flotation kinetics when Melbourne process water was used (Haran et al., 1996). In Canada the use of Kidd Creek process water containing 500 ppm thiosalt and 300 ppm calcium concentration for batch flotation of Cu-Zn ore from Kidd Creek was not detrimental to copper rougher flotation, it appears to improve the flotation by enhancing the depression of pyrite and recovery of copper due to the presence of thiosalt and calcium ions (Liu et al., 1993). In China a lab scale flotation test on galena and pyrite from Fankou mine using process water collected directly from the mine concentrator indicated that
Recycling of flotation effluents through the ore processing plant is one of the ways of reducing both plant-operating costs and industrial impact onto the local ecosystem. Such water originating from sulphide flotation are saturated with calcium and sulphate ions, and also contain several reduced sulphur compounds, cations of ferrous and non-ferrous metals, frothing molecules, residual chemical reagents and products of their degradation. The key step towards developing scientific approaches of recycling of the tailing waters is elucidation of how, in what extent, and why the chemical components, taken singly or collectively influence flotation of sulphides.

The influence of main process water components, calcium and sulphate ions, on chalcopyrite, galena, sphalerite, and pyrite flotation has been investigated through Hallimond flotation, zeta-potential and diffuse reflectance FTIR spectroscopy measurements using pure minerals sample as well as bench scale flotation tests using two complex sulphide ores. The significance of process water species in flotation has been assessed using deionised water, process water and simulated water containing calcium and sulphate ions in experiments. In addition, the effect of temperature in bench scale flotation tests has also been examined. The results are presented and discussed in this thesis.

**Description of Boliden concentrator**

Boliden is a leading European base metal producer, its main products are zinc and copper and other important metals include lead, gold and silver. The company has approximately 4,400 employees and the turnover is approximately SEK 30 billion annually (www.boliden.com).

The concentrator at Boliden Area processes approximately 1.6 million tonnes of ore and 0.19 million tonnes of slag per annum. The concentration of the ore is by autogenous grinding and flotation. The discharge from the autogenous grinding is directed through 3 mm sieve and the undersize is the feed into hydro-cyclone. The overflow from the hydrocyclone with K₈₀ ≤ 65 is fed to the first stage flotation circuit for Cu-Pb flotation. The flotation circuit is made up of two rougher flotation cells and one scavenger cell for each rougher cell, cleaner and re-cleaner cells. The first stage flotation circuit is for Cu-Pb flotation while the second stage circuit is for Zn flotation. The bulk Cu-Pb concentrate goes to the separation circuit. The scavenger tails of Cu-Pb flotation is conveyed to the Zn flotation circuit (Rao. et al., 1997).
**EXPERIMENTAL**

**Materials and reagents**

Pure chalcopyrite, galena, sphalerite and pyrite minerals used in Hallimond flotation tests, zeta-potential and FTIR measurements were procured from Gregory, Bottley & Lloyd Ltd., United Kingdom. The minerals were crushed, ground and classified into different size fractions. A size fraction of −150+38 μm was used in the Hallimond single mineral flotation tests and −5 μm fraction was used in both zeta-potential measurement and FTIR study. The chemical composition of the minerals is shown in Table 1.

Table 1. Chemical composition of the minerals used in the studies.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>% Cu</th>
<th>% Fe</th>
<th>% Zn</th>
<th>% Pb</th>
<th>% S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galena</td>
<td>0.2</td>
<td>1.38</td>
<td>1.26</td>
<td>73.69</td>
<td>6</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>25.8</td>
<td>29</td>
<td>0.54</td>
<td>0.22</td>
<td>29.5</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.02</td>
<td>44.4</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>49.7</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>0.17</td>
<td>4.2</td>
<td>39.92</td>
<td>1.32</td>
<td>20.7</td>
</tr>
</tbody>
</table>

Two complex sulphide ores from Boliden-Renström and Boliden-Kristineberg concentrators were used in the Bench-scale flotation tests. The ores were crushed and wet ground in a steel mill to obtain K80 ≤ 65 μm, the same flotation feed size in the process plant. The following flotation reagents were collected from Boliden (the same used in its flotation process): potassium amyl xanthate (KAX), isobutyl xanthate (IBX), Dowfroth (another collector), Danafloat (frother), dextrin, sodium hydrogen sulphite (NaHSO3), zinc sulphate (ZnSO4), copper sulphate (CuSO4) and calcium oxide (CaO). HCl and NaOH solutions were used as pH regulators and Na2SO4 and CaCl2 as sources of SO42− and Ca2+ ions respectively. Process water containing 128 mg/l Ca2+ and 63 mg/l SO42− ions concentrations was obtained from Renström ore concentrator and 186 mg/l Ca2+ and 153 mg/l SO42− ions concentrations from Kristineberg ore concentrator. Typical concentration range of various chemical species in Boliden process water is shown in Table 2.

**Hallimond flotation tests**

1 g of mineral is conditioned in a 100 ml standard volumetric flask and then transferred into a Hallimond tube flotation cell the upper part of the cell is filled with appropriate solution after addition of all reagents up to a total volume of 400 ml; this is followed by flotation under magnetic stirring. The sequence of reagent additions was pH regulators, calcium and/or sulphate species in water, collector, and frother. Conditioning time for species in water, collector and frother were 10 min, 5 min and 1 min respectively. Air was supplied at the rate a 200 cm³/min and the flotation time was 1 min. A 20 mg/l of KAX collector and 50 μg/l frother was used unless otherwise specified. All tests except the pH variation tests were carried out at pH ~10.5 for chalcopyrite, galena and pyrite and pH ~11.5 for sphalerite. The tests were performed under room temperature of approximately 22.5°C.
Table 2. Chemical species and their concentration range in Boliden process water.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentrations</th>
<th>From</th>
<th>To</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>SO₄²⁻</td>
<td>200</td>
<td>1500</td>
<td>mg/l</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>100</td>
<td>500</td>
<td>mg/l</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>0.1</td>
<td>1300</td>
<td>mg/l</td>
</tr>
<tr>
<td>COD (Cr)</td>
<td></td>
<td>&lt;30</td>
<td>130</td>
<td>mg/l</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>0.1</td>
<td>10</td>
<td>mg/l</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>P</td>
<td>&lt;0.050</td>
<td>0.7</td>
<td>mg/l</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>4.3</td>
<td>53</td>
<td>mg/l</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>4.4</td>
<td>8000</td>
<td>μg/l</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>12</td>
<td>3900</td>
<td>μg/l</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al</td>
<td>59</td>
<td>59000</td>
<td>μg/l</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>0.12</td>
<td>5.2</td>
<td>μg/l</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>4</td>
<td>540</td>
<td>μg/l</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>2.7</td>
<td>20000</td>
<td>μg/l</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td>&lt;0.1</td>
<td>&lt;0.13</td>
<td>μg/l</td>
</tr>
<tr>
<td>Conductivity at 25°C</td>
<td></td>
<td>96</td>
<td>160</td>
<td>ms/m</td>
</tr>
</tbody>
</table>

Zeta-potential measurements

The measurement was carried out on the mineral sample at different conditions based on the present study flotation requirements. Zeta potential measurements were carried out with the aid of ZetaCompact instrument equipped with a charge-couple device (CCD) video camera and Zeta4 software. The software allows the direct reading of zeta-potential calculated from the electrophoretic mobilities using Smoluchowski equation. The result is a particle distribution histogram, from which the mean mobility are recalculated to zeta-potential values. In each measurement, about 10 mg of −5 μm fraction of the mineral at a concentration of about 10 mg/100 ml of suspension was used. The ionic strength was maintained with KNO₃ at a concentration of about 0.01M and the pH was adjusted with solutions of HNO₃ and KOH accordingly. The required concentration of each solution was usually prepared followed by addition of the mineral, conditioning for 10 minutes and addition of other required reagent and species. The pH of the suspension after all conditioning prior to zeta-potential measurement is always regarded as the pH of the measurement.

Diffuse reflectance FTIR spectroscopy measurements

The measurement was carried out with the aid of Bruker FTIR spectrometer model IFS 66v/s. The −5 μm fraction of the mineral pre-treated at different conditions based on the present study flotation requirements were subjected to FTIR measurements. In each measurement, about 10 mg of −5 μm fraction of the mineral is pre-treated at a solids concentration of about 10 mg/100 ml of solution. The pH was adjusted with solutions of HNO₃ and KOH accordingly. The required concentration of each solution and species was usually prepared followed by addition of the mineral, conditioning for 10 minutes and addition of other required reagent and species. The pulp is subsequently filtered and the solids left to dry on the filter paper at room temperature. The pH of the suspension after all conditioning prior to
filtration is always regarded as the pH of the measurement. Diffuse reflectance infrared Fourier transform (DRIFT) method was used in the measurement with 2.8 wt% concentration in potassium bromide (KBr) matrix. Each spectrum was recorded after 256 scans.

**Bench-scale flotation tests**

In each test about 1 Kg of ore is wet ground with about 600 ml of tap water or process water in the steel mill with 8 Kg grinding medium followed by flotation in the WEMCO cell of 2.5 litre capacity. The sequences of reagent additions in Cu-Pb flotation were pH regulator, zinc and pyrite depressants, copper-lead collectors, frother, and copper-lead flotation. The dosages of zinc and pyrite depressants are; 1500 g/t ZnSO₄, 300 g/t NaHSO₃ and 200 g/t of dextrin. Dosages of copper-lead collectors in a three stage sequential flotation are 30+20+10 g/t Danafloat and 10+5+0 g/t KAX. The conditioning times for pH regulator, zinc and pyrite depressants, and copper-lead collectors are 5 min, 1 min and 2+1+1 min respectively. The sequences of reagent additions in Zn-flotation were pH regulator, zinc activator, zinc collector, frother and zinc flotation. Dosages of zinc activator and collector in a three stage flotation were 400 g/t CuSO₄ and 40+20+20 g/t IBX. The conditioning times for zinc activator and collector are 2 min and 1+1+1 min respectively. The frother dosage was 20 g/t Dowfroth in all cases. The pH was regulated to ~10.5 and ~11.5 for Cu-Pb and Zn-flotation respectively with powdered calcium oxide. Experiments were performed at room temperature of approximately 22.5°C, and at 11°C and 4°C using a specially designed double edged flotation cell where the temperature of the pulp is controlled with the circulation of cooled water inside the cell wall. Total flotation time in each stage was 4.5 min. The flotation products were chemically analysed for the metals content at Boliden analytical laboratories.
RESULTS AND DISCUSSION

Hallimond flotation studies

The recovery of chalcopyrite and galena at different pH ranging from 3 to 11.5 in both deionised (DW) and process (PW) water is shown in Fig. 1. It can be seen that the recovery of chalcopyrite decreases generally from low to high pH until pH 10 when it begins to rise again. The recovery of galena decreases generally from pH 3 to pH 6 and rises at pH 7, stabilises to pH 9 where it begins to rise again. The recovery of both minerals in process water is generally lower than in deionised water.

![Fig. 1: Recovery of chalcopyrite and galena at different pH in deionised and process water.](image)

The flotation of pyrite and recovery of sphalerite at different pH values ranging from 3 to 11.5 in both deionised and process water is shown in Fig. 2. It can be seen that the flotation of pyrite decreases generally from pH 3 to pH 9, rises slightly at pH 10.5 and decreases at pH 11.5. In addition it can be seen that the recovery of pyrite in process water is generally higher than in deionised water except at pH 11.5. The results show that pyrite flotation is depressed with increasing pH and the high flotation response in the acidic pH range 2 to 5 is due to the formation of ferric amyl xanthate about the same pH region (Eric Forssberg, 1985). The decrease in recovery with increasing pH value is due to formation of ferrous hydroxide and ferric hydroxyl xanthate compounds imparting hydrophilic character to the surface. A better flotation response of pyrite in process water than deionised water could be due to the adsorption of Cu and Pb ions, and the rest reagents that exist in process water. The recovery of galena decreases generally from pH 3 to pH 6 and rises at pH 7, stabilises to pH 9 where it begins to rise again. In addition the recovery of galena in process water is generally lower than in deionised water.
The effect of Ca\(^{2+}\) ions at different concentrations on recovery of pure chalcopyrite and galena in both deionised and process water at pH 10.5 is shown in Fig. 3. It can be seen in chalcopyrite that the presence of Ca\(^{2+}\) ions in deionised water depresses the flotation of chalcopyrite on the average the depression is stable through low to high concentration of Ca\(^{2+}\) ions in solution, however a slight increase in recovery can be observed from 300 mg/l calcium ions. This increase in flotation response could be similar to the metal ion activation of oxide minerals by adsorption of CaOH\(^+\) species at the flotation pH 10.5; these species adsorption enhances collector adsorption and hence improves the recovery (Fuerstenau, 1976). It can also be observed that the mineral is generally depressed in process water; this could be due to the presence of a number of species including SO\(_4^{2-}\), SO\(_3^{2-}\) (Houot and Duhamet, 1992), dissolved iron (Kant et al., 1994; Peng et al., 2003b) in the process water which could form hydrophilic layers or iron oxidation species on the surface of chalcopyrite, in addition to the formation of copper hydroxide (Fullston et al., 1999) and iron hydroxide; these hydrophilic species usually play major role in the depression of chalcopyrite flotation.

In galena it can be seen that the presence of Ca\(^{2+}\) ions in deionised water did not show any serious effect on the flotation of galena, however there is slight depression in process water at lower concentration of Ca\(^{2+}\) ions, the depression is more pronounced from 500 mg/l concentration of Ca\(^{2+}\) ions. This could be due to the presence of a number of species including SO\(_4^{2-}\), SO\(_3^{2-}\) in addition to the depressive effect of combination of calcium and sulphite species (Ca\(^{2+}\)-SO\(_3^{2-}\)), dissolved iron in the process water which could form hydrophilic layers or iron oxidation species on the surface of the minerals as mentioned above in case of chalcopyrite.
The effect of Ca$^{2+}$ ions concentration on flotation of pure pyrite (pH 10.5) and sphalerite (pH 11.5) in both deionised and process water is shown in Fig. 4. In pyrite, it can be seen that the presence of Ca$^{2+}$ ions in both deionised and process water slightly increases recovery at 50 mg/l concentration while it becomes unstable as the concentration increases until 400 mg/l where a slight increase is seen in process water and a slight decrease is seen in deionised water. The increase in recovery at lower concentration could be due to activating effects of Ca$^{2+}$ ions in deionised water, Cu$^{2+}$, Fe$^{2+}$ and Ca$^{2+}$ ions and oxidation species of lead and copper in process water (Peng et al., 2003a; Peng et al., 2003b; Zhang et al., 1997).

It can be seen in sphalerite that the presence of Ca$^{2+}$ ions in deionised water slightly depresses the recovery of sphalerite up to 200 mg/l and remains constant afterwards and gradual depression can also be seen in process water up to 600 mg/l calcium concentration, above which the recovery increases a little. In general the recoveries looks better in process water than in deionised water; this could be due to the presence of a number of species in the process water that could activates sphalerite such as copper ions (Chandra and Gerson, 2009; Laskowski et al., 1997), lead ions (Trahar et al., 1997), sulphite ions (Shen et al., 2001) and rest reagents (Chen et al., 2009). The activation in process water is seen to be marginal and insignificant.
The effect of SO$_{4}^{2-}$ ions concentrations on pure chalcopyrite and galena minerals recovery at pH 10.5 is shown in Fig. 5. It can be seen that the presence of SO$_{4}^{2-}$ ions in deionised water also depresses the flotation of chalcopyrite on the average and the depression is more stable through low to high concentration of SO$_{4}^{2-}$ ions in solution. It can also be observed that the mineral is generally depressed in process water; this could be due to the adsorption of a number of species including sulphate, sulphite and metal oxy-hydroxide hydrophilic species in process water as mentioned above. There is also an indication that the increased concentration of SO$_{4}^{2-}$ ions besides the sulphate ions in process water has some depressing effect on chalcopyrite. The sulphate ions compete with collector molecules for adsorption as stated earlier (Lefèvre and Fédoroff, 2006; Wu et al., 2002); the strongly bonded SO$_{4}^{2-}$ ions on the mineral surfaces inhibits collector adsorption.

It can also be seen that the presence of SO$_{4}^{2-}$ ions in deionised water depresses the flotation of galena on the average. In addition the mineral is generally more depressed in process water than in deionised water; this could be due to the presence of a number of species including SO$_{4}^{2-}$, SO$_{3}^{2-}$ (Houot and Duhamet, 1992), dissolved iron (Kant et al., 1994; Peng et al., 2003b) in the process water which could form hydrophilic layers or iron oxidation species on the surface of the minerals; this species can play major roles in the depression of galena flotation. This is also an indication that high concentration of SO$_{4}^{2-}$ ions may have some depressing effect on galena as mentioned above.
Fig. 5: Effect of sulphate ions on chalcopyrite and galena flotation in both deionised and process water.

The effect of $\text{SO}_4^{2-}$ ions concentrations on pure pyrite (pH 10.5) and sphalerite (pH 11.5) minerals flotation is shown in Fig. 6. On pyrite it can be seen that the presence of $\text{SO}_4^{2-}$ ions in deionised water on the average slightly increased the recovery of pyrite. While the recovery is generally decreased in process water, with a constant decrease from 100 to 1000 mg/l $\text{SO}_4^{2-}$ ions concentrations, however a slight increase can be seen from 1200 mg/l $\text{SO}_4^{2-}$ ions concentrations. The activating effect in deionised water could be similar to thiosulphate reduction of hydrophilic compounds on sulphides particles which leads to increased flotation recovery (Kirjavainen et al., 2002a; Kirjavainen et al., 2002b). The mineral is generally more depressed in process water than in deionised water; this could be due to the presence of a number of species including $\text{SO}_4^{2-}$, $\text{SO}_3^{2-}$, iron oxidation species in the process water which could form hydrophyllic layers or iron oxidation species on the surface of the mineral as mentioned above.

On sphalerite it can be seen that increasing $\text{SO}_4^{2-}$ ions concentration in deionised water has no effect on the flotation of sphalerite but depresses a little at a very high concentration. It can also be observed that the mineral is generally not depressed in process water and with a slight better recovery compared to deionised water.
The effects of both Ca$^{2+}$ and SO$_4^{2-}$ ions concentrations combined on the recovery of pure chalcopyrite and galena minerals at pH 10.5 are presented in Fig. 7. The combined effects on chalcopyrite is similar to observation with single effects above however the somewhat activation observed from 300 mg/l of Ca in deionised water is not seen here, indicating that the SO$_4^{2-}$ effect is dominating. The mineral is relatively depressed due to SO$_4^{2-}$ adsorption on the mineral surfaces and hence collector could not be adsorbed (because the collector is anionic) only loosely bound SO$_4^{2-}$ ions will be replaced by chemisorbing collector molecules. The combined effect in galena is almost similar to observation with single effects of SO$_4^{2-}$ions above also indicating that the mineral is relatively depressed due to SO$_4^{2-}$ adsorption on the mineral surfaces.
The combined effects of both Ca²⁺ and SO₄²⁻ ions concentrations on the flotation of pure pyrite (pH 10.5) and sphalerite (pH 11.5) minerals are presented in Fig. 8. The combined effects on pyrite shows a slight decrease in recovery at 50 and 100 mg/l Ca²⁺ and SO₄²⁻ ions concentrations respectively and thereafter the recovery increases gradually. The activation could be due to the activating effects of metal ions (Ca²⁺ ions in deionised water, Cu²⁺, Fe²⁺ and Ca²⁺ ions and oxidation species of lead and copper in process water (Peng et al., 2003a; Peng et al., 2003b; Zhang et al., 1997) mentioned above. This effect seems to be dominating after 50 and 100 mg/l Ca²⁺ and SO₄²⁻ ions concentrations in both deionised and process water in addition to the activating effect of thiosulphate reduction of hydrophilic compounds on sulphides particles (Kirjavainen et al., 2002a; Kirjavainen et al., 2002b).

The combined effects on sphalerite shows a slight depression with increasing calcium and sulphate ions for some time as the recovery reaches its minimum at 500 and 1000 mg/l Ca and SO₄ concentrations and slightly rise afterwards. Almost the same trend is observed in process water; however the recovery is little better in process water.
Fig. 8: Combined effect of calcium and sulphate ions on pyrite and sphalerite flotation in both deionised and process water (calcium concentration is not shown in the figure and calcium is added to half the concentration of sulphate in all the tests).

The above single mineral Hallimond flotation results showed that sphalerite is not floatable in either deionised water or process water and there is no distinct effect of either calcium or sulphate ions. The metal cations that exist in process water are also inadequate to activate sphalerite flotation noticeably and Cu ions activation as practiced to float sphalerite is necessary.

**Zeta-potential studies**

The zeta-potential response of chalcopyrite, galena, pyrite and sphalerite at different pH ranging from 3 to 11.5 in deionised water, process water, and deionised water containing different Ca$^{2+}$ ions concentrations is shown in Fig. 9. It can be seen that the zeta-potential of chalcopyrite reduces gradually (becomes highly negative) as the pH increases in deionised water while the reduction is not very obvious in process water. However the zeta-potential is higher (less negative) in process water and in the presence of calcium ions than in deionised water due to the presence of positively charged metal ions in process water which adsorb on the surfaces of the mineral particles. This is an indication that adsorption of negatively charged collector on chalcopyrite particles may be enhanced (Fuerstenau and Pradip, 2005; Zhang et al., 1997).

Chalcopyrite surface is negatively charged in the entire pH 3 to 12 region either in deionised or process water, and an extrapolation of these curves show an iso-electric point (iep) around pH 3. Similar iep for chalcopyrite at low pH 3.0 has been documented by several authors(Healy and Moignard, 1976). The negative surface charge arises due to the sulphide anions and copper and iron cations interacting with oxygen of hydroxyl species. The presence of calcium clearly showed an iep at about pH 3.5 and the positive charge below this pH is
obviously due to the adsorption of $\text{Ca}^{2+}$ ions on the surface. The negative charge density is mostly constant between pH 4 and 10 with a lesser negative charge at higher calcium concentration. Above pH 10, all the curves in the presence of calcium proceed towards positive charge and exhibiting an iep at pH 11 in the presence of 1000 ppm calcium concentration. An increase in zeta-potential above pH 10 can be attributed to the presence of $\text{CaOH}^+$ species and their adsorption on the surface.

In galena the zeta-potential reduces gradually (becomes highly negative) as the pH increases in deionised water while the reduction is not very obvious in process water until after pH 8. In addition the zeta-potential is becoming less negative at all pH values with increasing calcium concentration in deionised water. The zeta-potential curve in the presence of 500 ppm calcium closely matches to that of the curve in process water illustrating the same level of calcium ions in process water (Table 2). Calcium ions exist as $\text{Ca}^{2+}$ ions up to pH 12 and their adsorption decreases the magnitude of negative charge which is seen in the results of deionised water. This is also an indication that adsorption of negatively charged collector on galena particles may be enhanced as mentioned above. The usual pH of flotation in practice is 10.5 and at this pH, the hydrolysis of calcium ions forms the first product of calcium hydroxyl species ($\text{CaOH}^+$) and these species established to be more susceptible to adsorption.

Several authors reported the zeta-potential of galena in the past (Healy and Moignard, 1976) and galena exhibits an iso-electric point (iep) ranging from pH 2 to 4 depending on its conditioning time in water and whether the surface is clean or composed of oxidised sulfooxy anions. The results show that galena is negatively charged in the pH range studied both in deionised water and process water, and an extrapolation of these curves indicates that the iep

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Fig. 9: Zeta-potential response of chalcopyrite, galena, pyrite and sphalerite at different pH in the presence of deionised water (DW), process water (PW) and deionised water containing 200, 300 and 1000 ppm calcium
lies at about pH 2. In general the magnitude of negative zeta-potential is lesser in process water than in deionised water due to the adsorption of metal cations that exist in process water.

The zeta-potential for pyrite in the absence of calcium ions shows an iso-electric point of pyrite at about pH 7.0, which is slightly higher than the values of pH 6.2 and 6.4 reported in the literature (Healy and Moignard, 1976). In process water, pyrite is slightly negative in the entire acidic pH region and up to pH 9.5 and above which pH a charge reversal to positive potentials is seen. The negative potentials in acidic pH region indicate the adsorption of sulfoxyl species and the positive potentials at very high basic pH show the adsorption of positive first hydroxyl species of Cu, Pb and Ca ions that exist in process water. In the presence of Ca ions, the zeta-potentials are positive in the entire acidic to basic pH range and the higher the concentration of Ca ions, the higher is the magnitude of positive potentials. It is very clear that the positively charged calcium ions in deionised water adsorb on the surface of pyrite and activate in the basic flotation pH region. This is an indication that adsorption of negatively charged collector on pyrite particles may be enhanced.

Studies reported in the literature indicate that the iso-electric point (iep) of sphalerite is in the range of pH 2 to 7. The extent of surface oxidation of the samples besides their origin and iron impurity could probably explain wide variation in iep. The results of the present sphalerite sample show that it is negatively charged in the entire pH range studied and an iep at pH 2 can be noticed while extending the curve. It can be seen that the zeta-potential responses reduces gradually (becomes highly negative) as the pH increases in deionised water and greatly reduced after pH ~9.8 while the reduction is not obvious in process water until after pH 10. In addition the zeta-potential is higher (less negative) in process water than in tap water similarly due to the presence of positively charged metal ions in process water which adsorb on the surfaces of the mineral particles. This is also an indication that adsorption of negatively charged collector on sphalerite particles may be enhanced but such behaviour is not seen in Hallimond flotation. The responses are also higher in the presence of Ca ions (the higher the concentration of Ca ions the closer the curve to the positive zeta-potential) and it’s completely positive at pH 11.5 and 500 mg/l Ca ions concentration.

![Fig. 10: Zeta-potential of chalcopyrite, galena, pyrite and sphalerite in different calcium ions concentrations at pH 10.5 and sphalerite at pH 11.5.](image-url)
The zeta-potential response of chalcopyrite, galena, pyrite and sphalerite at pH 10.5 in the presence of increasing concentration of calcium is shown in Fig. 10. The concentration of calcium ions found in various Boliden process water ranges from about 50 to 500 mg/l therefore the range of measurements was taken from 0 to 600 mg/l. It can be seen that the zeta-potential increases (becomes less negative) with increase in calcium ions concentration and in pyrite at about 50 ppm calcium ions, a charge reversal occurs. The dominance effect of calcium over sulphate ions on the zeta-potential of the minerals are shown in appendixes I to IV.

Fig. 11: Zeta-potential of chalcopyrite, galena, pyrite and sphalerite in different sulphate ions concentration at pH 10.5 and sphalerite at pH 11.5.

The concentration of sulphate ions found in various Boliden process water ranges from about 150 to 1500 mg/l therefore the range of measurements was taken from 0 to 1600 mg/l. It can be seen in Fig. 11 that the zeta-potential of chalcopyrite is averagely stable between 0 and 1000 mg/l of sulphate ions but increases slightly afterwards and stabilises from 1200 to 1600. The zeta-potential of galena also increases slightly and gradually with increase in sulphate ions concentrations while that of pyrite and sphalerite increases insignificantly with increase in sulphate ions concentrations.

The dominance effect of calcium over sulphate ions on the zeta-potential of the minerals as well as the effects of zinc sulphate, sodium hydrogen sulphite, dextrin and copper sulphate on potassium amylxanthate and isobutyl xanthate adsorption are shown in appendixes I to IV.

**Diffuse reflectance FTIR studies**

The requisite size fractions of each mineral sample were prepared by intensive grinding in normal atmospheric condition and treated at low and high pH values in the experiments. Since
the sulphide minerals are prone to oxidation by molecular oxygen, the presences of sulfoxyanions on the minerals have been examined at the experimental conditions. Surface oxidation of sulphide minerals exposed to atmosphere and in flotation is an established fact (Buckley et al., 1985; Clarke et al., 1995; Dunn, 1997; Fullston et al., 1999; Vaughan et al., 1997) therefore the minerals were treated deliberately with H$_2$O$_2$ oxidant at different times so as to compare and judge the extent of surface oxidation of the samples.

The FTIR spectra of –5 μm pure chalcopyrite and chalcopyrite treated with H$_2$O$_2$ at different times are shown in Fig. 12. Untreated chalcopyrite spectrum exhibits two broad bands centred around 1008 cm$^{-1}$ and 471 cm$^{-1}$, and weak bands at 1195, 1166, 798, 776, 628 and 522 cm$^{-1}$ frequency. In addition to these bands, the oxidised chalcopyrite sample display bands at 3622, 3551, 3394, and 1090 cm$^{-1}$. The intensity of all bands in the H$_2$O$_2$ treated sample spectra increases with increasing time of treatment, implying that these bands relate to surface oxidised sulfoxyanion and hydroxide species. The bands at 1195 and 1008 cm$^{-1}$ can be assigned to S–O stretch vibrations in sulphate and sulphite structures respectively, while the band at 628 cm$^{-1}$ represents S–O bend vibrations. The superficial iron oxy-hydroxide species display bands in the 794-630 cm$^{-1}$ region and iron sulphate at 470 cm$^{-1}$; however the several bands around 470 and 780 cm$^{-1}$ could also arise due to Si–O vibrations caused by silicate impurity in the sample. The bands in the region 3000-3700 cm$^{-1}$ of the H$_2$O$_2$ treated sample characterize O–H stretching vibrations of surface hydroxyl groups.

The diffuse reflectance spectrum of –5 μm galena powder sample is shown in Fig. 13. The spectra of the same sample conditioned with H$_2$O$_2$ at different times are also presented in this figure. Since galena exhibit a fundamental vibration below 200 cm$^{-1}$, the several bands seen in the spectrum of pure sample are due to oxidized species on the surface. An increase in the intensity of these bands when the sample is treated with H$_2$O$_2$ oxidant substantiate that these bands are characteristic of oxidized species present on the sample.
The oxidized surface state of galena mainly consists of lead sulphate and thiosulphate, and lead carbonate. The bands at 598, 629, 1051, 1093 and 1160 cm$^{-1}$ can be assigned to S–O vibrations in lead sulphate. Lead thiosulphate bands that could appear at about 985 and 1120 cm$^{-1}$ are not really noticed in the spectra. Absorption bands characteristic of C–O vibrations in lead carbonate are seen at about 679, 838, 1051, 1409 and 1425 cm$^{-1}$. The spectra with increasing time of H$_2$O$_2$ treatment, the intensity of sulphate bands increased with no or little effect on carbonate bands. While comparing pure galena spectrum to the spectra oxidized by H$_2$O$_2$, it is clear that the pure galena sample used in experiments is partially oxidized and the surface is composed of not only sulphate but also carbonate species.

The oxidized surface state of pyrite mainly consists of ferrous sulphate and ferric sulphate, and superficial carbonate. Fundamental pyrite vibration bands exist below 600 cm$^{-1}$ (de Donato et al., 1999) therefore the absorbance bands seen in the pure pyrite spectrum in Fig. 14 are due to oxidised surface compounds. The band at 828 cm$^{-1}$ can be assigned to S–O vibrations in ferrous sulphate. The bands at 1017 to 1154 can be assigned to S-O vibrations in ferric sulphate, while the low intensity band at 1494 can be assigned to C-O vibration in superficial carbonate (de Donato et al., 1999; de Donato et al., 1993; Godociková et al., 2002). However with addition and increasing time of treatment in H$_2$O$_2$, the sulphate bands intensities marginally decreases and the carbonate band disappeared, this is indicating that the surfaces were initially covered by hydrated sulphates (de Donato et al., 1999). While comparing pure pyrite spectrum to the spectra oxidized by H$_2$O$_2$, it is clear that the pure pyrite sample used in the experiments is oxidized meagrely and the surface is mainly composed of hydrated sulphate species.
The diffuse reflectance spectrum of \(-5 \mu m\) sphalerite powder sample that is obtained after dry grinding in agate mortar and then micro-sieving in ultrasonic bath is shown in Fig. 15. The spectra of the same sample conditioned with H\(_2\)O\(_2\) at different times are also presented in this figure. Although sphalerite is a non-conductive solid which superficial oxidation is limited in the absence of surface activation (de Donato et al., 1999; Persson and Persson, 1991), however the several bands seen in the spectrum of pure sample are due to oxidized species on the surface since the sample was prepared open to atmosphere. An increase in the intensity of these bands when the sample is treated with H\(_2\)O\(_2\) oxidant substantiate that these bands are characteristic of oxidized species present on the sample.

The oxidized surface state of sphalerite mainly consists of zinc sulphate and thiosulphate, and zinc carbonate. The bands at 1056, 1101, and 1160 cm\(^{-1}\) can be assigned to S–O vibrations in zinc sulphate (Godociková et al., 2002). Absorption bands characteristic of C–O vibrations in zinc carbonate are seen at about 870, and 1441 cm\(^{-1}\) (de Donato et al., 1999; Godociková et al., 2002). The spectra with increasing time of H\(_2\)O\(_2\) treatment, the intensity of sulphate bands increased with no or little effect on carbonate bands. While comparing pure sphalerite spectrum to the spectra oxidized by H\(_2\)O\(_2\), it is clear that the pure sphalerite sample used in the experiments is partially oxidized and the surface is composed of both sulphate and carbonate species.
Fig. 15: DRIFT spectra of pure and H2O2 treated sphalerite.

The effect of calcium concentration on chalcopyrite spectra at the flotation pH 10.5 in de-ionised and process waters is shown in Figs. 16 and 17 respectively. The presence of calcium has no marked changes in the surface species bands in de-ionised water while additional strong bands at 1432 and 876 cm⁻¹ appeared in process water.

Fig. 16: Effect of calcium concentration on chalcopyrite at pH 10.5 in deionised water.
The intensity of these carbonate species bands is seen to increase with increased calcium concentration characterizing increased calcium carbonate coating on the surface. Since the solids are collected after filtration, any bulk calcium carbonate precipitation remain in the solids fraction and hence seen in the spectra. The band frequencies related to sulfoxyanion species, mainly sulphate and/or sulphites are the same in these spectra with a similar intensity with increasing calcium concentration. Since the solubility of calcium sulphate is much higher than calcium carbonate, the formation of calcium carbonate coating on the surface is understandable.

![Fig. 17: Effect of calcium concentration on chalcopyrite at pH 10.5 in process water.](image)

Figs. 18 and 19 show the influence of sulphate concentration on chalcopyrite in deionised and process waters respectively. The S–O stretching bands (1007 and 1195 cm\(^{-1}\)) in deionised water and in process water (1009, 1088, 1139, 1158 and 1186 cm\(^{-1}\)) are seen to increase with increasing sulphate concentration and the sulphate anions can be adsorbed on surface metal ion sites. Coordination of sulphate seems to be through the sulphur atom as SO stretching vibrations are being shifted to higher frequencies. Many peaks in process water compared to deionised water could be due to the presence of several reduced sulfoxyanions in process water and their adsorption.
In all the spectra, a shoulder band at 877 cm\(^{-1}\) and weak broad band at 1441 cm\(^{-1}\) can be assigned to carbonate anions. A strong adsorption of these anionic species on surface metal cations may largely inhibit anionic collector adsorption.

Fig. 19: Effect of sulphate concentration on chalcopyrite at pH 10.5 in process water.
The effect of calcium ions on galena surface composition in deionised and process waters at pH 10.5 depicted in Figs. 20 and 21 respectively. The spectra with increasing calcium in deionised water are comparable to the spectra conditioned at the same pH of 10.5 in the absence of calcium. The consumption of dissolved carbon dioxide in water from atmosphere leading to formation of lead carbonate (1410, 838, 680 cm\(^{-1}\)) has led no calcium carbonate precipitation with increasing calcium concentration where the low intensity of calcium carbonate bands (1430, 871 cm\(^{-1}\)) are unaffected.

![Fig. 20: Effect of calcium concentration on galena at pH 10.5 in deionised water.](image)

However, in the presence of process water, calcium carbonate bands have dominated than lead carbonate bands and with increasing calcium concentration, the bands characterizing calcium carbonate at 1432 and 877 cm\(^{-1}\) is seen to increase. In both cases, calcium ions have no effect on sulphate characteristic bands. Galena surface is mainly composed of lead carbonate in process water at pH 10.5 and higher level of calcium in process water leads to calcium carbonate precipitation on the surface.
Fig. 21: Effect of calcium concentration on galena at pH 10.5 in process water.

Figs. 22 and 23 respectively shows the spectra of galena conditioned with increasing concentration of sulphate ions in deionised and process waters at pH 10.5. The intensity of S-O stretching vibrations bands in sulfoxyanion species in deionised water is seen to increase a little with increasing sulphate ions until 700 ppm after which level they are decreased. The intensity level of these bands is close to the spectrum that is conditioned in water in the absence of sulphate suggesting that the surface is already oxidised to lead sulphate.

Fig. 22: Effect of sulphate concentration on galena at pH 10.5 in deionised water.
However, in process water these bands are seen at higher intensity level and there is no change in intensity with increasing sulphate concentration. The galena surface is totally composed of lead sulphate in process water containing several reduced sulfoxy species and there is no marked influence of additional sulphate concentration in process water.

![Fig. 23: Effect of sulphate concentration on galena at pH 10.5 in process water.](image)

The effect of calcium ions on pyrite surface composition in deionised and process waters at pH 10.5 are depicted in Figs. 24 and 25 respectively. The spectra with increasing calcium in deionised water are comparable to the spectra conditioned at the same pH of 10.5 and the presence calcium confer high intensity ferric sulphate bands at 1119 and 1151 cm⁻¹; the intensity is stronger when 50 ppm of Ca was present in the solution.

![Fig. 24: Effect of calcium concentration on pyrite at pH 10.5 in deionised water.](image)

However, in the presence of process water increase of calcium, dissolved organic reagents and carbon dioxide from air have lead to precipitation of calcium carbonate on the surface of the
pyrite (871 cm\(^{-1}\) and superficial carbonates broad bands at 1368 to 1461). The intensity of the bands is higher at 300 ppm concentration of calcium in solution. Pyrite surface is mainly composed of sulphate and carbonate in process water at pH 10.5 and higher level of calcium in process water leads to calcium carbonate precipitation on the surface.

![Effect of calcium concentration on pyrite at pH 10.5 in process water.](image)

Fig. 25: Effect of calcium concentration on pyrite at pH 10.5 in process water.

Fig. 26 and 27 respectively shows the spectra of pyrite conditioned with increasing concentration of sulphate ions in deionised and process waters at pH 10.5. The intensity of S-O stretching vibrations bands in sulfoxyanion species in deionised water is seen to increase at 400 ppm sulphate concentration after which level they are decreased. The intensity level of these bands is close to the spectrum that is conditioned in water in the absence of sulphate suggesting that the surface is already oxidised to ferric sulphate.

![Effect of sulphate concentration on pyrite at pH 10.5 in deionised water.](image)

Fig. 26: Effect of sulphate concentration on pyrite at pH 10.5 in deionised water.
However, in process water these bands are seen at higher intensity level and there is no change in intensity with increasing sulphate concentration. In addition a low intensity band of calcium carbonate can be seen at 871 cm⁻¹. The pyrite surface is mostly composed of ferric sulphate in process water containing several reduced sulfoxy species and there is no marked influence of additional sulphate concentration in process water.

Fig. 27: Effect of sulphate concentration on pyrite at pH 10.5 in process water.

The effect of calcium ions on sphalerite surface composition in deionised and process waters at pH 11.5 are depicted in Figs. 28 and 29. The spectra with increasing calcium in deionised water are comparable to the spectra conditioned at the same pH of 11.5 in the absence of calcium. The consumption of dissolved carbon dioxide in water from atmosphere leading to formation of zinc carbonate (1442, 870 cm⁻¹) has led to no calcium carbonate precipitation with increasing calcium concentration where the low intensity of calcium carbonate bands (1433, 870 cm⁻¹) are unaffected.
However, in the presence of process water, calcium carbonate bands have dominated zinc carbonate bands and with increasing calcium concentration, the bands characterizing calcium carbonate at 1441 and 871 cm\(^{-1}\) are seen to increase. In both cases, calcium ions have no effect on sulphate characteristic bands. Sphalerite surface is mainly composed of zinc carbonate in process water at pH 11.5 and higher level of calcium in process water leads to calcium carbonate precipitation on the surface.

Fig. 28: Effect of calcium concentration on sphalerite at pH 11.5 in deionised water.

Fig. 29: Effect of calcium concentration on sphalerite at pH 11.5 in process water
Figs. 30 and 31 shows the spectra of sphalerite conditioned with increasing concentration of sulphate ions in deionised and process waters at pH 11.5. The intensity of S-O stretching vibrations bands in sulfoxy species in deionised water is seen to increase a little with increasing sulphate ions until 400 ppm after which level they are decreased. The intensity level of 700 and 1000 ppm bands is close to the spectrum that is conditioned in water in the absence of sulphate suggesting that the surface is already oxidised to zinc sulphate.

Similarly, in process water the spectrum with 700 ppm sulphate and the spectrum without addition of sulphate are comparable while the remaining bands are also seen at higher intensity level.

Fig. 30: Effect of sulphate concentration on sphalerite at pH 11.5 in deionised water.

Fig. 31: Effect of sulphate concentration on sphalerite at pH 11.5 in process water.
The sphalerite surface is totally composed of zinc sulphate in process water containing several reduced sulfoxy species and there is no significant influence of additional sulphate concentration in process water.

**Figure 32:** Difference DRIFT spectra of sulphide minerals treated at 5x10^{-5}M xanthate concentration at pH 10.5 (ZnS pH 11.5) in deionised water after subtracting the respective pure mineral reference spectrum

The spectra of chalcopyrite, galena, sphalerite and pyrite treated with 5x10^{-5} M xanthate in deionised water after subtracting the pure mineral spectrum conditioned at the same experimental pH 10.5 (pH 11.5 for ZnS) without xanthate are shown in Fig. 32. The spectrum for chalcopyrite shows prominent bands at 1201, 1157, 1098 and 1011 cm^{-1}. These bands are obviously associated with adsorbed xanthate species where the higher intensity band 1098 cm^{-1} can be assigned to C–O–C vibrations and the bands at 1201 and 1011 cm^{-1} are due to S–C–S and C–O–C stretching vibrations (de Donato et al., 1999; Leppinen, 1990; Leppinen et al., 1989; Mielczarski et al., 1998; Persson, 1994). The bands characteristic of copper xanthate (1157 cm^{-1}) and dixanthogen (1201 cm^{-1}) are observed.

The spectrum for galena also exhibits C-O-C and S-C-S symmetric stretching vibration band at 1187 cm^{-1} and the stretching vibration band of the S-C-S group at 1024 cm^{-1} (Cases and De Donato, 1991; Cases et al., 1990; Chernyshova, 2002; Leppinen et al., 1989). Comparing the corresponding bands in lead amylxanthate (1:2) compound, these bands are shifted from 1220 cm^{-1} to a lower value of 1187 cm^{-1} and from 1022 to 1024 cm^{-1}. These bands can be assigned to monocoordinated form of lead xanthate.

The pyrite the spectrum exhibits C-O-C symmetric stretching vibration band at 1199 cm^{-1} and the stretching vibration band of the S-C-S group at 1062-1043 cm^{-1}. These xanthate species bands on pyrite are comparable to those of bulk dixanthogen with signals at 1239 and 1021 cm^{-1} wave numbers (Leppinen, 1990) but have shifted, and they can be assigned to iron xanthate. The ferric sulphate (1137, 1062, cm^{-1}) (Borda et al., 2004) and ferrous sulphate (808 cm^{-1}) bands although diminished can be seen in these spectra.
Bands of sphalerite oxidation products and low intensity C-O-C and S-C-S symmetric stretching vibration bands can be seen at 1200 cm\(^{-1}\) and 1047 (Larsson et al., 2000) respectively indicating amylxanthate adsorption on sphalerite surface.

The surface oxidized products of the minerals are expected to be removed during the abstraction of xanthate. The presence of oxidation products indicates that the maximum xanthate concentration of \(5 \times 10^{-5}\) M used is not adequate to form monolayer coverage.

![Difference DRIFT spectra of sulphide minerals treated at \(5 \times 10^{-5}\)M xanthate concentration at pH 10.5 (ZnS pH 11.5) in process water after subtracting the respective pure mineral reference spectrum](image)

Fig. 33: Difference DRIFT spectra of sulphide minerals treated at \(5 \times 10^{-5}\)M xanthate concentration at pH 10.5 (ZnS pH 11.5) in process water after subtracting the respective pure mineral reference spectrum

The spectra of chalcopyrite, galena, sphalerite and pyrite treated with \(5 \times 10^{-5}\) M xanthate in process water after subtracting the pure mineral spectrum conditioned at the same experimental pH 10.5 (pH 11.5 for ZnS) without xanthate are shown in Fig. 33. Chalcopyrite spectrum in process water shows that the S–O stretching band (1008 cm\(^{-1}\)) dominates over xanthate species bands, weak and low intensity bands (1181, 1144, 1084 cm\(^{-1}\)) inferring lower adsorption of xanthate. The galena spectrum shows weak xanthate bands and relatively high intensity lead carbonate bands at 873 and 1457 cm\(^{-1}\) inferring that the surface oxidation products in process water impeded xanthate adsorption. Pyrite spectrum show diminished xanthate bands. The presence of negative ferric sulphate band illustrates different level of surface oxidation compounds in the xanthate treated pyrite spectra compared to mineral spectrum that was subtracted. The sphalerite spectrum shows increased oxidised compound bands and mostly devoid of xanthate bands. The absence of xanthate bands could be that xanthate is in complex formation with the metal ions in process water or copper ions activation to sphalerite is necessary for xanthate adsorption.
Fig. 34: Difference DRIFT spectra of sulphide minerals treated at 300 ppm calcium and 5 x 10⁻⁵ M xanthate concentration at pH 10.5 (ZnS pH 11.5) in deionised water after subtracting the respective pure mineral reference spectrum.

The spectra of chalcopyrite, galena, sphalerite and pyrite treated with 5 x 10⁻⁵ M xanthate and 300 ppm calcium in deionised water after subtracting the pure mineral spectrum conditioned at the same experimental pH 10.5 (pH 11.5 for ZnS) without xanthate are shown in Fig. 34 depicting the effect of calcium ions on xanthate adsorption.

Chalcopyrite spectrum shows that the intensity of bands characteristic to copper (1) amyl xanthate and dixanthogen (1089, 1162, 1175, 1195 cm⁻¹) are unchanged; only the intensity of a band (1009 cm⁻¹) due to oxidised sulfoxyanions is diminished in the presence of calcium. The spectra illustrates that there is no influence of calcium on xanthate adsorption onto chalcopyrite in deionised water.

Galena spectrum displayed negative bands of surface oxidised compounds; this is as a result of sulfooxy and carbonate species forming soluble complexes with the calcium. Xanthate adsorption on galena is also reduced in the presence of calcium as shown by the decreasing intensity of xanthate bands (1187 and 1023 cm⁻¹).

Pyrite shows that the surface xanthate species bands at 1119 to 1172 cm⁻¹ broaden forms two peaks and increase in intensity in the presence of calcium. In addition a low intensity carbonate band appears at 848 cm⁻¹. The broad signal could be due to precipitation of a calcium xanthate complex on the pyrite surface. Xanthate adsorption on pyrite is also increased in the presence of calcium as shown by the increasing intensity of xanthate bands (1155 and 1124 cm⁻¹). Sphalerite spectrum shows decreased intensity of surface zinc sulphate and carbonate bands as well as reduced xanthates bands (1200-1047 cm⁻¹) in the presence of calcium. The successive decrease in surface oxidised compounds bands was due to the result of sulfooxy and carbonate species forming soluble complexes with the calcium.
Fig. 35: Difference DRIFT spectra of sulphide minerals treated at 300 ppm calcium and 5 x 10^{-5} M xanthate concentration at pH 10.5 (ZnS pH 11.5) in process water after subtracting the respective pure mineral reference spectrum.

The spectra of chalcopyrite, galena, sphalerite and pyrite treated with 5x10^{-5} M xanthate and 300 ppm calcium in process water after subtracting the pure mineral spectrum conditioned at the same experimental pH 10.5 (pH 11.5 for ZnS) without xanthate are shown in Fig. 35 depicting the effect of calcium ions on xanthate adsorption.

Chalcopyrite spectrum shows that the presence of both calcium ions and xanthate gives a negative carbonate bands at 1442 and 875 cm^{-1} indicating that the surface carbonate layer is more concentrated when treated in process water than in the presence of xanthate. This could be due to ion-exchange between carbonate anions and xanthate or surface metal ion carbonation/carbonate precipitation is impeded in the presence of xanthate.

Galena spectrum compared to in process water and in the presence of 5x10^{-5} M xanthate, the spectrum shows very intense carbonate bands at 873 and 1457 cm^{-1} (Fig. 33) this has not only disappeared but also show negative bands at the same region. These spectra indicate that calcium forms complexes with surface carbonate species and dissolved into the bulk of the solution.

Pyrite spectrum in process water and in the presence of 5x10^{-5} M xanthate, the spectrum shows a low intensity carbonate band at 873 cm^{-1} which is diminished at the same region on addition of calcium. These spectra indicate that calcium forms complexes with surface carbonate species and dissolved into the bulk of the solution. Sphalerite spectrum also shows that the surface oxidized compounds are removed from the surface in the presence of calcium. While in the presence of 5x10^{-5} M xanthate, the spectrum shows very intense carbonate bands at 1450 and 877 cm^{-1}, it also shows negative bands at the same region indicating that calcium forms complexes with surface carbonate species and dissolved into the bulk of the solution.
The spectra of chalcopyrite, galena, sphalerite and pyrite treated with $5 \times 10^{-5}$ M xanthate and 700 ppm sulphate in deionised water after subtracting the pure mineral spectrum conditioned at the same experimental pH 10.5 (pH 11.5 for ZnS) without xanthate are shown in Fig. 36 depicting the effect of sulphate ions on xanthate adsorption.

Chalcopyrite spectrum features in the presence of sulphate and xanthate is similar to features in the presence of only xanthate inferring no significant influence of sulphate ions on xanthate adsorption. However, higher concentration of sulphate reduced the intensity of S–O stretching band considerably and at the same time xanthate species bands intensity increased a little. The sulphate ions in this case could be in either complex or precipitate formation with dissolved Fe ions, therefore no competition for xanthate adsorption from sulphate anions.

Galena spectrum shows that the oxidised lead sulphate and carbonate is marginally removed from the surface in the presence of sulphate. Xanthate adsorption is not much affected with sulphate concentration. Pyrite spectrum shows that the carbonate is marginally removed from the surface in the presence of sulphate. Sphalerite spectrum shows increase in oxidised zinc sulphate and carbonate band. There is no significant effect of sulphate on xanthate adsorption.
The spectra of chalcopyrite, galena, sphalerite and pyrite treated with $5 \times 10^{-5}$ M xanthate and 700 ppm sulphate in process water after subtracting the pure mineral spectrum conditioned at the same experimental pH 10.5 (pH 11.5 for ZnS) without xanthate are shown in Fig. 37 depicting the effect of sulphate ions on xanthate adsorption.

In chalcopyrite the presence of sulphate ions and xanthate show a negative carbonate band at 875 cm$^{-1}$ indicating that the surface carbonate layer is more concentrated when treated in process water than in the presence of xanthate. This could be due to ion-exchange between carbonate anions and xanthate or surface metal ion carbonation/carbonate precipitation is impeded in the presence of xanthate. Xanthate bands at 1086 and 1201 cm$^{-1}$ in the presence of calcium and weak bands at 1086 and 1188 cm$^{-1}$ in the presence of lower sulphate concentration can however be seen in these spectra. However, at 1000 ppm sulphate concentration, the spectrum is almost devoid of xanthate bands. Thus, very high sulphate concentration impeded xanthate adsorption.

Galena spectrum shows that presence of sulphate entirely removed both oxidised lead sulphate and carbonate from the surface. Xanthate adsorption is not much affected in the presence of sulphate. In the case of pyrite, the presence of sulphate removes both ferric sulphate and carbonate from the surface. Xanthate adsorption is not much affected by the presence of sulphate. Sphalerite shows that presence of sulphate increase oxidised zinc sulphate and carbonate bands. There is no significant effect on xanthate adsorption in the presence of sulphate.

Spectra depicting the effects of zinc sulphate, sodium hydrogen sulphite, dextrin and copper sulphate on potassium amylxanthate and isobutyl xanthate adsorption on sulphides can be found in appendixes I to IV.
Bench-scale flotation studies

The bench scale flotation studies were carried out at different temperatures covering the range of seasonal temperatures in the process plant since the temperature in the process plants in the north of Sweden varies seasonally from winter to spring and summer through autumn. Renström ore grades 0.36% Cu, 6% Zn, and 1% Pb while Kristineberg ore grades 0.9% Cu, 2.4% Zn, and 0.15% Pb.

Table 3 shows the recovery and grade of metals from flotation of both Renström and Kristineberg ores at different temperature using both tap water and process water. It can be observed that the recovery of copper from Renström and Kristineberg ores decreases with temperature. This is most likely due to reduced thermodynamics of mineral-collector interaction as the temperature decreases. In addition, the grade and recovery of copper when process water is used are higher than the products when tap water is used on the average. The somewhat better results when the process water was used could be due to presence of high concentration of Ca²⁺ ions that enhances collector adsorption to KAX (an anionic collector) as seen in zeta-potential studies as well as other minor metal species and rest reagents that acts as activators (Chen et al., 2009; Finkelstein, 1997).

Table 3: Recovery and Grade of metals from flotation of Renström and Kristineberg ores at different temperature using both tapwater and process water.

<table>
<thead>
<tr>
<th></th>
<th>Tapwater</th>
<th>Process water</th>
<th>Tapwater</th>
<th>Process water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>22.5°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu 87.99</td>
<td>1.84</td>
<td>89.67</td>
<td>1.58</td>
<td>91.52</td>
</tr>
<tr>
<td>Pb 82.63</td>
<td>5.61</td>
<td>88.51</td>
<td>5.03</td>
<td>80.71</td>
</tr>
<tr>
<td>Zn 72.46</td>
<td>20.45</td>
<td>67.41</td>
<td>21.52</td>
<td>22.53</td>
</tr>
<tr>
<td><strong>11°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu 83.81</td>
<td>1.56</td>
<td>84.94</td>
<td>1.31</td>
<td>89.91</td>
</tr>
<tr>
<td>Pb 75.44</td>
<td>4.46</td>
<td>74.48</td>
<td>4.08</td>
<td>83.48</td>
</tr>
<tr>
<td>Zn 67.76</td>
<td>19.07</td>
<td>69.88</td>
<td>18.10</td>
<td>37.98</td>
</tr>
<tr>
<td><strong>4°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu 83.39</td>
<td>1.42</td>
<td>82.13</td>
<td>1.82</td>
<td>89.03</td>
</tr>
<tr>
<td>Pb 75.58</td>
<td>3.69</td>
<td>74.15</td>
<td>5.50</td>
<td>82.28</td>
</tr>
<tr>
<td>Zn 68.18</td>
<td>17.15</td>
<td>70.21</td>
<td>21.20</td>
<td>36.34</td>
</tr>
</tbody>
</table>

It can also be observed that the recovery of lead from Renström ore in tap water decreases as temperature decreased from 22°C to 11°C while it increases at 4°C however the grade at 11°C is better than at 4°C. The recovery of Renström ore in process water however decreases with temperature. In contrast the recovery and grade of Kristineberg ores in tap water increases as temperature decreases with highest increase at 11°C. In process water the grade increases with decreases in temperature whilst the recovery decreases and increase again from 22°C, to 11°C and 4°C respectively. The reduction in recovery as temperature decreases are most likely due to reduced thermodynamics of mineral-collector interaction as the temperature decreases as mentioned above. The increase in recovery and grade in Kristineberg ore when temperature reduces cannot be clearly explained. One possible reason for better grades in process water.
could be the presence of rest reagents and high concentration of Ca\textsuperscript{2+} ions that enhances collector adsorption as mentioned above.

It can as well be observed that the recovery and grade of zinc from Renström ore in tap water decreases as temperature decreases, while the reverse is almost the case in process water where the recovery increases with decrease in temperature. However in Kristineberg ore both the recovery and grade of zinc increases with decrease in temperature in both tap and process waters. The increase in recoveries and grades of zinc as the temperature decreases cannot be clearly explained. One possible reason for better grades in process water could be the presence of rest reagents (Chen et al., 2009).

Table 4: Comparison of recoveries and grades when Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2-} ions are added to tapwater, to tapwater and process water at 22.5°C.

<table>
<thead>
<tr>
<th></th>
<th>Tapwater</th>
<th>Process water</th>
<th>Ca\textsuperscript{2+}</th>
<th>SO\textsubscript{4}\textsuperscript{2-}</th>
<th>Ca\textsuperscript{2+}+SO\textsubscript{4}\textsuperscript{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rec. %</td>
<td>Grade %</td>
<td>Rec. %</td>
<td>Grade %</td>
<td>Rec. %</td>
</tr>
<tr>
<td>Renström</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>87.99</td>
<td>1.84</td>
<td>89.67</td>
<td>1.58</td>
<td>87.60</td>
</tr>
<tr>
<td>Pb</td>
<td>82.63</td>
<td>5.61</td>
<td>88.51</td>
<td>5.03</td>
<td>87.60</td>
</tr>
<tr>
<td>Zn</td>
<td>72.46</td>
<td>20.45</td>
<td>67.41</td>
<td>21.52</td>
<td>68.38</td>
</tr>
<tr>
<td>Kristineberg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>91.52</td>
<td>3.60</td>
<td>92.53</td>
<td>2.91</td>
<td>91.34</td>
</tr>
<tr>
<td>Pb</td>
<td>80.71</td>
<td>0.53</td>
<td>85.71</td>
<td>0.46</td>
<td>82.31</td>
</tr>
<tr>
<td>Zn</td>
<td>22.53</td>
<td>2.61</td>
<td>41.99</td>
<td>6.31</td>
<td>24.06</td>
</tr>
</tbody>
</table>

Table 4 shows a comparison between flotation results using tap water, process water and simulated water containing process water equivalent concentration of Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2-} ions singly and combined. It can be observed that the presence of Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2-} ions singly and combined in the water has some influence on both the recovery and grade of copper, galena and zinc. The somewhat better results when the process water was used could be due to presence of other minor metal species and rest reagents that acts as activators (Chen et al., 2009; Finkelstein, 1997). The difference in flotation response between process and tap water could also be caused by different grinding environments (Eric Forsberg et al., 1993; Grano, 1999; Göktepe and Williams, 1995; Martin et al., 1991; Peng et al., 2003a; Peng et al., 2003b), for example, the pH of process water is about 11 which is the grinding pH when using process water for flotation as against tap water in which grinding pH is about 8.

**Balance of calcium and sulphate species in pulp solution**

**Renström Ore**

The sulphate and calcium species concentration balance in solution for tests on Renström ore using tap water and process water at 22 °C, 10°C and 5 °C temperatures are presented in Table 5. The concentrations of Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2-} ions in the tap water are 22.5 and 7.4 mg/l respectively. The concentrations of Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2-} ions in the final solution after the flotation using tap water at 22.5 °C are 370 and 375 mg/l respectively. The concentration of Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2-} contributed by the reagents are 449 mg/l and 365 mg/l respectively. The shortage of 102 mg/l Ca\textsuperscript{2+} must have adsorbed on the mineral surfaces and/or precipitated as calcium carbonate, and the excess of 2 mg/l SO\textsubscript{4}\textsuperscript{2-} must have been contributed from the dissolved sulphur composition of the mineral. The concentrations of Ca\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2-} ions in the process.
water are 128 and 63 mg/l respectively. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using process water at 22 °C are 446 and 511 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 328 and 392 mg/l respectively. The shortage of 10 mg/l Ca$^{2+}$ must have been adsorbed on the mineral surfaces and the excess of 56 mg/l SO$_4^{2-}$ must have been contributed from the sulphur composition of the mineral.

Table 5. Calcium and sulfate species ions balance in solution from flotation of Renström ore at different temperature using both tapwater and process water.

<table>
<thead>
<tr>
<th>Pulp liquid</th>
<th>Tap water</th>
<th>Process water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~22 °C</td>
<td>~11 °C</td>
</tr>
<tr>
<td></td>
<td>SO$_4^{2-}$ mg/l</td>
<td>Ca$^{2+}$ mg/l</td>
</tr>
<tr>
<td>Initial</td>
<td>373</td>
<td>472</td>
</tr>
<tr>
<td>Final</td>
<td>375</td>
<td>370</td>
</tr>
<tr>
<td>Difference</td>
<td>2</td>
<td>-102</td>
</tr>
<tr>
<td>~11 °C</td>
<td>Initial</td>
<td>306</td>
</tr>
<tr>
<td>Final</td>
<td>281</td>
<td>155</td>
</tr>
<tr>
<td>Difference</td>
<td>-25</td>
<td>-112</td>
</tr>
<tr>
<td>~4 °C</td>
<td>Initial</td>
<td>249</td>
</tr>
<tr>
<td>Final</td>
<td>224</td>
<td>121</td>
</tr>
<tr>
<td>Difference</td>
<td>-25</td>
<td>-99</td>
</tr>
</tbody>
</table>

The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using tap water at 10 °C are 155 and 281 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 245 mg/l and 299 mg/l respectively. The shortage of 112 mg/l Ca$^{2+}$ must have been adsorbed on the mineral surfaces and the shortage of 25 mg/l SO$_4^{2-}$ must be due to competitive adsorption on the surfaces of the minerals. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using process water at 10 °C are 200 and 364 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 103 mg/l and 240 mg/l respectively. The shortage of 31 mg/l Ca$^{2+}$ must have been adsorbed on the mineral surface and the excess of 61 mg/l SO$_4^{2-}$ must have come from the sulphur concentration in the mineral.

The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using tap water at 5 °C are 121 and 224 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 198 mg/l and 241 mg/l respectively. The shortages of 99 mg/l Ca$^{2+}$ and 25 mg/l SO$_4^{2-}$ must be due to the adsorption of the species to the surfaces of the minerals. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using process water at 5 °C are 239 and 366 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 92 mg/l and 241 mg/l respectively. There is neither shortage nor excess of Ca$^{2+}$ ions. However the excess of 21 mg/l SO$_4^{2-}$ must have come from the sulphur concentration in the mineral.
The sulphate and calcium species concentration balance in solution and flotation results for tests on Kristineberg ore using tapwater and process water at 22 °C, 10 °C and 5 °C temperatures are presented in Table 6. The concentrations of Ca^{2+} and SO_{4}^{2-} ions in the tapwater are 22.5 and 7.4 mg/l respectively. The concentrations of Ca^{2+} and SO_{4}^{2-} ions in the final solution after the flotation using tapwater at 22 °C are 556 and 918 mg/l respectively. The concentration of Ca^{2+} and SO_{4}^{2-} contributed by the reagents are 493 mg/l and 409 mg/l respectively. The excess of 41 mg/l Ca^{2+} must have come from the ore and excess of 502 mg/l SO_{4}^{2-} must have been contributed from the sulphur composition of the mineral. The concentrations of Ca^{2+} and SO_{4}^{2-} ions in the process water are 186 and 153 mg/l respectively. The concentrations of Ca^{2+} and SO_{4}^{2-} ions in the final solution after the flotation using process water at 22 °C are 782 and 1090 mg/l respectively. The concentration of Ca^{2+} and SO_{4}^{2-} contributed by the reagents are 762 and 519 mg/l respectively. The shortage of 166 mg/l Ca^{2+} must have been adsorbed on the mineral surfaces and the excess of 418 mg/l SO_{4}^{2-} must have been contributed from the sulphur composition of the mineral.

Table 6. Calcium and sulfate species ions balance in solution from flotation of Kristineberg ore at different temperature using both tapwater and process water.

<table>
<thead>
<tr>
<th>Pulp liquid</th>
<th>Tap water</th>
<th>Process water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~22 °C</td>
<td>~10 °C</td>
</tr>
<tr>
<td></td>
<td>SO_{4}^{2-} mg/l</td>
<td>Ca^{2+} mg/l</td>
</tr>
<tr>
<td>Initial</td>
<td>416</td>
<td>515</td>
</tr>
<tr>
<td>Final</td>
<td>918</td>
<td>556</td>
</tr>
<tr>
<td>Difference</td>
<td>502</td>
<td>41</td>
</tr>
<tr>
<td>Initial</td>
<td>249</td>
<td>425</td>
</tr>
<tr>
<td>Final</td>
<td>556</td>
<td>394</td>
</tr>
<tr>
<td>Difference</td>
<td>308</td>
<td>-31</td>
</tr>
<tr>
<td>Initial</td>
<td>249</td>
<td>364</td>
</tr>
<tr>
<td>Final</td>
<td>506</td>
<td>346</td>
</tr>
<tr>
<td>Difference</td>
<td>257</td>
<td>-18</td>
</tr>
</tbody>
</table>

The concentrations of Ca^{2+} and SO_{4}^{2-} ions in the final solution after the flotation using tapwater at 10 °C are 394 and 556 mg/l respectively. The concentration of Ca^{2+} and SO_{4}^{2-} contributed by the reagents are 402 mg/l and 241 mg/l respectively. The shortage of 31 mg/l Ca^{2+} must have been adsorbed on the mineral surfaces and the excess of 308 mg/l SO_{4}^{2-} must have been contributed from the sulphur composition of the mineral. The concentrations of Ca^{2+} and SO_{4}^{2-} ions in the final solution after the flotation using process water at 10 °C are 565 and 704 mg/l respectively. The concentration of Ca^{2+} and SO_{4}^{2-} contributed by the reagents are 357 mg/l and 241 mg/l respectively. The excess of 22 mg/l Ca^{2+} could be due to excessive addition of calcium oxide or analytical error and the excess of 309 mg/l SO_{4}^{2-} must have come from the sulphur concentration in the mineral.

The concentrations of Ca^{2+} and SO_{4}^{2-} ions in the final solution after the flotation using tap water at 5 °C are 346 and 506 mg/l respectively. The concentration of Ca^{2+} and SO_{4}^{2-} contributed by the reagents are 342 mg/l and 257 mg/l respectively. The shortage of 18 mg/l Ca^{2+} must be due to the adsorption of the species to the surfaces of the minerals and the
excess of 257 mg/l SO₄²⁻ must have come from the sulphur concentration in the mineral. The concentrations of Ca²⁺ and SO₄²⁻ ions in the final solution after the flotation using process water at 5 °C are 559 and 665 mg/l respectively. The concentration of Ca²⁺ and SO₄²⁻ contributed by the reagents are 360 mg/l and 241 mg/l respectively. The excess of 13 mg/l Ca²⁺ could be due to excessive addition of calcium oxide or analytical error and the excess of 271 mg/l SO₄²⁻ must have come from the sulphur concentration in the mineral.
CONCLUSIONS

Hallimond flotation studies showed that calcium ions depress chalcopyrite and sphalerite in both deionised water and process water, and galena in process water. However, pyrite flotation improves in process water and chalcopyrite flotation at a very high concentration of calcium in deionised water. Sulphate ions are seen to depress chalcopyrite flotation in both deionised and process water and fluctuation in galena and sphalerite flotation in deionised water depending on the level of sulphate concentration while pyrite flotation enhances in deionised water but depresses in process water. Depression effects are closely associated to calcium carbonate coating and sulfooxy and hydroxide species presence on the minerals while the improvement could be due to activating effect of calcium and other metal ions as well as the thiosulphate reduction of hydrophilic compounds on sulphides particles.

Chalcopyrite, galena and sphalerite are negatively charged in the entire pH region, where the magnitude of negative charge is significantly higher in deionised water than in process water, illustrating the adsorption of metal ions that exist in process water. The adsorption of calcium ions is evidenced from the zeta-potentials of chalcopyrite, galena and sphalerite where the magnitude of negative charge is successively reduced with increasing calcium concentration. In the presence of calcium, the negative charge moving to positive at pH 10.5 and a charge reversal occurring at pH 11.5 for chalcopyrite and sphalerite accounted for the presence and adsorption of high surface active CaOH⁺ species. In the case of pyrite, the calcium and other metal ions in process water are seen to aid xanthate adsorption and activate pyrite flotation. In general, significant effect of calcium ions but not sulphate ions is observed on the zeta-potentials of all the minerals. The minerals zeta-potentials in the presence of Ca²⁺, SO₄²⁻, ZnSO₄, NaHSO₃ and dextrin independently and in the presence and absence of xanthate collector showed that the NaHSO₃ assisted xanthate adsorption and the other reagents has little or no effect for xanthate adsorption.

DRIFT spectra of chalcopyrite, galena, sphalerite and pyrite pure samples showed that the surfaces are partially oxidised depicting surface sulfooxy, oxy-hydroxide and carbonate species absorbance bands. These oxidised species bands are evidenced by the bands that developed when the samples are oxidised with H₂O₂ oxidant. The composition of surface species is found to be pH dependent. Depending on the experimental conditions of pH, type of water used, whether deionised water or process water and time of conditioning, chalcopyrite surface is composed of copper and iron sulfooxy, carbonate and oxy-hydroxide compounds, galena surface is composed of lead sulfooxy and carbonate compounds, sphalerite surface is composed of zinc sulfooxy and carbonate compounds while pyrite surface is composed of sulfooxy and superficial carbonate compounds.

In deionised water, calcium ions had little or no effect on surface composition of sulphides while calcium carbonate bands appeared in process water with increasing intensity with increasing calcium concentration. The intensity of sulfooxy species bands increased with increasing sulphate concentration both in deionised and process waters illustrating its adsorption on surface metal ion sites.

Xanthate adsorbs on chalcopyrite to form mono-coordinate copper xanthate (1157 cm⁻¹) and dixanthogen (1201 cm⁻¹) phases both in deionised and process waters, however process water suppressed xanthate adsorption where xanthate species bands intensities were lower. Mono-coordinate lead amylxanthate (1187 and 1024 cm⁻¹) both in deionised and process waters was distinguished in the case of galena, however process water suppressed xanthate adsorption.

52
where diminished xanthate species bands were seen. Xanthate bands are not apparent on sphalerite in deionised and process waters only surface oxidised compounds and low intensity xanthate bands are observed (1449, 1094, 1056 and 1161 cm\(^{-1}\)) at 5\(\times\)10\(^{-5}\) M xanthate. Xanthate adsorbs on pyrite to form mono-coordinate ferric and ferrous xanthate (1199, 1060-1043 cm\(^{-1}\)) and dixanthogen (1239 and 1021 cm\(^{-1}\)) in deionised water, and these species bands are diminished in process water. Calcium ions hardly affected xanthate adsorption while sulphate ions at a very high concentration inhibited xanthate adsorption. Upon xanthate adsorption, the intensity of surface oxidised species bands, mainly sulfoxyl species bands, are decreased illustrating ion-exchange mechanism of replacing surface oxidised species by xanthate.

Bench-scale flotation tests showed that the temperature has a significant influence on minerals recovery where a lower temperature decreases the recoveries. Recoveries are generally increased when process water was used, which is evidenced in the results when the tests were performed in the presence of calcium, sulphate and both species combined. An analysis for calcium and sulphate species in pulp liquid before and after flotation tests showed depleted calcium ions and excess sulphate ions in the pulp liquid after flotation. These results closely corroborate that the depletion of calcium ions are due to their adsorption on minerals as noticed in zeta-potential studies and as well caused by the calcium precipitation revealed in DRIFT spectra. The dissolved oxidised surface sulfoxyl species and also the release of these species up on xanthate adsorption contributed to the excess sulphate concentration in the flotation pulp liquid.
Future work

- Determinations of the atomic composition of surface species for all the minerals treated similarly as in zeta-potential and DRIFT spectroscopy studies presented in this thesis by subjecting them to XPS measurement.

- Effects of other minor species in process water, such as reduced sulphur compounds (RSC) (sulfoxamions with sulphur in the oxidation state below VI), on sulphides flotation by adsorption, zeta-potential, FTIR and XPS measurements.

- To find and adopt the best chemical recourses to overcome the detrimental effects of the process water components.

- Pilot flotation studies based on the new chemical recourses.
References


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Paper 1
Recycling of process water in sulphide flotation: Part 1. Effect of calcium and sulphate ions on chalcopyrite flotation

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Abstract

The influence of process water components on chalcopyrite flotation has been investigated through Hallimond flotation, zeta-potential and diffuse reflectance FTIR spectroscopy measurements using pure chalcopyrite sample as well as bench scale flotation tests using complex sulphide ore. The significance of process water species in flotation has been assessed using deionised water, process water and simulated water containing calcium and sulphate ions in experiments. In addition, the effect of temperature in bench scale flotation tests has also been examined.

Hallimond flotation indicated depression of chalcopyrite in the presence of calcium and sulphate ions with potassium amyl xanthate as collector. Calcium ions have significant influence on zeta-potential characteristics of chalcopyrite and xanthate adsorption behaviour compared to sulphate ions. FTIR studies revealed the presence of surface oxidised sulfoxy species on chalcopyrite and also surface iron and calcium carbonates at pH 10.5 in the presence of process water and water containing calcium ions, which surface species influenced xanthate adsorption. Bench scale flotation using two different complex sulphide ores showed that chalcopyrite recovery is better in process water than tap water. Flotation results also indicated general depression of chalcopyrite at temperatures lower than 22°C in either tap water or process water, activation of chalcopyrite at all temperatures in process water and depression of chalcopyrite when tap water containing calcium and sulphate ions was used at 22°C.

Keywords: Chalcopyrite, Complex sulphide ore, Hallimond flotation, Zeta-potential, Diffuse reflectance FTIR, Bench-scale flotation, Sulphate and calcium ions

Introduction

Increasing environmental friendly production practises mandated by strict environmental regulations have called for increased recycling of process water in sulphide minerals processing through flotation. However the presence of a number of components and species in the recycled water has raised questions of possible implications on the flotation recovery.

It is a common practise in the flotation stage of complex sulphide ore processing to float Cu and Pb in the first stage of flotation while Zn is activated and floated in the second stage (Liu and Zhang, 2000). The floatability of Cu is usually affected by a number of factors which includes electrochemical effects, components and species present in the pulp (Chen et al., 2009; Das et al., 1997; Göktepe and Williams, 1995; Houot and Duhamet, 1992; Peng and Gran), control of the grinding environment especially the presence of iron oxidation and species and metal deficient surface from chalcopyrite oxidation depending on the grinding
medium (Forssberg et al., 1988; Guy and Trahar, 1984; Martin et al., 1991; Peng et al., 2003a). The common major species in process water includes calcium and sulphate ions. Calcium ions originate from the ore and mainly from the lime used as pH regulator while sulphate originate from the oxidation of sulphide mineral and also from the sodium bisulphite used to control the surface properties. A number of studies carried out in the past dealt with the effect of calcium and sulphate ions on environmentally important organic and inorganic anions and metal cations on wide band-gap metal hydroxides and the results were interpreted as either competitive (Lefèvre and Fédoroff, 2006; Wu et al., 2002), promotive (Jia Y, 2005; Ostergren et al., 2000; Swedlund and Webster, 2001) or indifferent (Lefèvre and Fédoroff, 2006) adsorption depending on the speciation of the adsorbed anion and the formation of calcium bearing surface co-precipitates. However little is generally known about the effects of concentrated sulphate and calcium solutions on adsorption-reaction of collectors on sulphides in terms of kinetics of the reagent adsorption, adsorption isotherms, kinetic of the formation of dixanthogen, flotation kinetics and grade.

In particular previous work has shown that calcium activates copper and nickel in a Ni-Cu ore and improves the floatability of the sulphide by increasing the adsorption of xanthate on the sulphides (Kirjavainen et al., 2002). In addition the adsorption of calcium ions on chalcopyrite promotes adsorption of dextrin and depresses the flotation of chalcopyrite in the presence of galena, however citric acid can reactivate chalcopyrite (Liu and Zhang, 2000). In this study the influence of process water major species of calcium and sulphate ions on chalcopyrite flotation in single mineral as well as in flotation from complex sulphide ores were investigated.

**Experimental**

**Materials and reagents**

Pure chalcopyrite mineral (grading 25.8% Cu, 29% Fe, 29.5% S, 0.54% Zn and 0.22% Pb) used in Hallimond flotation tests, zeta-potential and FTIR measurements were procured from Gregory, Bottley & Lloyd Ltd. United Kingdom. The mineral was crushed, ground and classified into different size fractions. A size fraction of −150+38μm was used in the Hallimond single mineral flotation tests and −5μm fraction was used in both zeta-potential measurement and FTIR study.

Two complex sulfide ores from Boliden-Renström and Boliden-Kristineberg concentrators were used in the Bench-scale flotation tests. The ores were crushed and wet ground in a steel mill to obtain K<sub>50</sub> < 65 μm the common feed size in flotation practice.

All the flotation reagents that are being used at Boliden concentrator treating complex sulphide ores have been obtained. Potassium amyl xanthate (KAX) and Danafloat (dithiophosphate) were used in the experiment as collectors, Dowfroth 250 (polypropylene oxide methanol) was used as frother, dextrin, sodium hydrogen sulphite (NaHSO₃), and zinc sulphate (ZnSO₄) were used as depressant for any pyrite and sphalerite in the ore. Calcium oxide (CaO), HCl and NaOH solutions were used as pH regulators and K₂SO₄ and CaCl₂ as sources of SO₄²⁻ and Ca²⁺ ions respectively. Process water containing 128 mg/l Ca²⁺ and 63 mg/l SO₄²⁻ ions concentrations was obtained from Renström ore concentrator and 186 mg/l Ca²⁺ and 153 mg/l SO₄²⁻ ions concentrations from Kristineberg ore concentrator. The common concentration range of chemical species found in Boliden process water is shown in Table 1.
Table 1. Chemical species and their concentration range in Boliden process water.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentrations</th>
<th>From</th>
<th>To</th>
<th>Unit</th>
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<tr>
<td>Sulphate</td>
<td>SO₄²⁻</td>
<td>200</td>
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<td>mg/l</td>
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<tr>
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<td>Fe</td>
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<td>COD (Cr)</td>
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<td>&lt;30</td>
<td>130</td>
<td>mg/l</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>0.1</td>
<td>10</td>
<td>mg/l</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>P</td>
<td>&lt;0.050</td>
<td>0.7</td>
<td>mg/l</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>4.3</td>
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<td>mg/l</td>
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<td>Manganese</td>
<td>Mn</td>
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<td>8000</td>
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<tr>
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<td>12</td>
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<td>μg/l</td>
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<td>Al</td>
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<td>59000</td>
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<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>0.12</td>
<td>5.2</td>
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<tr>
<td>Cobolt</td>
<td>Co</td>
<td>4</td>
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<td>Cu</td>
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<td>Mercury</td>
<td>Hg</td>
<td>&lt;0.1</td>
<td>&lt;0.13</td>
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</tr>
<tr>
<td>Conductivity at 25°C</td>
<td></td>
<td>96</td>
<td>160</td>
<td>ms/m</td>
</tr>
</tbody>
</table>

**Hallimond flotation tests**

1 g of mineral is conditioned in a 100 ml standard volumetric flask and then transferred into a Hallimond tube flotation cell the upper part of the cell is filled with appropriate solution after addition of all reagents up to a total volume of 400 ml; this is followed by flotation under magnetic stirring. The sequence of reagent additions was pH regulators, calcium and/or sulphate species in water, collector, and frother. Conditioning time for species in water, collector and frother were 10 min, 5 min and 1 min respectively. Air was supplied at the rate of 200 cm³/min and the flotation time was 1 min. 20 mg/l of KAX and 50 μg/l frother was used. All tests except the pH variation tests were carried out at pH ~10.5 in room temperature of approximately 22.5°C.

**Zeta-potential measurements**

The measurement was carried out on the mineral sample at different conditions based on the present study flotation requirements. Zeta potential measurements were carried out with the aid of ZetaCompact instrument equipped with a charge-couple device (CCD) video camera and Zeta4 software. The software allows the direct reading of zeta-potential calculated from the electrophoretic mobilities using Smoluchowski equation. The result is a particle distribution histogram, from which the mean mobility are recalculated to zeta-potential values. In each measurement, about 10 mg of ~5 μm fraction of the mineral at a concentration of about 10 mg/100 ml of suspension was used. The ionic strength was maintained with KNO₃ at a concentration of about 0.01M and the pH was adjusted with solutions of HNO₃ and KOH accordingly. The required concentration of each solution was usually prepared followed by addition of the mineral, conditioning for 10 minutes and addition of other required reagent and species. The pH of the suspension after all conditioning prior to zeta-potential measurement is always regarded as the pH of the measurement.
Diffuse reflectance FTIR spectroscopy measurements

The measurement was carried out with the aid of Bruker FTIR spectrometer model IFS 66v/s. The ~5 μm fraction of the mineral pre-treated at different conditions based on the present study flotation requirements were subjected to FTIR measurements. In each measurement, about 10 mg of ~5 μm fraction of the mineral is pre-treated at a solids concentration of about 10 mg/100 ml. The pH was adjusted with solutions of HNO₃ and KOH accordingly. The required concentration of each solution and species was usually prepared followed by addition of the mineral, conditioning for 10 minutes and addition of other required reagent and species. The pulp is subsequently filtered and left to dry on the filter paper at room temperature. The pH of the suspension after all conditioning prior to filtration is always regarded as the pH of the measurement. Diffuse reflectance infrared Fourier transform (DRIFT) method was used in the measurement with 2.8 wt% concentration in potassium bromide (KBr) matrix. Each spectrum was recorded after 256 scans.

Bench-scale flotation tests

In each test about 1 Kg of ore is wet ground with about 600 ml of tap water or process water in the steel mill with 8 Kg grinding medium followed by flotation in the WEMCO cell of 2.5 litre capacity. The sequences of reagent additions were pH regulator, depressants, collectors, frother, and flotation. The dosages of depressants are; 1500 g/t ZnSO₄, 300 g/t NaHSO₃ and 200 g/t of dextrin. Dosages of copper collectors in a three stage sequential flotation are 30+20+10 g/t Danafloat and 10+5+0 g/t KAX. The conditioning times for pH regulator, depressants, and collectors are 5 min, 1 min and 2+1+1 min respectively. The frother dosage was 20 g/t Dowfroth. The pH was regulated to ~10.5 with powdered calcium oxide. Experiments were performed at room temperature of approximately 22.5 °C and at 11°C and 4°C using a specially designed double edged flotation cell where the temperature of the pulp is controlled with the circulation of temperature controlled water inside the cell wall. Total flotation time was 4.5 min.

Results and discussion

Hallimond flotation studies

The recovery of chalcopyrite at different pH ranging from 3 to 11.5 in both deionised and process water is shown in Fig. 1. It can be seen that the recovery decreases generally from low to high pH until pH 10 when it begins to rise again. This increase in flotation response at basic pH region could be due to oxidative pulp environment and dixanthogen formation making the surface more hydrophobic in character. The recovery in process water is generally lower than in deionised water. The process water components are thus inhibiting collector adsorption to some degree.
The effect of Ca$^{2+}$ ions at different concentrations on recovery of pure chalcopyrite in both deionised and process water is shown in Fig. 2. It can be seen that the presence of Ca$^{2+}$ ions in deionised water depresses the flotation of chalcopyrite on the average the depression is stable through low to high concentration of Ca$^{2+}$ ions in solution, however a slight increase in recovery can be observed from 300 mg/l calcium ions. This increase in flotation response could be similar to the metal ion activation of oxide minerals by adsorption of CaOH$^+$ species at the flotation pH 10.5; these species adsorption enhances collector adsorption and hence improves the recovery (Fuerstenau, 1976; Vergouw et al., 1998). It can also be observed that the mineral is generally depressed in process water; this could be due to the presence of a number of species including SO$_4^{2-}$, SO$_3^{2-}$ (Houot and Duhamet, 1992), dissolved iron (Kant et al., 1994; Peng et al., 2003b) in the process water which could form hydrophyllic layers or iron oxidation species on the surface of chalcopyrite, in addition to the formation of copper hydroxide (Fullston et al., 1999) and iron hydroxide; these hydrophilic species usually play major role in the depression of chalcopyrite flotation.
Fig. 2. Effect of calcium ions on chalcopyrite flotation in both deionised and process water.

The effect of SO$_4^{2-}$ ions concentrations on pure chalcopyrite mineral recovery is shown in Fig. 3. It can be seen that the presence of SO$_4^{2-}$ ions in deionised water also depresses the flotation of chalcopyrite on the average and the depression is more stable through low to high concentration of SO$_4^{2-}$ ions in solution. It can also be observed that the mineral is generally depressed in process water; this could be due to the adsorption of number species including sulphate, sulphite and metal oxy-hydroxide hydrophilic species in process water as mentioned above. There is also an indication that the increased concentration of SO$_4^{2-}$ ions besides the sulphate ions in process water has some depressing effect on chalcopyrite. The sulphate ions compete with collector molecules for adsorption as stated earlier (Lefèvre and Fédoroff, 2006; Wu et al., 2002); the strongly bonded SO$_4^{2-}$ ions on the mineral surfaces inhibits collector adsorption.
Fig. 3. Effect of sulphate ions on chalcopyrite flotation in both deionised and process water.

The effects of both Ca$^{2+}$ and SO$_4^{2-}$ ions concentrations on the recovery of pure chalcopyrite mineral are presented in Fig. 4. The combined effects is similar to observation with single effects above however the somewhat activation observed from 300 mg/l of Ca is not seen here, indicating that the SO$_4^{2-}$ effect is dominating. The mineral is relatively depressed due to SO$_4^{2-}$ adsorption on the mineral surfaces and hence collector could not be adsorbed (because the collector is anionic) only loosely bound SO$_4^{2-}$ ions will be replaced by chemisorbing collector molecules.

Fig. 4. Combined effect of calcium and sulphate ions on chalcopyrite flotation in both deionised and process water.
Zeta-potential studies

The zeta-potential response of chalcopyrite at different pH ranging from 2 to 11.5 in deionised water, process water, and deionised water containing different Ca\(^{2+}\) ions concentrations is shown in Fig. 5. It can be seen that the zeta-potential reduces gradually (becomes highly negative) as the pH increases in deionised water while the reduction is not very obvious in process water. However the zeta-potential is higher (less negative) in process water and in the presence of calcium ions than in deionised water due to the presence of positively charged metal ions in process water which adsorb on the surfaces of the mineral particles. This is an indication that adsorption of negatively charged collector on chalcopyrite particles may be enhanced (Fuerstenau and Pradip, 2005; Zhang et al., 1997). The usual pH of flotation in practice is 10.5 as indicated by the red broken arrow.

Fig. 5. Zeta-potential response of chalcopyrite at different pH in the presence of deionised water, process water and deionised water containing 200, 300 and 1000 ppm calcium.

Chalcopyrite surface is negatively charged in the entire pH 3 to 12 region either in deionised or process water, and an extrapolation of these curves show an iso-electric point (iep) around pH 3. Similar iep for chalcopyrite at low pH 3.0 has been documented by several authors (Fullston et al., 1999; Healy and Moignard, 1976). The negative surface charge arises due to the sulphide anions and copper and iron cations interacting with oxygen of hydroxyl species. The presence of calcium clearly showed an iep at about pH 3.5 and the positive charge below this pH is obviously due to the adsorption of Ca\(^{2+}\) ions on the surface. The negative charge density is mostly constant between pH 4 and 10 with a lesser negative charge at higher calcium concentration. Above pH 10, all the curves in the presence of calcium proceeding towards positive charge and exhibiting an iep at pH 11 in the presence of 1000 ppm calcium concentration. An increase in zeta-potential above pH 10 can be attributed to the presence of CaOH\(^{+}\) species and their adsorption on the surface.

The zeta-potential response of chalcopyrite at pH 10.5 in the presence of increasing concentration of calcium and in combination with a fixed concentration of sulphate is shown
in Fig. 6. The concentration of calcium ions found in various Boliden process water ranges from about 50 to 500 mg/l therefore the range of measurements was taken from 0 to 600 mg/l. It can be seen in Fig. 6 that the zeta-potential increases (becomes less negative) with increase in calcium ions concentration and the presence of 700 mg/l sulphate ions has no marked influence on the zeta potentials. This is an indication of a possible enhancement of adsorption of anionic collectors as well as dominance effect of calcium ions over sulphate ions in solution.

Fig. 6. Zeta-potential of chalcopyrite at different calcium ions concentration and in the presence of fixed concentration of sulphate ions at pH 10.5.

The concentration of sulphate ions found in various Boliden process water ranges from about 150 to 1500 mg/l therefore the range of measurements was taken from 0 to 1600 mg/l. It can be seen in Fig. 7 that the zeta-potential is averagely stable between 0 and 1000 mg/l of sulphate ions but increases slightly afterwards and stabilises from 1200 to 1600. The dominance effect of calcium ions over sulphate ions in solution can be clearly seen as the presence of 300 mg/l calcium ions sharply increases the zeta-potential in the presence of 0 through 1600 mg/l sulphate ions.
Fig. 7. Zeta-potential of chalcopyrite at different sulphate ions concentration and in the presence of fixed concentration of calcium ions at pH 10.5.

ZnSO₄ is usually used as a depressant for zinc minerals in sulphide flotation (Cao and Liu, 2006); therefore its effect at different concentration is studied in different waters. Fig. 8 shows the zeta-potential response of chalcopyrite in the presence of different concentration of ZnSO₄ and 3x10⁻⁵M of KAX (equivalent to the concentration of KAX in pulp solution in flotation practice) both in deionised and process water. It can be seen that the zeta-potentials were readily high in the process water but increases with increase in ZnSO₄ concentration in deionised water. The slight increase in zeta-potentials with increasing Zn²⁺ ions could be the adsorption of zinc ions and/or removal of surface oxidized species.

Fig. 8. Zeta-potential of chalcopyrite at different zinc sulphate concentrations and in the presence of fixed KAX concentration at pH 10.5 in deionised and process waters.
NaHSO₃ is a common depressant for pyrite (Grano et al., 1997; Khmeleva et al., 2003; Shen et al., 2001) usually in sulphide minerals flotation in practice; its effects on zeta-potential of chalcopyrite were also studied. Fig. 9 shows the zeta-potential response of chalcopyrite in the presence of different concentration of NaHSO₃, and 3x10⁻⁵M of KAX both in deionised and process water. It can be seen that the zeta-potentials were readily high (less negative) in the process water but increases with increase in NaHSO₃ concentration in deionised water although its much lower with addition of KAX in deionised water. In deionised water, the role of NaHSO₃ appears to be cleaning the chalcopyrite surface from oxidised products as the zeta-potentials is seen to increase with its increasing concentration. The presence of xanthate is thus seen to decrease the negative charge in this case. Such an effect of NaHSO₃ in process water is not observed and the zeta potentials are more or less the same.

![Fig. 9. Zeta-potential of chalcopyrite at different sodium hydrogen sulphite concentration and with a fixed concentration of KAX at pH 10.5 in deionised and process waters.](image)

Dextrin (C₆H₁₀O₆) is also a common polysaccharide used in sulphide minerals flotation as a non-toxic depressant of pyrite (Bogusz et al., 1997; Bolin and Laskowski, 1991; Laskowski et al., 1991; Liu et al., 1994; López Valdivieso et al., 2004), its effects on the zeta-potential response of chalcopyrite was also investigated. Fig. 10 shows the zeta-potential response of chalcopyrite in the presence of different concentration of dextrin (C₆H₁₀O₆) and 3x10⁻⁵M of KAX both in deionised and process waters. It can be seen that the zeta-potentials were readily high in the process water but increases slightly with increase in dextrin concentration in deionised water and also drops a little after 0.0006M of dextrin. It is rather stable with addition of KAX in deionised water. The initial decrease in negative potential in the presence of dextrin both in deionised and process waters could be due to its more neutral charge compared to negative oxidising surface species. Higher dosage of dextrin beyond 1x10⁻⁴M has no effect on zeta-potentials of chalcopyrite.
Fig. 10. Zeta-potential of chalcopyrite at different concentration of dextrin and with KAX, in both deionised and process waters.

Fig. 11 shows the zeta-potential response of chalcopyrite in the presence of different concentration of KAX in the presence of calcium, sulphate, zinc sulphate, sodium hydrogen sulphite and dextrin both in deionised and process water. High zeta-potential in the presence of calcium ions and in process water as well as low zeta-potential in the presence of sulphate ions are still clearly visible. Generally all the zeta-potentials measured in the presence of calcium ions seem to be identical, and are also identical to all zeta-potentials measured in process water. Increasing xanthate concentration, the zeta-potentials became less negative implying that the higher negative surface sulfoxyanions have been exchanged up on the adsorption of less negative xanthate species. However, in the presence of either sulphate or thiosulphate, the zeta potentials became marginally more negative with increasing xanthate concentration.
Fig. 11. Zeta-potential of chalcopyrite at different concentration of KAX and in the presence of zinc sulphate, sodium hydrogen sulphite, dextrin, in both deionised and process waters.

**Diffuse reflectance FTIR studies**

The requisite size fractions of pure chalcopyrite sample were prepared by intensive grinding in normal atmospheric condition and treated at low and high pH values in the experiments. Since the sulphide minerals are prone to oxidation by molecular oxygen, the presences of sulfoxyanions on chalcopyrite have been examined at the experimental conditions. In addition chalcopyrite was treated deliberately with H$_2$O$_2$ oxidant at different times so as to compare and judge the extent of surface oxidation of the samples.

The FTIR spectra of pure chalcopyrite and chalcopyrite treated with H$_2$O$_2$ at different times are shown in Fig. 12. Untreated chalcopyrite spectrum exhibits two broad bands centred around 1008 cm$^{-1}$ and 471 cm$^{-1}$, and weak bands at 1195, 1166, 776, 628 and 522 cm$^{-1}$ frequency. In addition to these bands, the oxidised chalcopyrite sample display bands at 3622, 3551, 3394, and 1090 cm$^{-1}$. The intensity of all bands in the H$_2$O$_2$ treated sample spectra increases with increasing time of treatment, implying that these bands relate to surface oxidised sulfoxyanion and hydroxide species. The bands at 1195 and 1008 cm$^{-1}$ can be assigned to S–O stretch vibrations in sulphate and sulphite structures respectively (Cases and De Donato, 1991; de Donato et al., 1999; Godociková et al., 2002; Leppinen, 1990; Mielczarski et al., 1998; Persson, 1994), while the band at 628 cm$^{-1}$ represents S–O bend vibrations (Persson, 1994; Smith, 1999; Socrates, 2001). The superficial iron oxy-hydroxide species display bands in the 794-630 cm$^{-1}$ region and iron sulphate at 470 cm$^{-1}$ (Parker et al., 2008); however the several bands around 470 and 780 cm$^{-1}$ could also arise due to Si–O vibrations caused by silicate impurity in the sample. The bands in the region 3000-3700 cm$^{-1}$ of the H$_2$O$_2$ treated sample characterize O–H stretching vibrations of surface hydroxyl groups.
Fig. 12. DRIFT spectra of pure and H$_2$O$_2$ treated at different times of chalcopyrite.

Fig. 13 presents the spectra of chalcopyrite conditioned in deionised water and process water at acidic (pH 3), neutral (pH 7) and basic (pH 10.5) pH values. In deionised water, the spectral features are similar to the bands depicting surface sulfoxyanions and oxy-hydroxide species as discussed above. The spectra in process water, in particular at pH 10.5, illustrate two additional bands, a broad band at 1432 and a sharp band 877 cm$^{-1}$, representing C–O stretch and C–O out-of-plane bend respectively in carbonate structural unit (Persson, 1994; Smith, 1999; Socrates, 2001). The bending bands are generally sharper than the stretching bands and can be seen in the spectra. Since the intensity of these bands is seen to increase with increasing calcium concentration in water (Fig. 14), they represent calcium carbonate precipitation on chalcopyrite surface or in bulk solution.
The effect of calcium concentration on chalcopyrite spectra at the flotation pH 10.5 in de-ionised and process waters is shown in Fig. 14. The presence of calcium has no marked changes in the surface species bands in de-ionised water while additional strong bands at 1432 and 876 cm\(^{-1}\) appeared in process water. The intensity of these carbonate species bands is seen to increase with increased calcium concentration characterizing increased calcium carbonate coating on the surface. Since the solids are collected after filtration, any bulk calcium carbonate precipitation remain in the solids fraction and hence seen in the spectra. The band
frequencies related to sulfoxyanion species, mainly sulphate and/or sulphites are the same in these spectra with a similar intensity with increasing calcium concentration. Since the solubility of calcium sulphate is much higher than calcium carbonate, the formation of calcium carbonate coating on the surface is understandable.

Fig. 14. DRIFT spectra of chalcopyrite treated with increasing calcium concentration at pH 10.5 in deionised (a) and process (b) waters.

Fig. 15 shows the influence of sulphate concentration in deionised and process waters. The S–O stretching bands (1007 and 1195 cm\(^{-1}\)) in deionised water and in process water (1009, 1088,
1139, 1158 and 1186 cm\(^{-1}\) are seen to increase with increasing sulphate concentration and the sulphate anions can be adsorbed on surface metal ion sites. Coordination of sulphate seems to be through the sulphur atom as SO stretching vibrations are being shifted to higher frequencies. Many peaks in process water compared to deionised water could be due to the presence of several reduced sulfoxyanions in process water and their adsorption. In all the spectra, a shoulder band at 877 cm\(^{-1}\) and weak broad band at 1441 cm\(^{-1}\) can be assigned to carbonate anions (Persson, 1994; Smith, 1999; Socrates, 2001). A strong adsorption of these anionic species on surface metal cations may largely inhibit anionic collector adsorption.

Fig. 15. DRIFT spectra of chalcopyrite treated with increasing sulphate concentration at pH 10.5 in deionised (a) and process (b) waters.
The spectra of chalcopyrite treated with xanthate in deionised and process waters after subtracting the pure mineral spectrum conditioned at the same experimental pH 10.5 without xanthate are shown in Fig. 16. Within a maximum xanthate concentration of $5 \times 10^{-5}$ M used, the difference spectra with increasing xanthate concentration in deionised water show three prominent bands at 1201, 1157 and 1098 cm$^{-1}$, and a band at 1011 cm$^{-1}$ appears at a higher concentration. These bands are obviously associated with adsorbed xanthate species where the higher intensity band 1098 cm$^{-1}$ can be assigned to C–O–C vibrations and the bands at 1201 and 1011 cm$^{-1}$ are due to S–C–S and C–O–C stretching vibrations (de Donato et al., 1999; Leppinen, 1990; Leppinen et al., 1989; Mielczarski et al., 1998; Persson, 1994). The bands characteristic of copper xanthate (1157 cm$^{-1}$) and dixanthogen (1201 cm$^{-1}$) are observed. In process water, the S–O stretching band (1008 cm$^{-1}$) dominates over xanthate species bands, weak and low intensity bands (1181, 1144, 1084 cm$^{-1}$) inferring lower adsorption of xanthate.

Fig. 16. Difference DRIFT spectra of chalcopyrite treated at different xanthate concentration at pH 10.5 in deionised (a) and process (b) waters after subtracting the respective pure mineral reference spectrum.
The effect of calcium and sulphate ions in deionised water on xanthate adsorption is presented in Fig. 17. In the presence of calcium, the intensity of bands characteristic to copper (1) amyl xanthate and dixanthogen (1089, 1162, 1175, 1195 cm⁻¹) are unchanged. It was also the case when the mineral spectrum is subtracted from the spectra after treating the sample with increasing calcium amounts at a fixed 5x10⁻⁵ M xanthate concentration. Only the intensity of a band (1009 cm⁻¹) due to oxidised sulfoxyanions is little diminished in the presence of calcium. The spectra illustrates that there is no influence of calcium on xanthate adsorption onto chalcopyrite. Similarly, the spectral features found to be exactly the same with increasing sulphate concentration inferring no significant influence of sulphate ions on xanthate adsorption. However, the difference spectra showed the adsorption of sulphate ions where the intensity of S–O stretching vibration band at 1011 cm⁻¹ is seen to depend on the level of sulphate ions concentration. At lower sulphate concentrations of 200 and 400 ppm, the spectra show that the intensity of sulfoxyanion species band (1011 cm⁻¹) has enhanced with xanthate species bands at 1157, 1188 and 1201 cm⁻¹. However, higher concentration of sulphate reduced the intensity of S–O stretching band considerably and at the same time xanthate species bands intensity increased a little. The sulphate ions in this case could be in either complex or precipitate formation with dissolved Fe ions, therefore no competition for xanthate adsorption from sulphate anions.
Fig. 17. DRIFT spectra of chalcopyrite treated with increasing calcium (a) and sulphate (b) ions in the presence of $5 \times 10^{-5} \text{M}$ xanthate after subtracting the mineral spectrum in deionised water at pH 10.5.

Analogous spectra as in Fig. 17 but the effect of calcium and sulphate ions in the presence of process water are shown in Fig. 18. In the difference spectra, the presence of both calcium or sulphate ions and xanthate show a negative carbonate band at 875 cm$^{-1}$ indicating that the surface carbonate layer is more concentrated when treated in process water than in the presence of xanthate. This could be due to ion-exchange between carbonate anions and
xanthate or surface metal ion carbonation/calcium carbonate precipitation is impeded in the presence of xanthate. Xanthate bands at 1086 and 1201 cm\(^{-1}\) in the presence of calcium and weak bands at 1086 and 1188 cm\(^{-1}\) in the presence of lower sulphate concentration can however be seen in these spectra. However, at 1000 ppm sulphate concentration, the spectrum is almost devoid of xanthate bands. Thus, very high sulphate concentration impeded xanthate adsorption.

Fig. 18. DRIFT spectra of chalcopyrite treated with increasing calcium (a) and sulphate (b) ions in the presence of 5x10\(^{-5}\)M xanthate after subtracting the mineral spectrum in process water at pH 10.5.
Bench-scale flotation studies

The bench scale flotation tests were carried out at different temperatures covering the seasonal temperature changes in beneficiation plant from winter to spring and summer through autumn in the north of Sweden. Renström ore grades 0.36 percent Cu, while Kristineberg ore grades 0.9 percent Cu. Table 2 shows the recovery and grade of copper from both Renström and Kristineberg ores at 22, 11 and 4°C using both tapwater and process water. It can be observed that the recovery of copper from Renström and Kristineberg ores decreases with temperature. This is most likely due to reduced thermodynamics of mineral-collector interaction as the temperature decreases. In addition, the grade and recovery of copper when process water is used are higher than the products when tapwater is used on the average. The somewhat better results when the process water was used could be due to presence of high concentration of Ca$^{2+}$ ions that enhances collector adsorption to KAX (an anionic collector) as seen in zeta-potential studies as well as other minor metal species and rest reagents that acts as activators (Chen et al., 2009; Finkelstein, 1997).

Table 2. Recovery and grade of copper from bench scale flotation using tapwater and process water at 22, 10 and 5°C temperatures.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Renström ore</th>
<th>Kristineberg ore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tap water</td>
<td>Process water</td>
</tr>
<tr>
<td></td>
<td>Recovery %</td>
<td>Grade %</td>
</tr>
<tr>
<td>22°C</td>
<td>87.99</td>
<td>1.84</td>
</tr>
<tr>
<td>11°C</td>
<td>83.81</td>
<td>1.56</td>
</tr>
<tr>
<td>4°C</td>
<td>83.39</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Table 3 shows a comparison between flotation results using tapwater, processwater and simulated water containing processwater equivalent concentration of Ca$^{2+}$ and SO$_4^{2-}$ ions singly and combined. It can be observed that the presence of Ca$^{2+}$ and SO$_4^{2-}$ ions singly and combined in the water has some influence on both the recovery and grade of copper. The somewhat better results when the process water was used could be due to presence of other minor metal species and rest reagents that acts as activators (Chen et al., 2009; Finkelstein, 1997).

Table 3. Comparison of recoveries and grades of chalcopyrite when Ca$^{2+}$ and SO$_4^{2-}$ ions are added to tapwater, and using only tapwater and process water at 22°C.

<table>
<thead>
<tr>
<th>Pulp liquid</th>
<th>Renström ore</th>
<th>Kristineberg ore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Recovery, %</td>
<td>Grade, %</td>
</tr>
<tr>
<td>Ca ions</td>
<td>89.31</td>
<td>1.44</td>
</tr>
<tr>
<td>Sulphate ions</td>
<td>87.60</td>
<td>1.50</td>
</tr>
<tr>
<td>Ca$^{2+}$+Sulphate ions</td>
<td>88.30</td>
<td>1.41</td>
</tr>
<tr>
<td>Tap water</td>
<td>87.99</td>
<td>1.84</td>
</tr>
<tr>
<td>Process water</td>
<td>89.67</td>
<td>1.58</td>
</tr>
</tbody>
</table>

The difference in flotation response between process and tap water could also be caused by different grinding environments (Eric Forssberg et al., 1993; Grano, 2009; Göktepe and
Williams, 1995; Martin et al., 1991; Peng et al., 2003a; Peng et al., 2003b), for example, the pH of process water is about 11 which is the grinding pH when using process water for flotation as against tap water in which grinding pH is about 8.

**Balance of calcium and sulphate species in pulp solution**

*Renström Ore*

The sulphate and calcium species concentration balance in solution for tests on Renström ore using tapwater and process water at 22 °C, 10 °C and 5 °C temperatures are presented in Table 4. The concentrations of Ca²⁺ and SO₄²⁻ ions in the tapwater are 22.5 and 7.4 mg/l respectively. The concentrations of Ca²⁺ and SO₄²⁻ ions in the final solution after the flotation using tapwater at 22.5 °C are 370 and 375 mg/l respectively. The concentration of Ca²⁺ and SO₄²⁻ contributed by the reagents are 449 mg/l and 365 mg/l respectively. The shortage of 102 mg/l Ca²⁺ must have adsorbed on the mineral surfaces and/or precipitated as calcium carbonate, and the excess of 2 mg/l SO₄²⁻ must have been contributed from the dissolved sulphur composition of the mineral. The concentrations of Ca²⁺ and SO₄²⁻ ions in the process water are 128 and 63 mg/l respectively. The concentrations of Ca²⁺ and SO₄²⁻ ions in the final solution after the flotation using process water at 22 °C are 446 and 511 mg/l respectively. The concentration of Ca²⁺ and SO₄²⁻ contributed by the reagents are 328 and 392 mg/l respectively. The shortage of 10 mg/l Ca²⁺ must have been adsorbed on the mineral surfaces and the excess of 56 mg/l SO₄²⁻ must have been contributed from the sulphur composition of the mineral.

### Table 4. Calcium and sulfate species ions balance in solution from flotation of Renström ore at different temperature using both tapwater and process water.

<table>
<thead>
<tr>
<th>Pulp liquid</th>
<th>Tap water</th>
<th>Process water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~22 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO₄²⁻ mg/l</td>
<td>Ca²⁺ mg/l</td>
</tr>
<tr>
<td>Initial</td>
<td>373</td>
<td>472</td>
</tr>
<tr>
<td>Final</td>
<td>375</td>
<td>370</td>
</tr>
<tr>
<td>Difference</td>
<td>2</td>
<td>-102</td>
</tr>
<tr>
<td>~11 °C</td>
<td>306</td>
<td>267</td>
</tr>
<tr>
<td>Final</td>
<td>281</td>
<td>155</td>
</tr>
<tr>
<td>Difference</td>
<td>-25</td>
<td>-112</td>
</tr>
<tr>
<td>~4 °C</td>
<td>249</td>
<td>220</td>
</tr>
<tr>
<td>Final</td>
<td>224</td>
<td>121</td>
</tr>
<tr>
<td>Difference</td>
<td>-25</td>
<td>-99</td>
</tr>
</tbody>
</table>

The concentrations of Ca²⁺ and SO₄²⁻ ions in the final solution after the flotation using tapwater at 10 °C are 155 and 281 mg/l respectively. The concentration of Ca²⁺ and SO₄²⁻ contributed by the reagents are 245 mg/l and 299 mg/l respectively. The shortage of 112 mg/l Ca²⁺ must have been adsorbed on the mineral surfaces and the shortage of 25 mg/l SO₄²⁻ must be due to competitive adsorption on the surfaces of the minerals. The concentrations of Ca²⁺ and SO₄²⁻ ions in the final solution after the flotation using process water at 10 °C are 200 and 364 mg/l respectively. The concentration of Ca²⁺ and SO₄²⁻ contributed by the reagents are 103 mg/l and 240 mg/l respectively. The shortage of 31 mg/l Ca²⁺ must have been adsorbed.
on the mineral surface and the excess of 61 mg/l SO$_4^{2-}$ must have come from the sulphur concentration in the mineral.

The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using tapwater at 5 °C are 121 and 224 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 198 mg/l and 241 mg/l respectively. The shortages of 99 mg/l Ca$^{2+}$ and 25 mg/l SO$_4^{2-}$ must be due to the adsorption of the species to the surfaces of the minerals. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using process water at 5 °C are 239 and 366 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 92 mg/l and 241 mg/l respectively. There is neither shortage nor excess of Ca$^{2+}$ ions. However the excess of 21 mg/l SO$_4^{2-}$ must have come from the sulphur concentration in the mineral.

Kristineberg Ore

The sulphate and calcium species concentration balance in solution and flotation results for tests on Kristineberg ore using tapwater and process water at 22 °C, 10 °C and 5 °C temperatures are presented in Table 3. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the tapwater are 22.5 and 7.4 mg/l respectively. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using tapwater at 22 °C are 556 and 918 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 493 mg/l and 409 mg/l respectively. The excess of 41 mg/l Ca$^{2+}$ must have came from the ore and excess of 502 mg/l SO$_4^{2-}$ must have been contributed from the sulphur composition of the mineral. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the process water are 186 and 153 mg/l respectively. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using process water at 22 °C are 782 and 1090 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 762 and 519 mg/l respectively. The shortage of 166 mg/l Ca$^{2+}$ must have been adsorbed on the mineral surfaces and the excess of 418 mg/l SO$_4^{2-}$ must have been contributed from the sulphur composition of the mineral.

Table 5 Calcium and sulfate species ions balance in solution from flotation of Kristineberg ore at different temperature using both tapwater and process water.

<table>
<thead>
<tr>
<th>Pulp liquid</th>
<th>Tap water</th>
<th>Process water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~22 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO$_4^{2-}$ mg/l</td>
<td>Ca$^{2+}$ mg/l</td>
</tr>
<tr>
<td>Initial</td>
<td>416</td>
<td>515</td>
</tr>
<tr>
<td>Final</td>
<td>918</td>
<td>556</td>
</tr>
<tr>
<td>Difference</td>
<td>502</td>
<td>41</td>
</tr>
<tr>
<td>~11 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>249</td>
<td>425</td>
</tr>
<tr>
<td>Final</td>
<td>556</td>
<td>394</td>
</tr>
<tr>
<td>Difference</td>
<td>308</td>
<td>-31</td>
</tr>
<tr>
<td>~4 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>249</td>
<td>364</td>
</tr>
<tr>
<td>Final</td>
<td>506</td>
<td>346</td>
</tr>
<tr>
<td>Difference</td>
<td>257</td>
<td>-18</td>
</tr>
</tbody>
</table>
The concentrations of Ca\(^{2+}\) and SO\(_{4}^{2-}\) ions in the final solution after the flotation using tapwater at 10 °C are 394 and 556 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_{4}^{2-}\) contributed by the reagents are 402 mg/l and 241 mg/l respectively. The shortage of 31 mg/l Ca\(^{2+}\) must have been adsorbed on the mineral surfaces and the excess of 308 mg/l SO\(_{4}^{2-}\) must have been contributed from the sulphur composition of the mineral. The concentrations of Ca\(^{2+}\) and SO\(_{4}^{2-}\) ions in the final solution after the flotation using process water at 10 °C are 565 and 704 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_{4}^{2-}\) contributed by the reagents are 357 mg/l and 241 mg/l respectively. The excess of 22 mg/l Ca\(^{2+}\) could be due to excessive addition of calcium oxide or analytical error and the excess of 309 mg/l SO\(_{4}^{2-}\) must have come from the sulphur concentration in the mineral.

The concentrations of Ca\(^{2+}\) and SO\(_{4}^{2-}\) ions in the final solution after the flotation using tapwater at 5 °C are 346 and 506 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_{4}^{2-}\) contributed by the reagents are 342 mg/l and 257 mg/l respectively. The shortage of 18 mg/l Ca\(^{2+}\) must be due to the adsorption of the species to the surfaces of the minerals and the excess of 257 mg/l SO\(_{4}^{2-}\) must have come from the sulphur concentration in the mineral. The concentrations of Ca\(^{2+}\) and SO\(_{4}^{2-}\) ions in the final solution after the flotation using process water at 5 °C are 559 and 665 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_{4}^{2-}\) contributed by the reagents are 360 mg/l and 241 mg/l respectively. The excess of 13 mg/l Ca\(^{2+}\) could be due to excessive addition of calcium oxide or analytical error and the excess of 271 mg/l SO\(_{4}^{2-}\) must have come from the sulphur concentration in the mineral.

Conclusions

Calcium and sulphate ions depress Hallimond flotation of chalcopyrite both in deionised water and process water. The depressing effect is evident at lower concentrations of about 100 mg/l of calcium and 200 mg/l of sulphate, above which concentration the flotation recoveries are either increase marginally or the same. Similar depressing effect is observed when both calcium and sulphate ions are used simultaneously. The effect was closely associated with calcium carbonate coating and sulfoxy species presence on chalcopyrite in the presence of calcium and sulphate ions respectively. A little increase in recovery at high calcium concentrations is thought to be due to the activating effect of calcium ions, which effect is not noticed in process water.

Chalcopyrite is negatively charged in the entire pH region, where the magnitude of negative charge is significantly higher than in process water, illustrating the adsorption of metal ions that exist in process water. The adsorption of calcium ions is evidenced from the zeta-potentials of chalcopyrite where the magnitude of negative charge is successively reduced with increasing calcium concentration. In the presence of calcium, the negative charge moving to positive at pH ≥ 10.5 and a charge reversal occurring at pH 11.5 is accounted for the presence and adsorption of high surface active CaOH\(^+\) species. Significant effect of calcium ions but not sulphate ions is observed on the zeta-potentials of chalcopyrite. Chalcopyrite zeta-potentials in the presence of Ca\(^{2+}\), SO\(_{4}^{2-}\), ZnSO\(_{4}\), NaHSO\(_{3}\) and dextrin independently and in the presence and absence of xanthate collector showed that the NaHSO\(_{3}\) assisted xanthate adsorption and the other reagents has little or no effect for xanthate adsorption.

DRIFT spectra of chalcopyrite pure sample showed that the surface is partially oxidised depicting surface sulfooxy species bands in the region 1200–1000 cm\(^{-1}\). These oxidised species bands are evidenced with the increased intensity of these bands when the sample is
oxidised with $\text{H}_2\text{O}_2$ oxidant. The composition of surface species found to be pH dependent, especially when chalcopyrite is conditioned in process water at pH 10.5 where calcium carbonate species bands appeared. Depending on the experimental conditions of pH, type of water used, whether deionised water or process water and time of conditioning, chalcopyrite surface is composed of copper and iron sulfooxy, carbonate and oxy-hydroxide compounds.

In deionised water, calcium ions had no effect on surface composition since the sulfooxy species bands have the same intensity with increasing calcium concentration, however in process water, very intense broad (1400 cm$^{-1}$) and sharp (877 cm$^{-1}$) bands appeared characterizing calcium carbonate on the surface. The intensity of sulfooxy species bands increased with increasing sulphate concentration both in deionised and process waters. Xanthate adsorbs on chalcopyrite to form mono-coordinate copper xanthate (1157 cm$^{-1}$) and dixanthogen (1201 cm$^{-1}$) phases both in deionised and process waters, however process water suppressed xanthate adsorption where xanthate species bands intensities were lower. Upon xanthate adsorption, the intensity of sulfooxy species bands decreased illustrating an ion-exchange adsorption mechanism. Calcium ions hardly affected xanthate adsorption and the carbonate species bands disappeared in deionised water while the spectra in process water showed negative bands. Thus xanthate replaces surface carbonate species upon adsorption. The DRIFT spectra in the presence of sulphate ions has no or little influence for xanthate adsorption at lower concentrations but at 1000 ppm, the spectra is almost devoid of xanthate species bands, elucidating xanthate cannot replace adsorbed sulphate when the bulk solution is more saturated with sulphate ions.

Chalcopyrite recoveries decrease as flotation temperature decreases in bench-scale flotation. Recoveries are generally increased when process water was used in bench-scale flotation, which is evidenced in the results when the tests were performed in the presence of calcium, sulphate and both species combined. An analysis for calcium and sulphate species in pulp liquid before and after flotation tests showed depleted calcium ions and excess sulphate ions in the pulp liquid after flotation. These results closely corroborate that the depletion of calcium ions are due to their adsorption on minerals as noticed in zeta-potential studies and as well caused by the calcium precipitation revealed in DRIFT spectra. The dissolved oxidised surface sulfooxy species and also the release of these species up on xanthate adsorption contributed to the excess sulphate concentration in the flotation pulp liquid.

Acknowledgements

The financial support from the Swedish VINNOVA foundation and, Boliden and Lundin Mining mineral companies for the research project on “Recycling of process water and influence of its chemistry on sulfide flotation and flotation selectivity” is gratefully acknowledged. One of the authors, Prof. KH Rao, also acknowledges the support from the “Centre for Advanced Mining and Metallurgy (CAMM)” recently established under the Swedish Strategic Research Initiative programme.

References


Paper 2
Recycling of process water in sulphide flotation: Part 2. Effect of calcium and sulphate ions on flotation of galena

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Abstract

The effects of major components of calcium and sulphate species present in recycled process water on galena flotation has been investigated through Hallimond flotation, zeta-potential and diffuse reflectance FTIR spectroscopy measurements using pure galena sample as well as bench scale flotation tests using complex sulphide ore. The significance of process water species in flotation has been assessed using deionised water, process water and simulated water containing calcium and sulphate ions in experiments. In addition, the effect of temperature in bench scale flotation tests has also been examined.

Hallimond flotation indicated depression of galena in the presence of major species of calcium and sulphate ions using potassium amyl xanthate as collector. Calcium ions have significant influence on zeta-potential characteristics of galena and xanthate adsorption behaviour compared to sulphate ions. FTIR studies revealed the presence of surface oxidised sulfoxy and carbonate species on galena at pH 10.5 in the presence of deionised water, process water and water containing calcium and sulphate ions, which surface species influenced xanthate adsorption. Bench scale flotation using two different complex sulphide ores showed that galena recovery is better in tap water than process water. Flotation results also indicated general depression of galena at temperatures lower than 22°C in either tap water or process water.

Keywords: Galena, Complex sulphide ore, Hallimond flotation, Zeta-potential, Diffuse reflectance FTIR, Bench-scale flotation, Sulphate and calcium ions

Introduction

Prevailing campaign for a cleaner and safer environment with clean surface and ground water has lead to increased recycling of process water within the production cycle of sulphide mineral flotation. Since the chemistry of process water is entirely different from fresh water; there is a concern about the possible effects of components contained in them on the efficiency of the flotation process (Rao and Finch, 1989). Calcium and sulphate ions are two very common components in the process water from flotation of sulphide minerals. The usual procedure in the flotation stage of complex sulphide ore processing is to float Cu and Pb in the first stage of flotation while Zn is activated and floated in the second stage (Liu and Zhang, 2000). The floatability of Pb is usually affected by a number of factors which includes electrochemical effects, components and species present in the pulp (Chen et al., 2009; Das et
al., 1997; Grano et al., 1990; Göktepe and Williams, 1995; Houot and Duhamet, 1992; Peng and Grano; Rao and Finch, 1989), grinding method (Eric Forssberg et al., 1993) and control of the grinding environment especially the metal oxidation species produced on galena and oxidation-reduction state which in turn influence the potential range of subsequent flotation (Chander, 2003; Forssberg et al., 1988; Guy and Trahar, 1984; Martin et al., 1991; Peng et al., 2003a; Peng et al., 2003b; Ralston, 1991). The origins of calcium and sulphate species in process water are the ore and flotation reagents (Broman, 1980). A number of studies carried out in the past dealt with the effect of calcium and sulphate ions on environmentally important organic and inorganic anions and metal cations on wide band-gap metal hydroxides and the results was interpreted as either competitive (Lefèvre and Fédoroff, 2006; Wu et al., 2002) promotive (Jia Y, 2005; Ostergren et al., 2000; Swedlund and Webster, 2001) or indifferent (Lefèvre and Fédoroff, 2006) adsorption depending on the speciation of the adsorbed anion and the formation of calcium bearing surface co-precipitates. However little is generally known about the effects of concentrated sulphate and calcium solutions on adsorption-reaction of collectors on sulphides in terms of kinetics of the reagent adsorption, adsorption isotherms, kinetic of the formation of dixanthogen, flotation kinetics and grade.

In particular previous work has shown that calcium ions promotes flotation of galena in a mixture of galena and chalcopyrite in the presence of dextrin however citric acid can reverse this process (Liu and Zhang, 2000). In this study the influence of major species of calcium and sulphate ions on galena flotation in single mineral as well as in flotation from complex sulphide ores were investigated.

**Experimental**

**Materials and reagents**

Pure galena mineral used (containing 73.69% Pb, 6% S, 1.38% Fe, 1.26% Zn and 0.2% Cu) in Hallimond flotation tests, zeta-potential and FTIR measurements were procured from Gregory, Bottley & Lloyd Ltd., United Kingdom. The mineral was crushed, ground and classified into different size fractions. A size fraction of ~150+38 μm was used in the Hallimond single mineral flotation tests and ~5 μm size fractions was used in both zeta-potential measurement and FTIR study. Two complex sulphide ores from Boliden-Renström and Boliden-Kristineberg concentrators were used in the Bench-scale flotation tests. The ores were crushed and wet ground in a steel mill to obtain K80 ≤ 65 μm the common feed size in practice.

Potassium amyl xanthate (KAX) and Danafoam were used in the experiment as collectors, Dowfoth 250 (polypropylene oxide methanol) was used as frother, dextrin (Boulton et al., 2001; López Valdivieso et al., 2004), sodium hydrogen sulphite (NaHSO3) (Khmaleva et al., 2003; Shen et al., 2001), and zinc sulphate (ZnSO4) (Cao and Liu, 2006) were used as depressant for pyrite and sphalerite in the ore. Calcium oxide (CaO), HCl and NaOH solutions were used as pH regulators and K2SO4 and CaCl2 as sources of SO42- and Ca2+ ions respectively. Process water containing 128 mg/l Ca2+ and 63 mg/l SO42- ions concentrations was obtained from Renström ore concentrator and 186 mg/l Ca2+ and 153 mg/l SO42- ions concentrations from Kristineberg ore concentrator. An analysis of Boliden process water for chemical species showed that calcium, sulphate and aluminium are the major species (Table 1).
Table 1. Chemical species and their concentration range in Boliden process water.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentrations From</th>
<th>Concentrations To</th>
<th>Unit</th>
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<tr>
<td>Sulphate</td>
<td>SO₄</td>
<td>200</td>
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<tr>
<td>Calcium</td>
<td>Ca</td>
<td>100</td>
<td>500 mg/l</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
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<td>1300 mg/l</td>
</tr>
<tr>
<td>COD (Cr)</td>
<td>&lt;30</td>
<td>130</td>
<td>mg/l</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>0.1</td>
<td>10 mg/l</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>P</td>
<td>&lt;0.050</td>
<td>0.7 mg/l</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>4.3</td>
<td>53 mg/l</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>4.4</td>
<td>8000 μg/l</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>12</td>
<td>3900 μg/l</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al</td>
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<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>0.12</td>
<td>5.2 μg/l</td>
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<td>Cobalt</td>
<td>Co</td>
<td>4</td>
<td>540 μg/l</td>
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<tr>
<td>Copper</td>
<td>Cu</td>
<td>2.7</td>
<td>20000 μg/l</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td>&lt;0.1</td>
<td>&lt;0.13 μg/l</td>
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<tr>
<td>Conductivity at 25°C</td>
<td>96</td>
<td>160</td>
<td>ms/m</td>
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**Hallimond flotation tests**

1 g of mineral is conditioned in a 100 ml standard volumetric flask and then transferred into a Hallimond tube flotation cell the upper part of the cell is filled with appropriate solution after addition of all reagents up to a total volume of 400 ml; this is followed by flotation under magnetic stirring. The sequence of reagent additions was pH regulators, species in water, collector, and frother. Conditioning time for species in water, collector and frother were 10 min, 5 min and 1 min respectively. The air supply rate was 200 cm³/min and the flotation time was 1 min. 20 mg/l of KAX and 50 μg/l frother was used. All tests except the pH variation test were carried out at pH ~10.5 in room temperature of approximately 22°C.

**Bench-scale flotation tests**

In each test about 1 Kg of ore is wet ground with about 600 ml of tap water or process water in the steel mill with 8 Kg grinding medium followed by flotation in the WEMCO cell of 2.5 litre capacity. The sequences of reagent additions were pH regulator, depressants, collectors, frother, and flotation. The dosages of depressants are; 1500 g/t ZnSO₄, 300 g/t NaHSO₃ and 200 g/t of dextrin. Dosages of lead collectors in a three stage sequential flotation are 30+20+10 g/t Danafloat and 10+5+0 g/t KAX. The conditioning times for pH regulator, depressants, and copper collectors are 5 min, 1 min and 2+1+1 min respectively. The frother dosage was 20 g/t Dowfroth. The pH was regulated to ~10.5 with powdered calcium oxide. Experiments were performed at room temperature of approximately 22°C, 11°C and 4°C. Total flotation time was 4.5 min.

**Zeta-potential measurements**

The measurement was carried out on the mineral sample at different conditions based on the present study flotation requirements. Zeta potential measurements were carried out with the aid of ZetaCompact instrument equipped with a charge-couple device (CCD) video camera.
and Zeta4 software. The software allows the direct reading of zeta-potential calculated from the electrophoretic mobilities using Smoluchowski equation. The result is a particle distribution histogram, from which the mean mobility are recalculated to zeta-potential values. In each measurement; about 10 mg of −5 μm fraction of the mineral at a concentration of about 10 mg/100 ml of solution was used. The ionic strength was maintained with KNO₃ at a concentration of about 0.01M the pH was adjusted with solutions of HNO₃ and KOH accordingly. The required concentration of each solution was usually prepared followed by addition of the mineral, conditioning for 10 minutes and addition of other required reagent and species. The pH of the suspension after all conditioning prior to zeta-potential measurement is always regarded as the pH of the measurement. All the measurements were carried out at the flotation pH 10.5 unless otherwise specified.

**FTIR (DRIFT) spectroscopy measurements**

The measurement was carried out with the aid of Bruker FTIR spectrometer model IFS 66v/s. The −5 μm fractions of the mineral pre-treated at different conditions based on the present study flotation requirements were subjected to FTIR measurements. In each measurement; about 10 mg of −5 μm fraction of the mineral is pre-treated at a concentration of about 10 mg/100 ml of solution. The pH was adjusted with solutions of HNO₃ and KOH accordingly. The required concentration of each solution and species was usually prepared followed by addition of the mineral, conditioning for 10 minutes and addition of other required reagent and species. The pulp is subsequently filtered and left to dry on the filter paper at room temperature. The pH of the suspension after all conditioning prior to filtration is always regarded as the pH of the measurement. Diffuse reflectance infrared Fourier transform (DRIFT) method was used in the measurement with 2.8 wt% concentration in potassium bromide (KBr) matrix. Each spectrum was recorded after 256 scans.

**Results and discussion**

**Hallimond flotation studies**

The recovery of galena at different pH ranging from 3 to 11.5 in both deionised and process water is shown in Fig.1. It can be seen that the recovery decreases generally from pH 3 to pH 6 and rises at pH 7, stabilises to pH 9 where it begins to rise again. In addition the recovery of galena in process water is generally lower than in deionised water.
The effect of Ca\(^{2+}\) ions at different concentrations on recovery of pure galena in both deionised and process water is shown in Fig. 2. It can be seen that the presence of Ca\(^{2+}\) ions in deionised water did not show any serious effect on the flotation of galena, however there is slight depression in process water at lower concentration of Ca\(^{2+}\) ions, the depression is more pronounced from 500 mg/l concentration of Ca\(^{2+}\) ions. This could be due to the presence of a number of species including SO\(_4^{2-}\), SO\(_3^{2-}\) in addition to the depressive effect of combination of calcium and sulphite species (Ca\(^{2+}\)-SO\(_3^{2-}\)) (Houot and Duhamet, 1992), dissolved iron (Kant et al., 1994; Peng et al., 2003b) in the process water which could form hydrophillic layers or iron oxidation species on the surface of the minerals.

The effect of SO\(_4^{2-}\) ions concentrations on pure galena mineral recovery is shown in Fig. 3. It can be seen that the presence of SO\(_4^{2-}\) ions in deionised water depresses the flotation of galena on the average. It can also be observed that the mineral is generally more depressed in process water than in deionised water; this could be due to the presence of a number of species including SO\(_4^{2-}\), SO\(_3^{2-}\) (Houot and Duhamet, 1992), dissolved iron (Kant et al., 1994; Peng et al., 2003b) in the process water which could form hydrophillic layers or iron oxidation species on the surface of the minerals; this species can play major roles in the depression of galena flotation. This is also an indication that high concentration of SO\(_4^{2-}\) ions may have some depressing effect on galena similar to oxides minerals by competing with collector molecules adsorption on the mineral surface (LeFèvre and Fédoroff, 2006; Wu et al., 2002), the strongly bonded SO\(_4^{2-}\) ions on the mineral surfaces inhibits collector adsorption.
The effects of both Ca\(^{2+}\) and SO\(_4\)^{2-}\) ions concentrations on the recovery of pure galena mineral are presented in Fig. 4. The combined effect is almost similar to observation with single effects of SO\(_4\)^{2-}\) ions above indicating that the SO\(_4\)^{2-}\) effect is dominating. The mineral is relatively depressed due to SO\(_4\)^{2-}\) adsorption on the mineral surfaces and hence collector could not be adsorbed (because the collector is anionic) only loosely bound SO\(_4\)^{2-}\) ions will be replaced by chemisorbing collector molecules.
Fig. 4: Combined effect of calcium and sulphate ions on galena flotation in both deionised and process water.

**Zeta-potential studies**

Fig. 5: Zeta-potential response of galena at different pH in the presence of tap water, process water and tap water containing 200, 300 and 1000 ppm Ca.

The zeta-potential response of galena at different pH ranging from 2 to 11.5 in deionised water, process water, and deionised water containing different Ca$^{2+}$ ions concentrations is shown in Fig. 5. Several authors reported the zeta-potential of galena in the past (Healy and Moignard, 1976), and galena exhibits an iso-electric point (iep) ranging from pH 2 to 4 depending on its conditioning time in water and whether the surface is clean or composed of
oxidised sulfoxy anions. The results show that galena is negatively charged in the pH range studied both in deionised water and process water, and an extrapolation of these curves indicates that the iep lies at about pH 2. In general the magnitude of negative zeta-potential is lesser in process water than in deionised water due to the adsorption of metal cations that exist in process water.

It can be seen that the zeta-potential reduces gradually (becomes highly negative) as the pH increases in deionised water while the reduction is not very obvious in process water until after pH 8. In addition the zeta-potential is becoming less negative at all pH values with increasing calcium concentration in deionised water. The zeta-potential curve in the presence of 500 ppm calcium closely matches to that of the curve in process water illustrating the same level of calcium ions in process water (Table 1). Calcium ions exist as Ca\(^{2+}\) ions up to pH 12 and their adsorption decreases the magnitude of negative charge which is seen in the results of Fig. 5. This is an indication that adsorption of negatively charged collector on galena particles may be enhanced (Fuerstenau and Pradip, 2005; Zhang et al., 1997). The usual pH of flotation in practice is 10.5 as indicated by the red broken arrow and at this pH, the hydrolysis of calcium ions forms the first product of calcium hydroxyl species (CaOH\(^{+}\)) and these species established to be more susceptible to adsorption.

![Figure 6: Zeta-potential of galenaA at different calcium ions concentration and with a fixed concentration of sulphate ions at pH 10.5.](image)

The zeta-potential response of galena at pH 10.5 in the presence of different concentration of calcium and with 700 mg/l concentration of sulphate is shown in Fig.6. The concentration of calcium ions found in various Boliden process water ranges from about 50 to 500 mg/l therefore the range of measurements was taken from 0 to 600 mg/l. It can be seen in Fig. 6 that the zeta-potential increases (becomes less negative) with increase in calcium ions concentration as well as in the presence of 700 mg/l sulphate ions but to a lesser extent. This shows that the presence of sulphate ions reduced the effect of calcium ions on surface charge. Overall, the effect of calcium ions is significantly higher than the sulphate ions and this
indicates a possible enhancement of anionic collector adsorption in the presence of calcium ions.

The concentration of sulphate ions found in various Boliden process water ranges from about 150 to 1500 mg/l therefore the range of measurements was taken from 0 to 1600 mg/l to determine the effect of these ions on galena. It can be seen in Fig. 7 that the zeta-potential increases slightly and gradually with increase in sulphate ions concentrations. The dominance effect of calcium ions over sulphate ions in solution can also be clearly seen as the presence of 300 mg/l calcium ions sharply increases the zeta-potential in the presence of 0 through 1600 mg/l sulphate ions.

![Graph showing zeta-potential of galena at different sulphate ions concentration and with a fixed concentration of calcium ions at pH 10.5.](image)

Fig. 7: Zeta-potential of galena at different sulphate ions concentration and with a fixed concentration of calcium ions at pH 10.5.

Fig. 8 shows the zeta-potential response of galena in the presence of different concentrations of ZnSO₄ in deionised water and process water. The surface charge is becoming less negative with increasing zinc ions in deionised water while the effect of zinc ions in process water is rather marginal at lower concentration and no effect at higher concentration. Since the zeta-potentials in process water were already high due to the presence of several cations, in particular Ca²⁺ ions, little or negligible effect of zinc ions is understandable. It can also be seen that the presence of 3x10⁻⁵M of KAX (equivalent to the concentration of KAX in pulp solution in practice) both in deionised and process water has no marked effect on the zeta-potentials. These results display that the adsorption of xanthate on galena is through an ion-exchange mechanism where the anionic surface carbonate or sulphate is replaced with xanthate anion explaining no change in surface charge. In essence, the zeta-potentials were less negative in the process water but the high negative charge in deionised water decreases with increase in ZnSO₄ concentration.
Fig. 8: Zeta-potential of galena at different zinc sulphate concentration and with a fixed concentration of KAX at pH 10.5 in deionised and process water.

Fig. 9: Zeta-potential of galena at different sodium hydrogen sulphite concentration and with a fixed concentration of KAX at pH 10.5 in deionised and process water. It can be seen that the zeta-potentials were readily high (less negative) in the process water but increases with increase in NaHSO₃ concentration in deionised water although its slightly
higher with addition of KAX in deionised water. The less negative charge in the presence of sodium bisulphite could be that sulphite removes the sulphur-rich anionic and/or carbonate species from galena surface.

Fig. 10 shows the zeta-potential response of galena at different concentrations of Dextrin (C6H10O6) and in the presence and absence of 3x10^-5M of KAX both in deionised and process water. It can be seen that the zeta-potentials were readily high in the process water but increases slightly in the presence of dextrin and remains constant with increase in dextrin concentration. Thus dextrin is seen to influence zeta-potentials only at low amounts and perhaps the surface is saturated with dextrin at 1x10^-4M due to very low surface area involved (dilute suspension) in the experiments. The reduction in negative zeta-potential up on the adsorption of dextrin is in agreement with literature (Liu and Laskowski, 1989) and primarily caused due to shifting the slipping plane away from the interface because of large macromolecules adsorption.

Fig. 10: Zeta-potential of galena at different concentration of dextrin and with KAX, in both deionised and process water at pH 10.5.

Fig. 11 shows the zeta-potential response of galena in the presence of different concentrations of KAX in deionised and process waters, and in the presence of fixed concentrations of calcium (300 mg/l), sulphate (700 mg/l), zinc sulphate (3.5x10^-3M), sodium hydrogen sulphite (1.2x10^-3M) and dextrin (5x10^-4M) independently in both waters. High zeta-potential in the presence of calcium ions and in process water as well as low zeta-potential in the presence of sulphate ions are still clearly visible. Generally all the zeta-potentials measured in the presence of calcium ions seem to be identical, and are also identical to all zeta-potentials measured in process water.
Fig. 11: Zeta-potential of galena at different concentration of KAX and in the presence of calcium, sulphate, zinc sulphate, sodium hydrogen sulphite, and dextrin, in both deionised and process water at pH 10.5.

Diffuse reflectance FTIR spectroscopy studies

The diffuse reflectance spectrum of a 5 μm galena powder sample that is obtained after dry grinding in a agate mortar and then micro-sieving in ultrasonic bath is shown in Fig. 12. Surface oxidation of sulphide minerals exposed to atmosphere and in flotation is an established fact (Buckley et al., 1985; Clarke et al., 1995; Dunn, 1997; Fullston et al., 1999; Vaughan et al., 1997). The spectra of the same sample conditioned with H2O2 at different times are also presented in this figure. Since galena exhibit a fundamental vibration below 200 cm⁻¹, the several bands seen in the spectrum of pure sample are due to oxidized species on the surface. An increase in the intensity of these bands when the sample is treated with H2O2 oxidant substantiate that these bands are characteristic of oxidized species present on the sample.
The oxidized surface state of galena mainly consists of lead sulphate and thiosulphate, and lead carbonate. The bands at 599, 629, 1052, 1093 and 1159 cm\(^{-1}\) can be assigned to S–O vibrations in lead sulphate. Lead thiosulphate bands that could appear at about 985 and 1120 cm\(^{-1}\) not really noticed in the spectra. Absorption bands characteristic of C–O vibrations in lead carbonate are seen at about 679, 838, 1052, 1408 and 1425 cm\(^{-1}\). The spectra with increasing time of H\(_2\)O\(_2\) treatment, the intensity of sulphate bands increased with no or little effect on carbonate bands. While comparing pure galena spectrum to the spectra oxidized by H\(_2\)O\(_2\), it is clear that the pure galena sample used in experiments is partially oxidized and the surface is composed of not only sulphate but also carbonate species.
Infrared spectra of galena conditioned at pHs 3, 7 and 10.5 in deionised water Fig. 13a show that the extent of surface oxidation is pH dependent. The sulphate and carbonate bands intensities are low at pH 3, increased at pH 7 and then marginally decreased at pH 10.5. The variation in surface lead sulphate and lead carbonate with a change in pH could explain the fluctuating negative zeta-potential of galena with increasing pH (Fig. 5). In Fig. 13b, it can be seen that the presence of process water has significant influence on the surface composition of galena and at pH 10.5 where high intensity lead carbonate bands (680, 838, 1051, 1425 cm\(^{-1}\))
and calcium carbonate bands (875, 1425 cm\(^{-1}\)) besides lead sulphate bands (1051, 1160 cm\(^{-1}\)) are observed. Thus the presence of calcium ions and sulphate species in process water is seen to form calcium carbonate and lead sulphate on galena surface more than in deionised water which may inhibit xanthate collector adsorption leading to lower flotation of galena.

Fig. 14: Effect of calcium concentration on galena at pH 10.5 in deionised (a) and process (b) waters.

The effect of calcium ions on galena surface composition in deionised and process waters at pH 10.5 is depicted in Fig. 14 (a) and (b) respectively. The spectra with increasing calcium in deionised water are comparable to the spectra conditioned at the same pH of 10.5 in the
absence of calcium. The consumption of dissolved carbon dioxide in water from atmosphere leading to formation of lead carbonate (1410, 838, 680 cm⁻¹) has led no calcium carbonate precipitation with increasing calcium concentration where the low intensity of calcium carbonate bands (1430, 871 cm⁻¹) are unaffected. However, in the presence of process water, calcium carbonate bands have dominated than lead carbonate bands and with increasing calcium concentration, the bands characterizing calcium carbonate at 1432 and 877 cm⁻¹ is seen to increase. In both the cases of waters, calcium ions have no effect on sulphate characteristic bands. Galena surface is mainly composed of lead carbonate in process water at pH 10.5 and higher level of calcium in process water leads to calcium carbonate precipitation on the surface.

Fig. 15: Effect of sulphate concentration on galena at pH 10.5 in deionised (a) and process (b) waters.

Fig. 15 (a) and (b) shows the spectra of galena conditioned with increasing concentration of sulphate ions in deionised (a) and process (b) waters at pH 10.5. The intensity of S-O stretching vibrations bands in sulfoxy species in deionised water is seen to increase a little
with increasing sulphate ions until 700 ppm after which level they are decreased. The intensity level of these bands is close to the spectrum that is conditioned in water in the absence of sulphate suggesting that the surface is already oxidised to lead sulphate. However, in process water these bands are seen at higher intensity level and there is no change in intensity with increasing sulphate concentration. The galena surface is totally composed of lead sulphate in process water containing several reduced sulfoxy species and there is no marked influence of additional sulphate concentration in process water.

Fig. 16: Pure mineral subtracted from galena treated at different xanthate concentration at pH 10.5 in deionised (a) and process (b) waters.

Spectra of galena after interaction with amylxanthate at $5 \times 10^{-6}$, $2 \times 10^{-5}$ and $5 \times 10^{-5}$ M concentrations in deionised (a) and process (b) waters are shown in Fig. 16. These were the difference spectra after subtracting the mineral spectrum from the xanthate treated spectra. In
deionised water, the spectra exhibits C-O-C and S-C-S symmetric stretching vibration band at 1187 cm\(^{-1}\) and the stretching vibration band of the S-C-S group at 1024 cm\(^{-1}\). Comparing the corresponding bands in lead amylxanthate (1:2) compound, these bands are shifted from 1220 cm\(^{-1}\) to a lower value of 1187 cm\(^{-1}\) and from 1022 to 1024 cm\(^{-1}\). These bands can be assigned to monocoordinated form of lead xanthate. Furthermore, increasing xanthate concentration to 5x10\(^{-5}\) M, the intensity of these bands is seen to increase illustrating increased amylxanthate adsorption on galena surface. However, the lead sulphate (1160, 1132, 1025 cm\(^{-1}\)) and lead carbonate (1051, 838 cm\(^{-1}\)) bands although diminished can be seen in these spectra. The surface oxidized products of galena are expected to be removed during the abstraction of xanthate. The presence of oxidation products indicates that the maximum initial xanthate concentration of 5x10\(^{-5}\) M used is not adequate to form monolayer coverage. In process water and at low xanthate concentrations of 5x10\(^{-6}\) and 2x10\(^{-5}\) M, the spectra show only the oxidised substrate bands and devoid of xanthate bands. The absence of xanthate bands could be that xanthate is in complex formation with the metal ions in process water. However at 5x10\(^{-5}\) M xanthate concentration spectrum, xanthate bands can be seen. The presence of positive and negative lead sulphate and lead carbonate bands illustrates different level of surface oxidation compounds in the xanthate treated galena spectra compared to mineral spectrum that was subtracted.
Fig. 17: Effect of calcium on adsorption of xanthate on galena; the spectra presented in this figure are the difference spectra obtained after the galena spectrum conditioned at pH 10.5 is subtracted from the spectra of galena conditioned in the presence of increasing calcium and at a constant 5x10⁻⁵ M xanthate concentration at pH 10.5 in deionised (a) and process (b) waters.

The influence of calcium concentration on xanthate adsorption in deionised and process waters is shown in Fig. 17. The spectra presented in this figure are the difference spectra, i.e., the galena spectrum that is conditioned at pH 10.5 is subtracted from the spectra of galena conditioned in the presence of increasing calcium and at a constant 5x10⁻⁵ M xanthate concentration. In the presence of calcium and at 50 and 100 ppm concentration, the intensity of surface lead sulphate, hydroxide and carbonate bands are seen to decrease, and at higher levels of calcium (200 and 300 ppm), the spectra displayed negative bands. The successive decrease in surface oxidised compounds bands with increasing calcium was due to the result of sulfooxy and carbonate species forming soluble complexes with the calcium. Xanthate adsorption on galena is also reduced in the presence of calcium as shown by the decreasing intensity of xanthate bands (1187 and 1023 cm⁻¹) with increasing calcium concentration. Similar spectra but in process water show that the surface oxidized compounds, in particular lead carbonate, is removed from the surface with increasing calcium concentration. In process...
water and in the presence of $5 \times 10^{-5}$ M xanthate, the spectrum shows very intense carbonate bands at 1448 and 876 cm$^{-1}$, which not only disappeared but also show negative bands at the same region. These spectra indicate that calcium forms complexes with surface carbonate species and dissolved into the bulk of the solution.

Fig. 18: Effect of sulphate on adsorption of xanthate on galena; the spectra presented in this figure are the difference spectra obtained after the galena spectrum conditioned at pH 10.5 is subtracted from the spectra of galena conditioned in the presence of increasing calcium and at a constant $5 \times 10^{-5}$ M xanthate concentration at pH 10.5 in deionised (a) and process (b) waters.

The increase in sulphate concentration shows that the oxidised lead sulphate and carbonate is marginally removed from the surface in deionised water and entirely removed in process
water (Fig. 18). Xanthate adsorption is not much affected with increasing in sulphate concentration either in deionised or process water.

### Bench-scale flotation studies

The bench scale flotation studies was carried out at different temperatures covering the seasonal temperature changes in process plant from winter to spring and summer through autumn in the north of Sweden. Renström ore grades 1% Pb, while Kristineberg ore grades 0.1% Pb. Table 2 shows the recovery and grade of lead from both Renström and Kristineberg ores at 22, 11 and 4°C in both tap and process water. It can be observed that the recovery of lead from Renström ore in tap water decreases as temperature decreased from 22°C to 11°C while it increases at 4°C however the grade at 11°C is better than at 4°C. The recovery of Renström ore in process water however decreases with temperature. In contrast the recovery and grade of Kristineberg ores in tap water increases as temperature decreases with highest increase at 11°C. In process water the grade increases with decreases in temperature whilst the recovery decreases and increase again from 22°C, to 11°C and 4°C respectively. The reduction in recovery as temperature decreases are most likely due to reduced thermodynamics of mineral-collector interaction as the temperature decreases. The increase in recovery and grade in Kristineberg ore when temperature reduces cannot be clearly explained. One possible reason for better grades in process water could be the presence of rest reagents and high concentration of Ca²⁺ ions that enhances collector adsorption to KAX (an anionic collector) as seen in zeta-potential studies (Chen et al., 2009; Finkelstein, 1997)

**Table 2: Recovery and grade of lead from bench scale flotation using both tap water and process water at 22, 10 and 5°C temperatures.**

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<tr>
<th>Temp.</th>
<th>Renström ore</th>
<th>Kristineberg ore</th>
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<tr>
<td></td>
<td>Tap water</td>
<td>Process water</td>
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<tr>
<td></td>
<td>Recovery, %</td>
<td>Grade, %</td>
</tr>
<tr>
<td>22°C</td>
<td>82.63</td>
<td>5.61</td>
</tr>
<tr>
<td>11°C</td>
<td>75.44</td>
<td>4.46</td>
</tr>
<tr>
<td>4°C</td>
<td>75.58</td>
<td>3.69</td>
</tr>
</tbody>
</table>

**Table 3 shows a comparison between flotation results using tap water, process water and tap water containing Ca²⁺ and SO₄²⁻ ions singly and combined that were added equivalent to the concentrations in process water.** It can be observed that the presence of Ca²⁺ and SO₄²⁻ ions singly and combined in the water has some influence on both the recovery and grade of lead. The somewhat better results when the process water was used could be due to presence of other minor metal species and rest reagents that acts as activators (Chen et al., 2009; Finkelstein, 1997).

**Table 3: Comparison of recoveries and grades in tap water, process water and when Ca²⁺ and SO₄²⁻ ions are added to tap water at 22°C temperature.**

<table>
<thead>
<tr>
<th>Pulp liquid (species added)</th>
<th>Renström ore</th>
<th>Kristineberg ore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Recovery, %</td>
<td>Grade, %</td>
</tr>
<tr>
<td>Ca ions</td>
<td>87.60</td>
<td>4.91</td>
</tr>
<tr>
<td>Sulphate ions</td>
<td>89.44</td>
<td>5.20</td>
</tr>
<tr>
<td>Ca+Sulphate ions</td>
<td>87.04</td>
<td>4.57</td>
</tr>
<tr>
<td>Tap water</td>
<td>82.63</td>
<td>5.61</td>
</tr>
<tr>
<td>Process water</td>
<td>88.51</td>
<td>5.03</td>
</tr>
</tbody>
</table>
The difference in flotation response between process and tap water could also be caused by different grinding environments (Eric Forssberg et al., 1993; Grano, 2009; Göktepe and Williams, 1995; Martin et al., 1991; Peng et al., 2003a; Peng et al., 2003b), for example, the pH of process water is about 11 which is the grinding pH when using process water for flotation as against tap water in which grinding pH is about 8.

**Balance of calcium and sulphate species in pulp solution**

**Renström Ore**

The sulphate and calcium species concentration balance in solution for tests on Renström ore using tap water and process water at 22 °C, 11 °C and 4 °C temperatures are presented in Table 4. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the tap water are 22.5 and 7.4 mg/l respectively. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using tap water at 22 °C are 370 and 375 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 449 mg/l and 365 mg/l respectively. The shortage of 102 mg/l Ca$^{2+}$ must have adsorbed on the mineral surfaces and the excess of 2 mg/l SO$_4^{2-}$ must have been contributed from the dissolved sulphur composition of the mineral. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the process water are 128 and 63 mg/l respectively. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using process water at 22 °C are 446 and 511 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 328 and 392 mg/l respectively. The shortage of 10 mg/l Ca$^{2+}$ must have been adsorbed on the mineral surfaces and the excess of 56 mg/l SO$_4^{2-}$ must have been contributed from the sulphur composition of the mineral.

Table 4. Calcium and sulphate species ions balance in solution from flotation of Renström ore at different temperature using both tap water and process water.

<table>
<thead>
<tr>
<th></th>
<th>Tap water</th>
<th>Process water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~22 °C</td>
<td>~11 °C</td>
</tr>
<tr>
<td></td>
<td>SO$_4^{2-}$ mg/l</td>
<td>Ca$^{2+}$ mg/l</td>
</tr>
<tr>
<td>Initial</td>
<td>373</td>
<td>472</td>
</tr>
<tr>
<td>Final</td>
<td>375</td>
<td>370</td>
</tr>
<tr>
<td>Difference</td>
<td>2</td>
<td>-102</td>
</tr>
<tr>
<td>~11 °C</td>
<td>Initial</td>
<td>306</td>
</tr>
<tr>
<td>Final</td>
<td>281</td>
<td>155</td>
</tr>
<tr>
<td>Difference</td>
<td>-25</td>
<td>-112</td>
</tr>
<tr>
<td>~4 °C</td>
<td>Initial</td>
<td>249</td>
</tr>
<tr>
<td>Final</td>
<td>224</td>
<td>121</td>
</tr>
<tr>
<td>Difference</td>
<td>-25</td>
<td>-99</td>
</tr>
</tbody>
</table>

The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using tap water at 11 °C are 155 and 281 mg/l respectively. The concentration of Ca$^{2+}$ and SO$_4^{2-}$ contributed by the reagents are 245 mg/l and 299 mg/l respectively. The shortage of 112 mg/l Ca$^{2+}$ must have been adsorbed on the mineral surfaces and the shortage of 25 mg/l SO$_4^{2-}$ must be due to competitive adsorption on the surfaces of the minerals. The concentrations of Ca$^{2+}$ and SO$_4^{2-}$ ions in the final solution after the flotation using process water at 11 °C are 200 and
The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 103 mg/l and 240 mg/l respectively. The shortage of 31 mg/l Ca\(^{2+}\) must have been adsorbed on the mineral surface and the excess of 61 mg/l SO\(_4^{2-}\) must have come from the sulphur concentration in the mineral.

The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using tap water at 4 °C are 121 and 224 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 198 mg/l and 241 mg/l respectively. The shortages of 99 mg/l Ca\(^{2+}\) and 25 mg/l SO\(_4^{2-}\) must be due to the adsorption of the species to the surfaces of the minerals. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using process water at 4 °C are 239 and 366 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 92 mg/l and 241 mg/l respectively. There is neither shortage nor excess of Ca\(^{2+}\) ions. However the excess of 21 mg/l SO\(_4^{2-}\) must have come from the sulphur concentration in the mineral.

**Kristineberg Ore**

The sulphate and calcium species concentration balance in solution and flotation results for tests on Kristineberg ore using tap water and process water at 22 °C, 11 °C and 4 °C temperatures are presented in Table 3. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the tap water are 22.5 and 7.4 mg/l respectively. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using tap water at 22 °C are 556 and 918 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 493 mg/l and 409 mg/l respectively. The excess of 41 mg/l Ca\(^{2+}\) must have came from the ore and excess of 502 mg/l SO\(_4^{2-}\) must have been contributed from the sulphur composition of the mineral. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the process water are 186 and 153 mg/l respectively. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using process water at 22 °C are 782 and 1090 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 762 and 519 mg/l respectively. The shortage of 166 mg/l Ca\(^{2+}\) must have been adsorbed on the mineral surfaces and the excess of 418 mg/l SO\(_4^{2-}\) must have been contributed from the sulphur composition of the mineral.

Table 5. Calcium and sulphate species ions balance in solution from flotation of Kristineberg ore at different temperature using both tap water and process water.

<table>
<thead>
<tr>
<th></th>
<th>Tap water</th>
<th></th>
<th>Process water</th>
</tr>
</thead>
<tbody>
<tr>
<td>~22°C</td>
<td>SO(_4^{2-}) mg/l</td>
<td>Ca(^{2+}) mg/l</td>
<td>SO(_4^{2-}) mg/l</td>
</tr>
<tr>
<td>Initial</td>
<td>416</td>
<td>515</td>
<td>672</td>
</tr>
<tr>
<td>Final</td>
<td>918</td>
<td>556</td>
<td>1090</td>
</tr>
<tr>
<td>Difference</td>
<td>502</td>
<td>41</td>
<td>418</td>
</tr>
<tr>
<td>~11°C</td>
<td>Initial</td>
<td>249</td>
<td>425</td>
</tr>
<tr>
<td>Final</td>
<td>556</td>
<td>394</td>
<td>704</td>
</tr>
<tr>
<td>Difference</td>
<td>308</td>
<td>-31</td>
<td>309</td>
</tr>
<tr>
<td>~4°C</td>
<td>Initial</td>
<td>249</td>
<td>364</td>
</tr>
<tr>
<td>Final</td>
<td>506</td>
<td>346</td>
<td>665</td>
</tr>
<tr>
<td>Difference</td>
<td>257</td>
<td>-18</td>
<td>271</td>
</tr>
</tbody>
</table>
The concentrations of Ca\(^{2+}\) and SO\(_{4}^{2-}\) ions in the final solution after the flotation using tapwater at 11 °C are 394 and 556 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_{4}^{2-}\) contributed by the reagents are 402 mg/l and 241 mg/l respectively. The shortage of 31 mg/l Ca\(^{2+}\) must have been adsorbed on the mineral surfaces and the excess of 308 mg/l SO\(_{4}^{2-}\) must have been contributed from the sulphur composition of the mineral. The concentrations of Ca\(^{2+}\) and SO\(_{4}^{2-}\) ions in the final solution after the flotation using process water at 11 °C are 565 and 704 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_{4}^{2-}\) contributed by the reagents are 357 mg/l and 241 mg/l respectively. The excess of 22 mg/l Ca\(^{2+}\) could be due to excessive addition of calcium oxide or analytical error and the excess of 309 mg/l SO\(_{4}^{2-}\) must have come from the sulphur concentration in the mineral.

The concentrations of Ca\(^{2+}\) and SO\(_{4}^{2-}\) ions in the final solution after the flotation using tapwater at 4 °C are 346 and 506 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_{4}^{2-}\) contributed by the reagents are 342 mg/l and 257 mg/l respectively. The shortage of 18 mg/l Ca\(^{2+}\) must be due to the adsorption of the species to the surfaces of the minerals and the excess of 257 mg/l SO\(_{4}^{2-}\) must have come from the sulphur concentration in the mineral. The concentrations of Ca\(^{2+}\) and SO\(_{4}^{2-}\) ions in the final solution after the flotation using process water at 4 °C are 559 and 665 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_{4}^{2-}\) contributed by the reagents are 360 mg/l and 241 mg/l respectively. The excess of 13 mg/l Ca\(^{2+}\) could be due to excessive addition of calcium oxide or analytical error and the excess of 271 mg/l SO\(_{4}^{2-}\) must have come from the sulphur concentration in the mineral.

Conclusions

Calcium ions depress Hallimond flotation of galena in process water while it has no significant effect in deionised water. The depression is evident at concentrations above 400 mg/l of calcium. Sulphate ions show both improvement and depression of galena in both deionised and process water. The depression is observed in deionised water at 100, 700 to 1400 and 2000 mg/l sulphate, while the improvement is observed at 200 to 400 and 1600 mg/l sulphate. Similar trend is observed when both calcium and sulphate ions are used simultaneously. The depressing effect was closely associated with calcium carbonate coating and sulfoxy species presence on galena in the presence of calcium and sulphate ions respectively, while the improvement could be due to activating effect of calcium and other metal ions.

Galena is negatively charged in the entire pH region, where the magnitude of negative charge is significantly higher than in process water, illustrating the adsorption of metal ions that exist in process water. The adsorption of calcium ions is evidenced from the zeta-potentials of galena where the magnitude of negative charge is successively reduced with increasing calcium concentration. Significant effect of calcium ions but not sulphate ions is observed on the zeta-potentials of galena. Galena zeta-potentials in the presence of Ca\(^{2+}\), SO\(_{4}^{2-}\), ZnSO\(_{4}\), NaHSO\(_{3}\) and dextrin independently and in the presence and absence of xanthate collector showed that the NaHSO\(_{3}\) assisted xanthate adsorption and the other reagents has little or no effect for xanthate adsorption.

DRIFT spectra of galena pure sample showed that the surface is partially oxidised depicting surface sulfooxy species bands in the regions 598–629, 1051–1193 cm\(^{-1}\) and carbonate species bands at 679, 838, 1051, 1409 and 1425 cm\(^{-1}\). These oxidised species bands are evidenced with the increased intensity of these bands when the sample is oxidised with H\(_{2}\)O\(_{2}\) oxidant. The composition of surface species is found to be pH dependent evidently at pH 7 and 10.5 in
deionised water and pH 10.5 in process water where high intensity carbonate species bands appeared. Depending on the experimental conditions of pH, type of water used, whether deionised water or process water and time of conditioning, galena surface is composed of lead sulfooxy and carbonate compounds. In deionised and process water, calcium and sulphate ions had some effect on surface composition since the sulfooxy and carbonate species bands increased in intensity with increase in their concentration.

Xanthate adsorbs on galena to form mono-coordinate lead amylxanthate (1187 and 1024 cm\(^{-1}\)) both in deionised and process waters, however process water suppressed xanthate adsorption where xanthate species bands intensities were lower. Upon xanthate adsorption, the intensity of sulfooxy species bands decreased illustrating an ion-exchange adsorption mechanism. Calcium and sulphate ions form soluble complexes with sulfooxy and carbonate species leading to decreased and disappearance of the surface oxidised compounds bands. Xanthate adsorption on galena is also reduced in the presence of calcium and sulphate ions as shown by the decreasing intensity of xanthate bands (1187 and 1023 cm\(^{-1}\)).

Galena recoveries decrease as flotation temperature decreases in bench-scale flotation in tap water. Recoveries both increased and decreased when process water was used in bench-scale flotation, which is evidenced in the results when the tests were performed in the presence of calcium, sulphate and both species combined. An analysis for calcium and sulphate species in pulp liquid before and after flotation tests showed depleted calcium ions and excess sulphate ions in the pulp liquid after flotation. These results closely corroborate that the depletion of calcium ions are due to their adsorption on minerals as noticed in zeta-potential studies and as well caused by the calcium precipitation revealed in DRIFT spectra. The dissolved oxidised surface sulfooxy species and also the release of these species up on xanthate adsorption contributed to the excess sulphate concentration in the flotation pulp liquid.

Acknowledgements

The financial support from the Swedish VINNOVA foundation and, Boliden and Lundin Mining mineral companies for the research project on “Recycling of process water and influence of its chemistry on sulfide flotation and flotation selectivity” is gratefully acknowledged. One of the authors, Prof. KH Rao, also acknowledges the support from the “Centre for Advanced Mining and Metallurgy (CAMM)” recently established under the Swedish Strategic Research Initiative programme.

References


Paper 3
Recycling of process water in sulphide flotation. Part 3: Effect of calcium and sulphate ions on sphalerite flotation

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*Corresponding author, e-mail: hanumantha.rao@ltu.se

Abstract

The influence of process water components on sphalerite flotation has been investigated through Hallimond flotation, zeta-potential and diffuse reflectance FTIR spectroscopy measurements using pure sphalerite sample as well as bench scale flotation tests using complex sulphide ore. The significance of process water species in flotation has been assessed using deionised water, process water and simulated water containing calcium and sulphate ions in experiments. In addition, the effect of temperature in bench scale flotation tests has also been examined.

Hallimond flotation indicated depression of sphalerite in the presence of major species of calcium and sulphate ions using potassium amyl xanthate as collector. Calcium ions have significant influence on zeta-potential characteristics of sphalerite and xanthate adsorption behaviour compared to sulphate ions. FTIR studies revealed the presence of surface oxidised sulfoxy and carbonate species on sphalerite at pH 11.5 in the presence of deionised water, process water and water containing calcium and sulphate ions, which surface species does not influenced xanthate adsorption. Bench scale flotation using two different complex sulphide ores showed that sphalerite recovery is better in process water than in tap water. Flotation results also indicated better recovery of sphalerite at temperatures lower than 22°C in either tap water or process water.

Keywords: Sphalerite, Complex sulphide ore, Hallimond flotation, Zeta-potential, Diffuse reflectance FTIR, Bench-scale flotation, Sulphate and calcium ions

Introduction

The quest for a cleaner and safer environment with clean surface and ground water has lead to increased recycling of process water within the production cycle of sulphide minerals processing. Since the chemistry of process water is entirely different from fresh water; there is a concern about the possible effects of components contained in them on the efficiency of the flotation process (Rao and Finch, 1989). Calcium and sulphate ions are two very common major components in the process water from flotation of sulphide minerals. The usual procedure in the flotation stage of complex sulphide ore processing is to float Cu and Pb in the first stage of flotation while Zn is activated and floated in the second stage (Liu and Zhang, 2000). The floatability of Zn is usually affected by a number of factors which includes electrochemical effects, components and species present in the solution phase of the pulp (Chandra and Gerson, 2009; Chen et al., 2009; Chen et al., 2010; Das et al., 1997; Grano et al., 1990; Göktepe and Williams, 1995; H louot and Duhamet, 1992; Peng and Grano; Rao and Finch, 1989; Trahar et al., 1997), grinding method (Eric Forssberg et al., 1993; Palm et al., 2010) and control of the grinding environment especially the metal oxidation species produced on other undesired components such as pyrite (Shen et al., 2001), galena, and
chalcopyrite and oxidation-reduction state which in turn influence the potential range of subsequent flotation (Boulton et al., 2005; Chander, 2003; Forssberg et al., 1988; Grano, 2009; Martin et al., 1991; Ralston, 1991). The origins of calcium and sulphate species in process water are the ore and flotation reagents (Broman, 1980). A number of studies carried out in the past dealt with the effect of calcium and sulphate ions on environmentally important organic and inorganic anions and metal cations on wide band-gap metal hydroxides and the results was interpreted as either competitive (Lefèvre and Fédoroff, 2006; Wu et al., 2002) promotive (Jia Y, 2005; Ostergren et al., 2000; Swedlund and Webster, 2001) or indifferent (Lefèvre and Fédoroff, 2006) adsorption depending on the speciation of the adsorbed anion and the formation of calcium bearing surface co-precipitates. However little is generally known about the effects of concentrated sulphate and calcium solutions on adsorption-reaction of collectors on sulphides in terms of kinetics of the reagent adsorption, adsorption isotherms, kinetic of the formation of dixanthogen, flotation kinetics and grade. In particular previous work has shown that dry comminution (Palm et al., 2010), iron ions (Boulton et al., 2005), sulphite ions (Shen et al., 2001), lead ions and hydroxide (Trahar et al., 1997) and increased air distribution profile (Aslan and Boz, 2010) promotes flotation of sphalerite.

In this study the influence of major species of calcium and sulphate ions on sphalerite flotation in single mineral as well as in flotation from complex sulphide ores were investigated.

Experimental

Materials and reagents

Pure sphalerite mineral (containing 39.92% Zn, 20.7% S, 4.2% Fe, 1.32% Pb and 0.17% Cu) used in Hallimond flotation tests, zeta-potential and FTIR measurements was procured from Gregory, Bottley & Lloyd Ltd., United Kingdom. The mineral was crushed, ground and classified into different size fractions. A size fraction of ~150+38 μm was used in the Hallimond single mineral flotation tests and ~5 μm size fraction was used in both zeta-potential measurement and FTIR study. Two complex sulphide ores from Boliden-Renström and Boliden-Kristineberg mines were used in the Bench-scale flotation tests. The ores were crushed and wet ground in a stainless steel mill to obtain K80 ≤ 65 μm, the common feed size in practice.

Technical grade Isobutyl xanthate (IBX) was used in the experiment as a collector, Dowfroth 250 (polypropylene oxide methanol) was used as frother, dextrin (Boulton et al., 2001; López Valdivieso et al., 2004), sodium hydrogen sulphite (NaHSO3) (Khmeleva et al., 2003; Shen et al., 2001) was used as a depressant for any pyrite in the ore, copper sulphate (CuSO4) (Chandra and Gerson, 2009; Laskowski et al., 1997) was used as an activator for the sphalerite. Calcium oxide (CaO), HCl, HNO3, KOH and NaOH solutions were used as pH regulators and K2SO4 and CaCl2 as sources of SO42- and Ca2+ ions respectively, potassium nitrate (KNO3) was used to maintain ionic strength in zeta-potential measurement. Process water containing various Ca2+ and SO42- ions concentrations was obtained from Renström and Kristineberg ore concentrator (common concentration range of species found in Boliden process water is shown in Table 1).
Table 1: Chemical species and their concentration range in Boliden process water.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentrations</th>
<th>From</th>
<th>To</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>SO$_4^{2-}$</td>
<td>200</td>
<td>1500</td>
<td>mg/l</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>100</td>
<td>500</td>
<td>mg/l</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>0.1</td>
<td>1300</td>
<td>mg/l</td>
</tr>
<tr>
<td>COD (Cr)</td>
<td>&lt;30</td>
<td>130</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>0.1</td>
<td>10</td>
<td>mg/l</td>
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<tr>
<td>Phosphorus</td>
<td>P</td>
<td>&lt;0.050</td>
<td>0.7</td>
<td>mg/l</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>4.3</td>
<td>53</td>
<td>mg/l</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>4.4</td>
<td>8000</td>
<td>μg/l</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>12</td>
<td>3900</td>
<td>μg/l</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al</td>
<td>59</td>
<td>59000</td>
<td>μg/l</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>0.12</td>
<td>5.2</td>
<td>μg/l</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>4</td>
<td>540</td>
<td>μg/l</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>2.7</td>
<td>20000</td>
<td>μg/l</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td>&lt;0.1</td>
<td>&lt;0.13</td>
<td>μg/l</td>
</tr>
<tr>
<td>Conductivity at 25°C</td>
<td></td>
<td>96</td>
<td>160</td>
<td>ms/m</td>
</tr>
</tbody>
</table>

**Hallimond flotation tests**

1 g of mineral is conditioned in a 100 ml standard volumetric flask and then transferred into a Hallimond tube flotation cell the upper part of the cell is filled with appropriate solution after addition of all reagents up to a total volume of 400 ml; this is followed by flotation under magnetic stirring. The sequence of reagent additions was pH regulators, species in water, collector, and frother. Conditioning time for species in water, collector and frother were 10 min, 5 min and 1 min respectively. Air was supplied at the rate of 200 cm$^3$/min and the flotation time was 1 min. 20 mg/l of IBX and 50 μg/l frother was used. All tests except the pH variation test were carried out at pH ~11.5 in room temperature of approximately 22.5°C.

**Zeta-potential measurements**

The measurement was carried out on the mineral sample at different conditions based on the present study flotation requirements. Zeta potential measurements were carried out with the aid of ZetaCompact instrument equipped with a charge-couple device (CCD) video camera and Zeta4 software. The software allows the direct reading of zeta-potential calculated from the electrophoretic mobilities using Smoluchowski equation. The result is a particle distribution histogram, from which the mean mobility are recalculated to zeta-potential values. In each measurement; about 10 mg of ~5 μm fraction of the mineral at a concentration of about 10 mg/100 ml of solution was used. The ionic strength was maintained with KNO$_3$ at a concentration of about 0.01M and the pH was adjusted with solutions of HNO$_3$ and KOH accordingly. The required concentration of each solution was usually prepared followed by addition of the mineral, conditioning for 10 minutes and addition of other required reagent and species. The pH of the suspension after all conditioning prior to zeta-potential measurement is always regarded as the pH of the measurement. All the zeta-potential measurements were performed at the flotation pH 11.5 unless otherwise specified.
**Diffuse reflectance FTIR spectroscopy measurements**

The measurement was carried out with the aid of Bruker FTIR spectrometer model IFS 66v/s. The ~5 μm fractions of the mineral pre-treated at different conditions based on the present zeta-potential and flotation studies were subjected to FTIR measurements. In each measurement; about 10 mg of ~5 μm fraction of the mineral is pre-treated at a concentration of about 10 mg/100 ml of solution. The pH was adjusted with solutions of HNO₃ and KOH accordingly. The required concentration of each solution and species was usually prepared followed by addition of the mineral, conditioning for 10 minutes and addition of other required reagent and species. The pulp is subsequently filtered and left to dry on the filter paper at room temperature. The pH of the suspension after all conditioning prior to filtration is always regarded as the pH of the measurement. Diffuse reflectance infrared Fourier transform (DRIFT) method was used in the measurement with 2.8 wt% concentration in potassium bromide (KBr) matrix. Each spectrum was recorded after 256 scans.

**Bench-scale flotation tests**

In each test about 1 Kg of ore is wet ground with about 600 ml of tap water or process water in the steel mill with 8 Kg grinding medium followed by flotation in the WEMCO cell of 2.5 litre capacity. The sequences of reagent additions were pH regulator, activator, collector, frother followed by flotation. Dosages of zinc activator and collector in a three stage flotation were 400 g/t CuSO₄ and 40+20+20 g/t IBX. The conditioning times for zinc activator and collector are 2 min and 1+1+1 min respectively. The frother dosage was 20 g/t Dowfroth in all cases. The pH was regulated to ~11.5 with powdered calcium oxide. Experiments were performed at room temperature of approximately 22.5°C, 11°C and 4°C. Total flotation time in successive three stages was 4.5 min (1+1.5+2).

**Results and discussion**

**Hallimond flotation studies**

The recovery of sphalerite at different pH ranging from 3 to 11.5 in both deionised and process water is shown in Fig. 1. It can be seen that the recovery decreases sharply from pH 3 and remains averagely constant from pH 4 and 5 in process water and deionised water respectively. It can also be observed that the recovery of sphalerite in process water is generally lower than in deionised water. In general, the flotation response of sphalerite is only marginal at all basic pH values. It is clear that the collector is not adsorbed even in process water containing various metal ions and activation with Cu ions as followed for sphalerite flotation is necessary.
The effect of Ca\textsuperscript{2+} ions at different concentrations on recovery of pure sphalerite in both deionised and process water is shown in Fig. 2. It can be seen that the presence of Ca\textsuperscript{2+} ions in deionised water slightly depresses the recovery of sphalerite up to 200 mg/l and remains constant afterwards and gradual depression can also be seen in process water up to 600 mg/l calcium concentration, above which the recovery increases a little. In general the recoveries looks better in process water than in deionised water; this could be due to the presence of a number of species in the process water that could activates sphalerite such as copper ions (Chandra and Gerson, 2009; Laskowski et al., 1997), lead ions (Trahar et al., 1997), sulphite ions (Shen et al., 2001) and rest reagents (Chen et al., 2009). The activation in process water is seen to be marginal and insignificant.

The effect of SO\textsubscript{4}\textsuperscript{2-} ions concentrations on pure sphalerite mineral recovery is shown in Fig. 3. It can be seen that increasing SO\textsubscript{4}\textsuperscript{2-} ions concentration in deionised water has no effect on the flotation of sphalerite but depresses a little at a very high concentration. It can also be observed that the mineral is generally not depressed in process water and with a slight better recovery compared to deionised water.
Fig. 3: Effect of sulphate ions on sphalerite flotation in both deionised and process water at pH 11.5.

The effects of both Ca$^{2+}$ and SO$_4^{2-}$ ions concentrations on the recovery of pure sphalerite mineral are presented in Fig. 4. The combined effects shows a slight depression with increasing calcium and sulphate ions which reaches its minimum at 500 and 1000 mg/l Ca and SO$_4$ concentrations and slightly rise afterwards. Almost the same trend is observed in process water; however the recovery is little better in process water.

Fig. 4: Combined effect of calcium and sulphate ions on sphalerite flotation in both deionised and process water at pH 11.5.

The above single mineral Hallimond flotation results showed that sphalerite is not floatable in either deionised water or process water and there is no distinct effect of either calcium or sulphate ions. The metal cations that exist in process water are also inadequate to activate sphalerite flotation noticeably and Cu ions activation as practiced to float sphalerite is necessary.
**Zeta-potential studies**

The zeta-potential response of sphalerite at different pH ranging from 3 to 11.5 in deionised water, process water, and deionised water containing different Ca²⁺ ions concentrations is shown in Fig. 5. Studies reported in the literature indicate that the iso-electric point (iep) of sphalerite is in the range of pH 2 to 7. The extent of surface oxidation of the samples besides their origin and iron impurity could probably explain wide variation in iep. The results of the present sphalerite sample show that it is negatively charged in the entire pH range studied and an iep at pH 2 can be noticed while extending the curve.

![Zeta-potential response of sphalerite at different pH in the presence of deionised water, process water and deionised water containing 200, 300 and 1000 ppm Ca.](image)

Fig. 5: Zeta-potential response of sphalerite at different pH in the presence of deionised water, process water and deionised water containing 200, 300 and 1000 ppm Ca..

It can be seen that the zeta-potential responses reduces gradually (becomes highly negative) as the pH increases in deionised water and greatly reduced after pH ~9.8 while the reduction is not very obvious in process water until after pH 10. In addition the zeta-potential is higher (less negative) in process water than in tap water due to the presence of positively charged metal ions in process water which adsorb on the surfaces of the mineral particles. This is an indication that adsorption of negatively charged collector on sphalerite particles may be enhanced (Fuerstenau and Pradip, 2005; Zhang et al., 1997), but such behaviour is not seen in Hallimond flotation. The usual pH of flotation in practice is 11.5 as indicated by the red broken arrow. The responses are also higher in the presence of Ca ions (the higher the concentration of Ca ions the closer the curve to the positive zeta-potential) and it’s completely positive at pH 11.5 and 500 mg/l Ca ions concentration.
The zeta-potential response of sphalerite at pH 11.5 in the presence of different concentrations of calcium and with 700 mg/l concentration of sulphate is shown in Fig. 6. The concentration of calcium ions found in various Boliden process water ranges from about 50 to 500 mg/l therefore the range of measurements was taken from 0 to 600 mg/l. It can be seen in Fig. 6 that the zeta-potential increases (becomes less negative) with increase in calcium ions concentration as well as in the presence of 700 mg/l sulphate ions. This is also indicating possible enhancement of adsorption to anionic collectors as well as dominance effect of calcium ions over sulphate ions in solution. Since sphalerite is highly negative at pH 11.5, anionic sulphate ions could hardly influence its surface charge. Calcium ions exists as divalent cations and calcium hydroxyl (CaOH\(^+\)) ions as predominant species at pH 11.5 and their adsorption is seen to decrease the magnitude of negative surface charge.
The concentration of sulphate ions found in various Boliden process water ranges from about 150 to 1500 mg/l therefore the range of measurements was taken from 0 to 1600 mg/l. It can be seen in Fig. 7 that the zeta-potential increases insignificantly with increase in sulphate ions concentrations. The dominance effect of calcium ions over sulphate ions in solution can be clearly seen as the presence of 300 mg/l calcium ions sharply increases the zeta-potential in the presence of 0 through 1600 mg/l sulphate ions.

Fig. 8 shows the zeta-potential response of sphalerite in the presence of different concentration of CuSO₄, and in the presence of 9x10⁻⁵M of IBX (equivalent to the concentration of IBX in pulp solution in practice) both in deionised and process water. It can be seen that the zeta-potentials increase with increasing Cu²⁺ ions until 5x10⁻⁴M and above this concentration, there is no effect with more or less the same zeta-potentials. In this case, the presence of IBX caused the zeta-potentials to become more negative up to 5x10⁻⁴M copper ions concentration illustrating pronounced IBX adsorption. Further increase in concentration, the zeta-potentials are becoming less negative indicating a change in surface composition which could be due to copper hydroxide formation and its coating on the surface. The zeta-potential in process water were readily high and in the presence of IBX.
Fig. 8: Zeta-potential of sphalerite at different copper sulphate concentration and with a fixed $9 \times 10^{-5}$M concentration of IBX at pH 11.5 in deionised and process water.

Fig. 9 shows the zeta-potential response of sphalerite in the presence of different concentrations of NaHSO$_3$ and $9 \times 10^{-5}$M of IBX both in deionised and process water. It can be seen that the zeta-potentials were readily high (less negative) in the process water but increases with increase in NaHSO$_3$ concentration in deionised water and where the presence of IBX is seen no influence on the zeta-potentials.

Fig. 9: Zeta-potential of sphalerite at different sodium hydrogen sulphite concentration and with a fixed concentration of IBX at pH 11.5 in deionised and process water.

Fig. 10 shows the zeta-potential response of sphalerite in the presence of different concentrations of dextrin (C$_6$H$_{10}$O$_6$) and $9 \times 10^{-5}$M of IBX both in deionised and process water, it can be seen that the zeta-potentials were readily high in the process water but increases...
slightly in the presence of dextrin and remains constant with increase in dextrin concentration. The initial increase until 1x10^-4 M dextrin could be due to a more neutral dextrin molecule adsorption on negative sphalerite.

Fig. 10: Zeta-potential of sphalerite at different concentration of dextrin and with IBX, in both deionised and process water.

Fig. 11 shows the zeta-potential response of sphalerite in the presence of different concentration of IBX and fixed concentrations of copper sulphate (1x10^-3 M), sodium hydrogen sulphite (1.2x10^-3 M) and dextrin (5x10^-4 M) singly and combined. The activation of sphalerite by copper ions for IBX adsorption can be clearly seen with a sharp decrease in zeta-potentials with increasing IBX concentration in the presence of copper ions. It can be observed that the zeta-potentials are much lower in the presence of sulphate ions while no serious effect can be seen in the presence of only sodium hydrogen sulphite and dextrin. The effect of IBX concentration, in particular at high concentration, in the presence of three reagents combined is closely similar to that of copper ions alone.
Fig. 11: Zeta-potential of sphalerite at different concentration of IBX and in the presence of copper sulphate, sodium hydrogen sulphite, and dextrin singly and combined.

**Diffuse reflectance FTIR studies**

The diffuse reflectance spectrum of –5 µm sphalerite powder sample that is obtained after dry grinding in agate mortar and then micro-sieving in ultrasonic bath is shown in Fig. 12. The spectra of the same sample conditioned with H₂O₂ at different times are also presented in this figure. Although sphalerite is a non-conductive solid which superficial oxidation is limited in the absence of surface activation (de Donato et al., 1999; Persson and Persson, 1991), however the several bands seen in the spectrum of pure sample are due to oxidized species on the surface since the sample was prepared open to atmosphere. An increase in the intensity of these bands when the sample is treated with H₂O₂ oxidant substantiate that these bands are characteristic of oxidized species present on the sample.
The oxidized surface state of sphalerite mainly consists of zinc sulphate and thiosulphate, and zinc carbonate. The bands at 1056, 1101, and 1160 cm\(^{-1}\) can be assigned to S–O vibrations in zinc sulphate (Godocíková et al., 2002). Absorption bands characteristic of C–O vibrations in zinc carbonate are seen at about 870, and 1441 cm\(^{-1}\) (de Donato et al., 1999; Godocíková et al., 2002). The spectra with increasing time of H\(_2\)O\(_2\) treatment, the intensity of sulphate bands increased with no or little effect on carbonate bands. While comparing pure sphalerite spectrum to the spectra oxidized by H\(_2\)O\(_2\), it is clear that the pure sphalerite sample used in the experiments is partially oxidized and the surface is composed of both sulphate and carbonate species.

Fig. 12: Spectra of pure and H\(_2\)O\(_2\) treated sphalerite.
Infrared spectra of sphalerite conditioned at pHs 3, 7 and 11.5 in deionised water (Fig. 13a) show that the extent of surface oxidation is pH dependent. The sulphate and carbonate bands intensities are low at pH 3, increased at pH 7 and then marginally decreased at pH 11.5. The variation in surface zinc sulphate and zinc carbonate with a change in pH could explain the fluctuating negative zeta-potential of sphalerite with increasing pH (Fig. 5). In Fig. 13b, it can be seen that the presence of process water has some influence on the surface composition of sphalerite.
sphalerite especially at pH 11.5 where high intensity zinc carbonate bands (870 and 1442 cm\(^{-1}\)) are observed. Thus the presence of carbonate species in process water is seen to form zinc carbonate on sphalerite surface more than in deionised water which may inhibit xanthate collector adsorption leading to lower flotation of sphalerite.

Fig. 14: Effect of calcium concentration on sphalerite at pH 11.5 in deionised (a) and process (b) waters.

The effect of calcium ions on sphalerite surface composition in deionised and process waters at pH 11.5 is depicted in Fig. 14 (a) and (b). The spectra with increasing calcium in deionised
water are comparable to the spectra conditioned at the same pH of 11.5 in the absence of calcium. The consumption of dissolved carbon dioxide in water from atmosphere leading to formation of zinc carbonate (1442, 870 cm\(^{-1}\)) has led to no calcium carbonate precipitation with increasing calcium concentration where the low intensity of calcium carbonate bands (1433, 870 cm\(^{-1}\)) are unaffected. However, in the presence of process water, calcium carbonate bands have dominated zinc carbonate bands and with increasing calcium concentration, the bands characterizing calcium carbonate at 1441 and 871 cm\(^{-1}\) is seen to increase. In both water cases, calcium ions have no effect on sulphate characteristic bands. Sphalerite surface is mainly composed of zinc carbonate in process water at pH 11.5 and higher level of calcium in process water leads to calcium carbonate precipitation on the surface.
Fig. 15: Effect of sulphate concentration on sphalerite at pH 11.5 in deionised (a) and process (b) waters.

Fig. 15 (a) and (b) shows the spectra of sphalerite conditioned with increasing concentration of sulphate ions in deionised (a) and process (b) waters at pH 11.5. The intensity of S-O stretching vibrations bands in sulfoxy species in deionised water is seen to increase a little with increasing sulphate ions until 400 ppm after which level they are decreased. The intensity level of 700 and 1000 ppm bands is close to the spectrum that is conditioned in water in the absence of sulphate suggesting that the surface is already oxidised to zinc sulphate. Similarly, in process water the spectrum with 700 ppm sulphate and the spectrum without
addition of sulphate are comparable while the remaining bands are also seen at higher intensity level. The sphalerite surface is totally composed of zinc sulphate in process water containing several reduced sulfoxy species and there is no significant influence of additional sulphate concentration in process water.

Fig. 16: Pure mineral subtracted from sphalerite treated at different xanthate concentration at pH 11.5 in deionised (a) and process (b) waters.

Spectra of sphalerite after interaction with amylxanthate at 5x10^-6, 2x10^-5 and 5x10^-5 M concentrations in deionised (a) and process (b) waters are shown in Fig. 16. These were the difference spectra after subtracting the mineral spectrum from the xanthate treated spectra. In deionised water and at low xanthate concentrations of 5x10^-6 and 2x10^-5 M, the spectra show only the diminished oxidised surface compound bands and devoid of xanthate bands. The
absence of xanthate bands could be that xanthate cannot be adsorbed on sphalerite without copper ions activation or xanthate is in complex formation with the oxidised components that are missing from the mineral surface in the aqueous solution. However the bands of oxidation products can be seen when the xanthate concentration is increased to 5x10^{-5} M. In addition low intensity C-O-C and S-C-S symmetric stretching vibration band can be seen at 1200 cm^{-1} and 1047 respectively (Larsson et al., 2000; Leppinen, 1990), indicating a minute adsorption of amylxanthate on sphalerite surface. The surface oxidized products of sphalerite are expected to be removed during the abstraction of xanthate. The presence of oxidation products indicates that the maximum initial xanthate concentration of 5x10^{-5} M used is not adequate to form monolayer coverage. The presence of positive and negative zinc sulphate and zinc carbonate bands in the low concentration spectra illustrates different level of surface oxidation compounds in the xanthate treated sphalerite spectra compared to mineral spectrum that was subtracted. In process water, the three xanthate concentrations spectra show only the oxidised compound bands increasing with increase xanthate concentration and devoid of xanthate bands. The absence of xanthate bands could be that xanthate is in complex formation with the metal ions in process water.
Fig. 17: Effect of calcium on adsorption of xanthate on sphalerite; the spectra presented in this figure are the difference spectra obtained after the sphalerite spectrum conditioned at pH 11.5 is subtracted from the spectra of sphalerite conditioned in the presence of increasing calcium and at a constant 5x10^{-5} M xanthate concentration at pH 11.5 in deionised (a) and process (b) waters.

The influence of calcium concentration on xanthate adsorption in deionised (a) and process (b) waters is shown in Fig. 17. The spectra presented in this figure are the difference spectra, i.e., the sphalerite spectrum that is conditioned at pH 11.5 is subtracted from the spectra of
sphalerite conditioned in the presence of increasing calcium and at a constant $5 \times 10^{-5}$ M xanthate concentration. In the presence of calcium the intensity of surface zinc sulphate and carbonate bands are seen to decrease and they display negative bands at 50 and 100 ppm. The successive decrease in surface oxidised compounds bands with increasing calcium was due to the result of sulfooxy and carbonate species forming soluble complexes with the calcium.

In process water the band shows that the surface oxidized compounds are removed from the surface with increasing calcium concentration. While in the presence of $5 \times 10^{-5}$ M xanthate, the spectrum shows very intense carbonate bands at 1450 and 877 cm$^{-1}$, which not only disappeared but also show negative bands at the same region at increasing calcium concentration. These spectra indicate that calcium forms complexes with surface carbonate species and dissolved into the bulk of the solution.
Fig. 18: Effect of sulphate on adsorption of xanthate on sphalerite; the spectra presented in this figure are the difference spectra obtained after the sphalerite spectrum conditioned at pH 10.5 is subtracted from the spectra of sphalerite conditioned in the presence of increasing sulphate and at a constant 5x10^{-5} M xanthate concentration at pH 11.5.

In deionised water the oxidised zinc sulphate and carbonate bands are marginally absent at 200 ppm sulphate concentration while it increases at 400 to 1000 ppm (Fig. 18). The same trend is observed in process water. There is no significant effect on xanthate adsorption with increase in sulphate concentration either in deionised or process water.
Bench-scale flotation studies

The bench scale flotation studies was carried out at different temperatures covering the seasonal temperature changes in process plant from winter to spring and summer through autumn in the north of Sweden. Renström ore grades 6% Zn, while Kristineberg ore grades 2.4% Zn. Table 2 shows the recovery and grade of zinc from both Renström and Kristineberg ores at 22, 11 and 4°C in both tap and process water. It can be observed that the recovery and grade of zinc from Renström ore in tap water decreases as temperature decreases, while the reverse is almost the case in process water where the recovery increases with decrease in temperature. However in Kristineberg ore both the recovery and grade of zinc increases with decrease in temperature in both tap and process waters. The increase in recoveries and grades of zinc as the temperature decreases cannot be clearly explained. One possible reason for better grades in process water could be the presence of rest reagents (Chen et al., 2009).

Table 2: Recovery and grade of zinc from bench scale flotation using both tap and process water at 22.5, 11 and 4°C temperatures.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Renström ore Tap water</th>
<th>Process water</th>
<th>Kristineberg ore Tap water</th>
<th>Process water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Recovery, %</td>
<td>Grade, %</td>
<td>Recovery, %</td>
<td>Grade, %</td>
</tr>
<tr>
<td>22.5°C</td>
<td>72.46</td>
<td>20.45</td>
<td>67.41</td>
<td>21.52</td>
</tr>
<tr>
<td>11°C</td>
<td>67.76</td>
<td>19.07</td>
<td>69.88</td>
<td>18.10</td>
</tr>
<tr>
<td>4°C</td>
<td>68.18</td>
<td>17.15</td>
<td>70.21</td>
<td>21.20</td>
</tr>
</tbody>
</table>

Table 3 shows a comparison between flotation results using tap water, process water and tap water containing process water equivalent concentration of added Ca\(^{2+}\) and SO\(_4^{2-}\) ions singly and combined. It can be observed that the presence of Ca\(^{2+}\) and SO\(_4^{2-}\) ions singly and combined in the water has some influence on both the recovery and grade of zinc. The somewhat better results when the process water was used in Renström ore could be due to presence of other minor metal species and rest reagents that acts as activators (Chen et al., 2009; Finkelstein, 1997).

Table 3: Comparison of recoveries and grades in tap water, process water and when Ca\(^{2+}\) and SO\(_4^{2-}\) ions are added to tap water at 22.5°C.

<table>
<thead>
<tr>
<th>Pulp liquid (species added)</th>
<th>Renström ore Recovery, %</th>
<th>Grade, %</th>
<th>Kristineberg ore Recovery, %</th>
<th>Grade, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca ions</td>
<td>68.38</td>
<td>16.00</td>
<td>24.06</td>
<td>7.40</td>
</tr>
<tr>
<td>Sulphate ions</td>
<td>68.78</td>
<td>17.10</td>
<td>28.02</td>
<td>7.40</td>
</tr>
<tr>
<td>Ca(^{2+})+ Sulphate ions</td>
<td>70.19</td>
<td>17.60</td>
<td>25.90</td>
<td>3.90</td>
</tr>
<tr>
<td>Tap water</td>
<td>72.46</td>
<td>20.45</td>
<td>22.53</td>
<td>2.61</td>
</tr>
<tr>
<td>Process water</td>
<td>67.41</td>
<td>21.52</td>
<td>41.99</td>
<td>6.31</td>
</tr>
</tbody>
</table>

The difference in flotation response between process and tap water could also be caused by different grinding environments (Eric Forssberg et al., 1993; Grano, 2009; Göktepe and Williams, 1995; Martin et al., 1991; Peng et al., 2003a; Peng et al., 2003b) for example the pH of process water is about 11 which is the grinding pH when using process water for flotation as against tap water in which grinding pH is about 8.
Balance of calcium and sulphate species in pulp solution

Renström Ore

The sulphate and calcium species concentration balance in solution for tests on Renström ore using tap water and process water at 22 °C, 11 °C and 4 °C temperatures are presented in Table 4. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the tap water are 22.5 and 7.4 mg/l respectively. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using tap water at 22 °C are 370 and 375 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 449 mg/l and 365 mg/l respectively. The shortage of 102 mg/l Ca\(^{2+}\) must have adsorbed on the mineral surfaces and the excess of 2 mg/l SO\(_4^{2-}\) must have been contributed from the dissolved sulphur composition of the mineral. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the process water are 128 and 63 mg/l respectively. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using process water at 22 °C are 446 and 511 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 328 and 392 mg/l respectively. The shortage of 10 mg/l Ca\(^{2+}\) must have been adsorbed on the mineral surfaces and the excess of 56 mg/l SO\(_4^{2-}\) must have been contributed from the sulphur composition of the mineral.

Table 4: Calcium and sulphate species ions balance in solution from flotation of Renström ore at different temperature using both tap water and process water.

<table>
<thead>
<tr>
<th></th>
<th>Tap water</th>
<th></th>
<th>Process water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~22.5 °C</td>
<td></td>
<td>~11 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~4 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(_4^{2-}) mg/l</td>
<td>Initial</td>
<td>373</td>
<td>Initial</td>
<td>306</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>375</td>
<td>Final</td>
<td>281</td>
</tr>
<tr>
<td>SO(_4^{2-}) mg/l</td>
<td>Difference</td>
<td>2</td>
<td>Difference</td>
<td>-25</td>
</tr>
<tr>
<td>Ca(^{2+}) mg/l</td>
<td>Initial</td>
<td>472</td>
<td>Initial</td>
<td>267</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>370</td>
<td>Final</td>
<td>155</td>
</tr>
<tr>
<td>Ca(^{2+}) mg/l</td>
<td>Difference</td>
<td>-102</td>
<td>Difference</td>
<td>-112</td>
</tr>
<tr>
<td></td>
<td>~11 °C</td>
<td></td>
<td>~4 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial</td>
<td>306</td>
<td>Initial</td>
<td>249</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>281</td>
<td>Final</td>
<td>224</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
<td>-25</td>
<td>Difference</td>
<td>-99</td>
</tr>
<tr>
<td></td>
<td>~4 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial</td>
<td>455</td>
<td>Initial</td>
<td>344</td>
</tr>
<tr>
<td></td>
<td>Final</td>
<td>511</td>
<td>Final</td>
<td>366</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
<td>56</td>
<td>Difference</td>
<td>21</td>
</tr>
</tbody>
</table>

The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using tap water at 11 °C are 155 and 281 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 245 mg/l and 299 mg/l respectively. The shortage of 112 mg/l Ca\(^{2+}\) must have been adsorbed on the mineral surfaces and the shortage of 25 mg/l SO\(_4^{2-}\) must be due to competitive adsorption on the surfaces of the minerals. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using process water at 11 °C are 200 and 364 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 103 mg/l and 240 mg/l respectively. The shortage of 31 mg/l Ca\(^{2+}\) must have been adsorbed on the mineral surface and the excess of 61 mg/l SO\(_4^{2-}\) must have come from the sulphur concentration in the mineral.

The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using tap water at 4 °C are 121 and 224 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\)
contributed by the reagents are 198 mg/l and 241 mg/l respectively. The shortages of 99 mg/l Ca\(^{2+}\) and 25 mg/l SO\(_4^{2-}\) must be due to the adsorption of the species to the surfaces of the minerals. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using process water at 4 °C are 239 and 366 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 92 mg/l and 241 mg/l respectively. There is neither shortage nor excess of Ca\(^{2+}\) ions. However the excess of 21 mg/l SO\(_4^{2-}\) must have come from the sulphur concentration in the mineral.

**Kristineberg Ore**

The sulphate and calcium species concentration balance in solution and flotation results for tests on Kristineberg ore using tap water and process water at 22 °C, 11 °C and 4 °C temperatures are presented in Table 5.

Table 5: Calcium and sulphate species ions balance in solution from flotation of Kristineberg ore at different temperature using both tap water and process water.

<table>
<thead>
<tr>
<th></th>
<th>Tap water</th>
<th>Process water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~22.5°C</td>
<td></td>
</tr>
<tr>
<td>SO(_4^{2-}) mg/l</td>
<td>Ca(^{2+}) mg/l</td>
<td>SO(_4^{2-}) mg/l</td>
</tr>
<tr>
<td>Initial</td>
<td>416</td>
<td>515</td>
</tr>
<tr>
<td>Final</td>
<td>918</td>
<td>556</td>
</tr>
<tr>
<td>Difference</td>
<td>502</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>~11°C</td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>249</td>
<td>425</td>
</tr>
<tr>
<td>Final</td>
<td>556</td>
<td>394</td>
</tr>
<tr>
<td>Difference</td>
<td>308</td>
<td>-31</td>
</tr>
<tr>
<td></td>
<td>~4°C</td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>249</td>
<td>364</td>
</tr>
<tr>
<td>Final</td>
<td>506</td>
<td>346</td>
</tr>
<tr>
<td>Difference</td>
<td>257</td>
<td>-18</td>
</tr>
</tbody>
</table>

The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the tap water are 22.5 and 7.4 mg/l respectively. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using tap water at 22 °C are 556 and 918 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 493 mg/l and 409 mg/l respectively. The excess of 41 mg/l Ca\(^{2+}\) must have came from the ore and excess of 502 mg/l SO\(_4^{2-}\) must have been contributed from the sulphur composition of the mineral. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the process water are 186 and 153 mg/l respectively. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using process water at 22 °C are 782 and 1090 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 762 and 519 mg/l respectively. The shortage of 166 mg/l Ca\(^{2+}\) must have been adsorbed on the mineral surfaces and the excess of 418 mg/l SO\(_4^{2-}\) must have been contributed from the sulphur composition of the mineral.

The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using tap water at 11 °C are 394 and 556 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 402 mg/l and 241 mg/l respectively. The shortage of 31 mg/l Ca\(^{2+}\) must have been adsorbed on the mineral surfaces and the excess of 308 mg/l SO\(_4^{2-}\) must have been contributed from the sulphur composition of the mineral. The concentrations of
Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using process water at 11 °C are 565 and 704 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 357 mg/l and 241 mg/l respectively. The excess of 22 mg/l Ca\(^{2+}\) could be due to excessive addition of calcium oxide or analytical error and the excess of 309 mg/l SO\(_4^{2-}\) must have come from the sulphur concentration in the mineral.

The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using tap water at 4 °C are 346 and 506 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 342 mg/l and 257 mg/l respectively. The shortage of 18 mg/l Ca\(^{2+}\) must be due to the adsorption of the species to the surfaces of the minerals and the excess of 257 mg/l SO\(_4^{2-}\) must have come from the sulphur concentration in the mineral. The concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) ions in the final solution after the flotation using process water at 4°C are 559 and 665 mg/l respectively. The concentration of Ca\(^{2+}\) and SO\(_4^{2-}\) contributed by the reagents are 360 mg/l and 241 mg/l respectively. The excess of 13 mg/l Ca\(^{2+}\) could be due to excessive addition of calcium oxide or analytical error and the excess of 271 mg/l SO\(_4^{2-}\) must have come from the sulphur concentration in the mineral.

**Conclusions**

Calcium ions depress Hallimond flotation of sphalerite both in deionised water and process water. The depressing effect is evident at lower concentrations up to 200 mg/l of calcium in deionised water and 600 mg/l calcium in process water, above which concentration the flotation recoveries are either increased marginally or averagely constant. Similar depressing effect is observed when both calcium and sulphate ions are used simultaneously. Sulphate ions show no significant effect except at concentration of 2000 mg/l sulphate when the recovery drops significantly.

Sphalerite is negatively charged in the entire pH region, where the magnitude of negative charge is significantly higher than in process water, illustrating the adsorption of metal ions that exist in process water. The adsorption of calcium ions is evidenced from the zeta-potentials of sphalerite where the magnitude of negative charge is successively reduced with increasing calcium concentration. In the presence of calcium, the negative charge moving to positive at pH 10.5 and a charge reversal occurring at pH 11.5 is accounted for the presence and adsorption of high surface active CaOH\(^+\) species. Significant effect of calcium ions but not sulphate ions is observed on the zeta-potentials of sphalerite. Sphalerite zeta-potentials in the presence of Ca\(^{2+}\), SO\(_4^{2-}\), CuSO\(_4\), NaHSO\(_3\) and dextrin independently and in the presence and absence of xanthate collector showed that CuSO\(_4\) and NaHSO\(_3\) assisted xanthate adsorption and the other reagents has little or no effect for xanthate adsorption.

DRIFT spectra of sphalerite pure sample showed that the surface is partially oxidised depicting surface sulfooxy and carbonate species bands in the region 1056–1160 cm\(^{-1}\). These oxidised species bands are evidenced with the increased intensity of these bands when the sample is oxidised with H\(_2\)O\(_2\) oxidant. The composition of surface species is found to be pH dependent. Depending on the experimental conditions of pH, type of water used, whether deionised water or process water and time of conditioning, sphalerite surface is composed of zinc sulfooxy and carbonate compounds.

In deionised water, calcium ions had no effect on surface composition since the sulfooxy species bands have the same intensity with increasing calcium concentration, however in process water, very intense broad (1441, 871 cm\(^{-1}\)) bands appeared characterizing calcium
carbonate on the surface. Sulphate ions have no significant effects on surface compound bands both in deionised and process water.

Xanthate bands are not apparent in deionised water only surface oxidised compounds and low intensity xanthate bands are observed (1449, 1094, 1056 and 1161 cm⁻¹) at 5×10⁻⁵ M xanthate. In process water only the surface oxidised compound bands are observed, where the intensities are decreased with xanthate concentration, probably due to xanthate species forming soluble complexes with components. Calcium ions decreases and removes the sulfoxy and carbonate bands due to formation of soluble complexes with calcium in both deionised and process water. Sulphate ions at 200 mg/l removes the sulfoxy and carbonate bands, the bands intensity increase from 400 to 1000 mg/l sulphate in both deionised and process water. No significant effect on xanthate adsorption is observed.

Sphalerite recoveries generally increased as flotation temperature decreases in bench-scale flotation. Recoveries are generally increased when process water was used in bench-scale flotation due to presence of rest reagents. The increase in recoveries and grades of zinc as the temperature decreases cannot be clearly explained. An analysis for calcium and sulphate species in pulp liquid before and after flotation tests showed depleted calcium ions and excess sulphate ions in the pulp liquid after flotation. These results closely corroborate that the depletion of calcium ions are due to their adsorption on minerals as noticed in zeta-potential studies and as well caused by the calcium precipitation revealed in DRIFT spectra. The dissolved oxidised surface sulfoxy species and also the release of these species up on xanthate adsorption contributed to the excess sulphate concentration in the flotation pulp liquid.

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The financial support from the Swedish VINNOVA foundation and, Boliden and Lundin Mining mineral companies for the research project on “Recycling of process water and influence of its chemistry on sulfide flotation and flotation selectivity” is gratefully acknowledged. One of the authors, Prof. KH Rao, also acknowledges the support from the “Centre for Advanced Mining and Metallurgy (CAMM)” recently established under the Swedish Strategic Research Initiative programme.

References


Paper 4


Recycling of process water in sulphide flotation: Part 4. Effect of calcium and sulphate ions on pyrite depression

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Abstract

The influence of process water components on pyrite depression has been investigated through Hallimond flotation, zeta-potential and diffuse reflectance FTIR spectroscopy measurements using pure pyrite sample. The significance of process water species in flotation has been assessed using deionised water, process water and simulated water containing calcium and sulphate ions in experiments.

Hallimond flotation indicated activation of pyrite in the presence of calcium and sulphate ions with potassium amyl xanthate as collector. Calcium ions have significant influence on zeta-potential characteristics of pyrite and xanthate adsorption behaviour compared to sulphate ions. FTIR studies revealed the presence of hydrated surface oxidised species on pyrite and also surface iron and calcium carbonates at pH 10.5 in the presence of process water and water containing calcium ions, which surface species influenced xanthate adsorption.

Keywords: Pyrite, Hallimond flotation, Zeta-potential, Diffuse reflectance FTIR, Sulphate and calcium ions

Introduction

Global campaign for environmental friendly production practises has lead to increased recycling of process water within the production cycle of sulphide mineral flotation. However the difference in the chemistry compared to fresh water raised a concern about the possible effects of components contained in them on the efficiency of the flotation process (Rao and Finch, 1989). Calcium and sulphate ions are two very common components in the process water from flotation of sulphide minerals. The usual procedure in the flotation stage of complex sulphide ore processing is to float Cu and Pb in the first stage of flotation, Zn is activated and floated in the second stage (Liu and Zhang, 2000) while pyrite is usually selectively depressed at high pH in both stages (Boulton et al., 2001). Pyrite is a very important gangue mineral in complex sulphide ores. The depression of pyrite is usually affected by a number of factors which includes; the presence of oxidised and metal deficient surfaces (Chander, 1991) the use of appropriate modifier such as polyacrylamide, dextrin, sulfoxyl, cyanide and carefully controlled flotation conditions (Boulton et al., 2001; Chandra and Gerson, 2009; López Valdivieso et al., 2004; Matis et al., 1992) the presence of other sulphide mineral such as galena and chalcopyrite from which sulphur can be transferred to the pyrite surface (Trahar et al., 1994), extent of pyrite oxidation (Monte et al., 2002; Monte et al., 1997) electrochemical effects, components and species present in the pulp (Chander, 1991; Ekmecki and Demirel, 1997; Janetski et al., 1977) grinding method (Eric Forssberg et al., 1993; Peng and Grano, 2010) and control of the grinding environment especially the metal oxidation species produced on iron, chalcopyrite and galena (Cases et al., 1993; Peng et al., 2003a; Peng et al., 2003b), conditioning pH and gases (Shen et al., 1998). Biomodulation with
Acidithiobacillus ferrooxidans have been shown to depress pyrite to a very large extent (Chandraprabha et al., 2004a; Chandraprabha et al., 2004b; Chandraprabha et al., 2005; Mehrabani et al., 2010). The origins of calcium and sulphate species in process water are the ore and flotation reagents (Broman, 1980). A number of studies carried out in the past dealt with the effect of calcium and sulphate ions on environmentally important organic and inorganic anions and metal cations on wide band-gap metal hydroxides and the results was interpreted as either competitive (Lefèvre and Fédoroff, 2006; Wu et al., 2002) promotive (Jia Y, 2005; Ostergren et al., 2000; Swedlund and Webster, 2001) or indifferent (Lefèvre and Fédoroff, 2006) adsorption depending on the speciation of the adsorbed anion and the formation of calcium bearing surface co-precipitates. However little is generally known about the effects of concentrated sulphate and calcium solutions on adsorption-reaction of collectors on sulphides in terms of kinetics of the reagent adsorption, adsorption isotherms, kinetic of the formation of dixanthogen, flotation kinetics and grade.

In particular previous work has shown that sulphite ions promotes depression of pyrite (Khmeleva et al., 2003) while the presence of calcium ions alone activates pyrite, however calcium in the presence of sphalerite depresses pyrite (Zhang et al., 1997). Zinc sulphate was confirmed as a depressant of pyrite at high Eh (275 mV SHE) value but has little or no effect at low Eh values (He et al., 2006). In this study the influence of major species of calcium and sulphate ions on pyrite depression in single mineral was investigated.

**Experimental**

**Materials and reagents**

Pure pyrite mineral (containing 44.4 %Fe, 49.7 %S, and 0.02 %Cu) used in Hallimond flotation tests, zeta-potential and FTIR measurements were procured from Gregory, Bottley & Lloyd Ltd., United Kingdom. The mineral was crushed, ground and classified into different size fractions. A size fraction of -150+ 38 μm was used in the Hallimond single mineral flotation tests and -5 μm fractions were used in both zeta-potential measurement and FTIR study.

**Hallimond flotation tests**

1 g of mineral is conditioned in a 100 ml standard volumetric flask and then transferred into a Hallimond tube flotation cell the upper part of the cell is filled with appropriate solution after addition of all reagents up to a total volume of 400 ml; this is followed by flotation under magnetic stirring. The sequence of reagent additions was pH regulators, species in water, collector, and frother. Conditioning time for species in water, collector and frother were 10 min, 5 min and 1 min respectively. Air was supplied at the rate of 200 cm³/min and the flotation time was 1 min. 20 mg/l of KAX and 50 µg/l frother was used. All tests except the pH variation tests were carried out at pH ~10.5 in room temperature of approximately 22.5°C.

**Zeta-potential measurements**

The measurement was carried out on the mineral sample at different conditions based on the present study flotation requirements. Zeta potential measurements were carried out with the aid of ZetaCompact instrument equipped with a charge-couple device (CCD) video camera and Zeta4 software. The software allows the direct reading of zeta-potential calculated from the electrophoretic mobilites using Smoluchowski equation. The result is a particle
distribution histogram, from which the mean mobility are recalculated to zeta-potential values. In each measurement; about 10 mg of -5 μm fraction of the mineral at a concentration of about 10 mg/100 ml of solution was used. The ionic strength was maintained with KNO₃ at a concentration of about 0.01M and the pH was adjusted with solutions of HNO₃ and KOH accordingly. The required concentration of each solution was usually prepared followed by addition of the mineral, conditioning for 10 minutes and addition of other required reagent and species. The pH of the suspension after all conditioning prior to zeta-potential measurement is always regarded as the pH of the measurement.

**Diffuse reflectance FTIR spectroscopy measurements**

The measurement was carried out with the aid of Bruker FTIR spectrometer model IFS 66v/s. The -5 μm fractions of the mineral pre-treated at different conditions based on the present study flotation requirements were subjected to FTIR measurements. In each measurement; about 10 mg of -5 μm fraction of the mineral is pre-treated at a concentration of about 10 mg/100 ml of solution. The pH was adjusted with solutions of HNO₃ and KOH accordingly. The required concentration of each solution and species was usually prepared followed by addition of the mineral, conditioning for 10 minutes and addition of other required reagent and species. The pulp is subsequently filtered and left to dry on the filter paper at room temperature. The pH of the suspension after all conditioning prior to filtration is always regarded as the pH of the measurement. Diffuse reflectance infrared Fourier transform (DRIFT) method was used in the measurement with 2.8 wt% concentration in potassium bromide (KBr) matrix. Each spectrum was recorded after 256 scans.

**Results and discussion**

**Hallimond flotation studies**

The flotation of pyrite at different pH values ranging from 3 to 11.5 in both deionised and process water is shown in Fig. 1. It can be seen that the recovery decreases generally from pH 3 to pH 9, rises slightly at pH 10.5 and decreases at pH 11.5. In addition it can be seen that the recovery of pyrite in process water is generally higher than in deionised water except at pH 11.5. The results show that pyrite flotation is depressed with increasing pH and the high flotation response in the acidic pH range 2 to 5 is due to the formation of ferric amyl xanthate about the same pH region (Eric Forssberg, 1985). The decrease in recovery with increasing pH value is due to formation of ferrous hydroxide and ferric hydroxyl xanthate compounds imparting hydrophilic character to the surface. A better flotation response of pyrite in process water than deionised water could be due to the adsorption of Cu and Pb ions, and the rest reagents that exist in process water.
The effect of Ca$^{2+}$ ions concentration on flotation of pure pyrite in both deionised and process water is shown in Fig. 2. It can be seen that the presence of Ca$^{2+}$ ions in both deionised and process water slightly increases recovery at 50 mg/l concentration while it becomes unstable as the concentration increases until 400 mg/l where a slight increase is seen in process water and a slight decrease is seen in deionised water. The increase in recovery at lower concentration could be due to activating effects of Ca$^{2+}$ ions in deionised water, Cu$^{2+}$, Fe$^{2+}$ and Ca$^{2+}$ ions and oxidation species of lead and copper in process water (Peng et al., 2003a; Peng et al., 2003b; Zhang et al., 1997).

Fig. 1. Recovery of pyrite at different pH in deionised and process water

Fig. 2. Effect of calcium ions on pyrite depression in both deionised and process water at pH 10.5.
The effect of SO$_4^{2-}$ ions concentrations on pure pyrite mineral flotation is shown in Fig. 3. It can be seen that the presence of SO$_4^{2-}$ ions in deionised water on the average slightly increased the recovery of pyrite. While the recovery is generally decreased in process water, with a constant decrease from 100 to 1000 mg/l SO$_4^{2-}$ ions concentrations, however a slight increase can be seen from 1200 mg/l SO$_4^{2-}$ ions concentrations. The activating effect in deionised water could be similar to thiosulphate reduction of hydrophilic compounds on sulphides particles which leads to increased flotation recovery (Kirjavainen et al., 2002a; Kirjavainen et al., 2002b).

The mineral is generally more depressed in process water than in deionised water; this could be due to the presence of a number of species including SO$_4^{2-}$, SO$_3^{2-}$ (Houot and Duhamet, 1992), iron oxidation species (Peng et al., 2003b) in the process water which could form hydrophilic layers or iron oxidation species on the surface of the minerals; these species can play major roles in the depression of pyrite flotation. This is also an indication that high concentration of SO$_4^{2-}$ ions may have some depressing effect on pyrite similar to oxides minerals by competing with collector molecules adsorption on the mineral surface (Lefèvre and Fédoroff, 2006; Wu et al., 2002), the strongly bonded SO$_4^{2-}$ ions on the mineral surfaces which inhibits collector adsorption.

![Fig. 3. Effect of sulphate ions on pyrite depression in both deionised and process water.](image)

The effects of both Ca$^{2+}$ and SO$_4^{2-}$ ions concentrations on the flotation of pure pyrite mineral are presented in Fig. 4. The combined effects shows a slight decrease in recovery at 50 and 100 mg/l Ca$^{2+}$ and SO$_4^{2-}$ ions concentrations respectively and there after the recovery increases gradually. The activation could be due to the activating effects of metal ions (Ca$^{2+}$ ions in deionised water, Cu$^{2+}$, Fe$^{2+}$ and Ca$^{2+}$ ions and oxidation species of lead and copper in process water (Peng et al., 2003a; Peng et al., 2003b; Zhang et al., 1997)) mentioned above. This effect seems to be dominating after 50 and 100 mg/l Ca$^{2+}$ and SO$_4^{2-}$ ions concentrations in both deionised and process water in addition to the activating effect of thiosulphate.
reduction of hydrophilic compounds on sulphides particles (Kirjavainen et al., 2002a; Kirjavainen et al., 2002b).

Fig. 4. Combined effect of calcium and sulphate ions on pyrite depression in both deionised and process water.

Zeta-potential studies

The zeta-potential response of pyrite at different pH ranging from 3 to 11.5 in deionised water, process water, and deionised water containing different Ca\(^{2+}\) ions concentrations is shown in Fig. 5. In the absence of calcium ions, the results show an iso-electric point of pyrite at about pH 7.0, which is slightly higher than the values of pH 6.2 and 6.4 reported in the literature (Healy and Moignard, 1976). In process water, pyrite is slightly negative in the entire acidic pH region and up to pH 9.5 and above which pH a charge reversal to positive potentials is seen. The negative potentials in acidic pH region indicate the adsorption of sulfoxyl species and the positive potentials at very high basic pH show the adsorption of positive first hydroxyl species of Cu, Pb and Ca ions that exist in process water. In the presence of Ca ions, the zeta-potentials are positive in the entire acidic to basic pH range and the higher the concentration of Ca ions, the higher is the magnitude of positive potentials. It is very clear that the positively charged calcium ions in deionised water adsorb on the surface of pyrite and activate in the basic flotation pH region. This is an indication that adsorption of negatively charged collector on pyrite particles may be enhanced (Fuerstenau and Pradip, 2005; Zhang et al., 1997). The usual pH of flotation in practise is 10.5 as indicated by the red broken arrow.
Fig. 5. Zeta-potential response of pyrite at different pH in the presence of deionised water, process water and deionised water containing 200, 300 and 1000 ppm Ca.

The zeta-potential response of pyrite at pH 10.5 in the presence of different concentration of calcium and with 700 mg/l concentration of sulphate is shown in Fig. 6. The calcium ions concentration contained in various process water from Boliden mineral company locations in the north of Sweden ranges from about 50 to 500 mg/l therefore the range of measurements was taken from 0 to 600 mg/l. It can be seen in Fig. 6 that the zeta-potential increases (becomes less negative) with increase in calcium ions concentration and at about 50 ppm calcium ions, a charge reversal occurs. It was also the case when 700 mg/l sulphate ions are added in the presence of calcium ions. However the magnitude of positive charge is reduced with sulphate ions since the calcium ions could form soluble complexes with sulphate ions thereby minimising the effect of calcium ions on pyrite positive charge. Nonetheless the activation of pyrite by calcium ions even in the presence of sulphate ions is clearly observed.
Fig. 6. Zeta-potential of pyrite at different calcium ions concentration and together with a fixed concentration of sulphate ions at pH 10.5.

The concentration of sulphate ions found in various Boliden process water ranges from about 150 to 1500 mg/l therefore the range of measurements was taken from 0 to 1600 mg/l. It can be seen in Fig. 7 that the zeta-potential only increases slightly after 400 ppm concentration of sulphate ions. The dominance effect of calcium ions over sulphate ions in solution can also be clearly seen as the presence of 300 mg/l calcium ions sharply increases the zeta-potential in the presence of 0 through 1600 mg/l sulphate ions. However the increment was slightly reduced when the mineral was conditioned first with sulphate ions before addition of calcium ions, showing that sulphate ions had occupied most of the surface area of pyrite but calcium ions still dominates thereafter.
Fig. 7. Zeta-potential of pyrite at different sulphate ions concentration and with a fixed concentration of calcium ions at pH 10.5.

Fig. 8 shows the zeta-potential response of pyrite in the presence of different concentrations of ZnSO$_4$ both in deionised and process water. It can be seen that the zeta-potentials were readily high in the process water but increases with increase in ZnSO$_4$ concentration in deionised water. The presence of ZnSO$_4$ in process water decreased the zeta potential from positive to negative indicating the transfer of cationic species from surface to bulk of the solution or the adsorption sulphate anions on surface positive sites. The increase in zeta-potential until 1x10$^{-3}$ M ZnSO$_4$ concentration in deionised water is clearly due to the adsorption of zinc ions.

Fig. 8. Zeta-potential of pyrite at different zinc sulphate concentration at pH 10.5 in deionised and process water.
Fig. 9 shows the zeta-potential response of pyrite in the presence of different concentration of NaHSO₃ both in deionised and process water. It can be seen that the zeta-potentials were readily high (less negative) in the process water but low in deionised water. In both the cases, the zeta-potentials are seen to decrease with increasing NaHSO₃ concentration until about 8x10⁻⁴M, after which there is no further influence. Sodium bisulphite reacts with pyrite surface where the cationic ferric sites could transform to iron hydroxides reducing the surface charge.

Fig. 10 shows the zeta-potential response of pyrite in the presence of different concentrations of dextrin (C₆H₁₀O₆) both in deionised and process water, it can be seen that the zeta-potentials were readily high in the process water and low in deionised water. There is no major influence of dextrin on pyrite in deionised water but the initial decrease in zeta-potential in process water could be due to the adsorption neutral dextrin molecule on positive surface sites.
Fig. 10. Zeta-potential of pyrite at different concentration of dextrin in both deionised and process water.

Fig. 11. Zeta-potential of pyrite at different concentration of KAX and in the presence of calcium and sulphate in both deionised and process water.

Fig. 11 shows the zeta-potential response of pyrite in the presence of different concentration of KAX and fixed concentrations of calcium (300 mg/l) and sulphate (700 mg/l), both in deionised and process water. High zeta-potential in the presence of calcium ions and in process water as well as low zeta-potential in the presence of sulphate ions are still clearly
visible. Generally all the zeta-potentials measured in the presence of calcium ions seem to be identical, and are also identical to all zeta-potentials measured in process water.

**Diffuse reflectance FTIR studies**

![Diffuse reflectance FTIR studies](image)

The oxidized surface state of pyrite mainly consists of ferrous sulphate and ferric sulphate, and superficial carbonate. Fundamental pyrite vibrations band exists below 600 cm\(^{-1}\) (de Donato et al., 1999) therefore the absorbance bands seen in the pure pyrite spectrum in Fig.12 are due to oxidised surface compounds. The band at 828 cm\(^{-1}\) can be assigned to S–O vibrations in ferrous sulphate. The bands at 1017 to 1154 can be assigned to S-O vibrations in ferric sulphate, while the low intensity band at 1494 can be assigned to C-O vibration in superficial carbonate (Borda et al., 2004; de Donato et al., 1999; de Donato et al., 1993; Godocíková et al., 2002). However with addition and increasing time of treatment in H\(_2\)O\(_2\), the sulphate bands intensities marginally decreases and the carbonate band disappeared, this is indicating that the surfaces were initially covered by hydrated sulphates (de Donato et al., 1999). While comparing pure pyrite spectrum to the spectra oxidized by H\(_2\)O\(_2\), it is clear that the pure pyrite sample used in the experiments is partially oxidized and the surface is composed of not only hydrated sulphate but also carbonate species.
Fig. 13. Spectra of pyrite conditioned at pH 3, 7 and 10.5 in deionised (a) and process (b) waters.

Infrared spectra of pyrite conditioned at pHs 3, 7 and 10.5 in deionised water (Fig. 13a) shows that the extent of surface oxidation is pH dependent. The ferric sulphate bands (1025 - 1187) intensities are low at pH 3, increased at pH 7 and then marginally increased at pH 10.5, while the carbonate ferrous sulphate bands (1494, 828) are not seen at all pH. The variation in surface ferric and ferrous sulphate and carbonate with a change in pH could explain the high (more positive) zeta-potential of pyrite at lower pH and low (more negative) zeta-potential at
higher pH (Fig. 5). In Fig. 13b, it can be seen that the presence of process water at different pH has significant influence on the surface composition of pyrite at lower pHs 3 and 7 the intensity of the ferric and ferrous sulphates were very low and devoid of carbonate band while at pH 10.5 high intensity of ferric sulphate can be seen at 1122 and 1151 cm⁻¹, ferrous sulphate at 871 and low intensity carbonate band at 1441 cm⁻¹. The intensities of the bands are stronger in process water than in the deionised, this is due to the presence of calcium and sulphate species in process water which form calcium carbonate and ferric and ferrous sulphate on pyrite surface at high pH which may inhibit xanthate collector adsorption leading to lower flotation recovery of pyrite at high pH in (Fig.1).

Fig. 14. Effect of calcium concentration on pyrite at pH 10.5 in deionised (a) and process (b) waters.
The effect of calcium ions on pyrite surface composition in deionised and process waters at pH 10.5 is depicted in Fig. 14 (a) and (b). The spectra with increasing calcium in deionised water are comparable to the spectra conditioned at the same pH of 10.5 in the absence of added calcium in process water high intensity of ferric sulphate bands can be seen at 1119 and 1151 cm\(^{-1}\) the intensity is stronger when 50 ppm of Ca was present in the solution. However, in the presence of process water increase of calcium, dissolved organic reagents and carbon dioxide from air have lead to precipitation of calcium carbonate on the surface of the pyrite (871 cm\(^{-1}\) and superficial carbonates broad bands at 1368 to 1461). The intensity of the bands is higher at 300 ppm concentration of calcium in solution. Pyrite surface is mainly composed of sulphate and carbonate in process water at pH 10.5 and higher level of calcium in process water leads to calcium carbonate precipitation on the surface.

Fig. 15. Effect of sulphate concentration on pyrite at pH 10.5 in deionised (a) and process (b) waters.
Fig. 15 (a) and (b) shows the spectra of pyrite conditioned with increasing concentration of sulphate ions in deionised (a) and process (b) waters at pH 10.5. The intensity of S-O stretching vibrations bands in sulfoxy species in deionised water is seen to increase at 400 ppm sulphate concentration after which level they are decreased. The intensity level of these bands is close to the spectrum that is conditioned in water in the absence of sulphate suggesting that the surface is already oxidised to ferric sulphate. However, in process water these bands are seen at higher intensity level and there is no change in intensity with increasing sulphate concentration. In addition a low intensity band of calcium carbonate can be seen at 871 cm⁻¹. The pyrite surface is mostly composed of ferric sulphate in process water containing several reduced sulfoxy species and there is no marked influence of additional sulphate concentration in process water.

Fig. 16. Pure mineral subtracted from pyrite treated at different xanthate concentration at pH 10.5 in deionised (a) and process (b) waters.
Spectra of pyrite after interaction with amylxanthate at $5 \times 10^{-6}$, $2 \times 10^{-5}$ and $5 \times 10^{-5}$ M concentrations in deionised (a) and process (b) waters are shown in Fig. 16. These were the difference spectra after subtracting the mineral spectrum from the xanthate treated spectra. In deionised water, the spectra exhibits C-O-C symmetric stretching vibration band at 1199 cm$^{-1}$ (weak intensity at $5 \times 10^{-6}$M and high intensity at $2 \& 5 \times 10^{-5}$M KAX concentrations) and the stretching vibration band of the S-C-S group at 1062-1043 cm$^{-1}$. These xanthate species bands on pyrite are comparable to those of bulk dixanthogen with signals at 1239 and 1021 cm$^{-1}$ wave numbers (Leppinen, 1990) but have shifted, and they can be assigned to iron xanthate. The ferric sulphate (1137, 1062, cm$^{-1}$) and ferrous sulphate (808 cm$^{-1}$) bands although diminished can be seen in these spectra. The surface oxidized products of pyrite are expected to be removed during the abstraction of xanthate. The presence of oxidation products indicates that the maximum initial xanthate concentration of $5 \times 10^{-5}$ M used is not adequate to form monolayer coverage.

In process water and at low xanthate concentrations of $5 \times 10^{-6}$ and $2 \times 10^{-5}$ M, the spectra show only the oxidised compound bands and devoid of xanthate bands. The absence of xanthate bands could be that xanthate is in complex formation with the metal ions in process water. However at $5 \times 10^{-5}$ M xanthate concentration spectrum, xanthate bands can be seen in the spectrum. The presence of negative ferric sulphate band illustrates different level of surface oxidation compounds in the xanthate treated pyrite spectra compared to mineral spectrum that was subtracted.
Fig. 17. Effect of calcium on adsorption of xanthate on pyrite in deionised (a) and process (b) waters; the spectra presented in this figure are the difference spectra obtained after the pyrite spectrum conditioned at pH 10.5 is subtracted from the spectra of pyrite conditioned in the presence of increasing calcium and at a constant $5\times10^{-5}$ M xanthate concentration at pH 10.5.

The influence of calcium concentration on xanthate adsorption in deionised (a) and process (b) waters is shown in Fig. 17. The spectra presented in this figure are the difference spectra, i.e., the pyrite spectrum that is conditioned at pH 10.5 is subtracted from the spectra of pyrite conditioned in the presence of increasing calcium and at a constant $5\times10^{-5}$ M xanthate.
concentration. In deionised water the pyrite surface species band at 1119 to 1172 cm\(^{-1}\) broadens, forms two peaks and increase in intensity with increase in calcium ions concentration from 100 to 300 ppm. In addition a low intensity of carbonate band appears on the 300 ppm band at 848 cm\(^{-1}\) wavenumber. The broad signal could be due to precipitation of a calcium xanthate complex on the pyrite surface which increases in intensity with increase in calcium ions concentration. Xanthate adsorption on pyrite is also increased in the presence of calcium as shown by the increasing intensity of xanthate bands (1155 and 1124 cm\(^{-1}\)) with increasing calcium concentration. In process water the intensity of the iron xanthate band at 1143 cm\(^{-1}\) reduces slightly at 300 ppm calcium ions concentration. In addition the surface oxidised products are removed from the surface in the presence of calcium. In process water and in the presence of 5x10\(^{-3}\) M xanthate, the spectrum shows a low intensity carbonate band at 873 cm\(^{-1}\) which is diminished at the same region on addition of calcium. These spectra indicate that calcium forms complexes with surface carbonate species and dissolved into the bulk of the solution.

Fig. 18. Effect of sulphate on adsorption of xanthate on pyrite in deionised (a) and process (b) waters; the spectra presented in this figure are the difference spectra obtained after the pyrite spectrum conditioned at pH 10.5 is subtracted from the spectra of pyrite conditioned in the presence of increasing sulphate and at a constant 5x10\(^{-3}\) M xanthate concentration at pH 10.5.
The increase in sulphate concentration shows that the oxidised ferric sulphate drastically increases at 1000 ppm sulphate concentration while the carbonate is marginally removed from the surface in deionised water and both are entirely removed in process water (Fig. 18). Xanthate adsorption is not much affected with increasing in sulphate concentration in process water.

Conclusions

Calcium ions generally have no effects on Hallimond flotation of pyrite in deionised water. An increase in recovery is observed in process water after 400 mg/l calcium. Sulphate ions generally improve Hallimond flotation of pyrite in deionised water and depress it in process water. A general increase in recovery is observed when both calcium and sulphate ions are used simultaneously. The effect was closely associated with calcium carbonate coating and sulfooxy species presence on pyrite in the presence of calcium and sulphate ions respectively. The increase in recovery is thought to be due to the activating effect of calcium ions and other metal ions as well as the thiosulphate reduction of hydrophilic compounds on sulphides particles.

Pyrite is positively charged in the entire acidic pH region with iep at pH 7 where it remains negatively charged until pH 11.5 in deionised water. In process water it has negative potentials in acidic pH region due to adsorption of sulfooxy species and positive potentials after pH 9.5 due to adsorption of first hydroxyl species of Cu, Pb and Ca ions present in process water. The adsorption of calcium ions is evidenced from the zeta-potentials of pyrite where the magnitude of positive charge is successively increased with increasing calcium concentration. Significant effect of calcium ions but not sulphate ions is observed on the zeta-potentials of pyrite. Pyrite zeta-potentials in the presence of Ca$^{2+}$, SO$_4^{2-}$, ZnSO$_4$, NaHSO$_3$ and dextrin independently and in the presence and absence of xanthate collector showed that the NaHSO$_3$ assisted xanthate adsorption and the other reagents has little or no effect for xanthate adsorption.

DRIFT spectra of pure pyrite sample showed that the surface is partially covered by hydrated sulphates species bands in the region 828, 1017-1154 cm$^{-1}$ and carbonate band at 1494 cm$^{-1}$. These hydrated species bands are evidenced with the disappearance of these bands when the sample is oxidised with H$_2$O$_2$ oxidant. The composition of surface species found is to be pH dependent, with highest intensity of sulfooxy species band at pH 7 in deionised water and pH 10.7 in process water. Depending on the experimental conditions of pH, type of water used, and time of conditioning, pyrite surface is composed of sulfooxy and superficial carbonate compounds.

In deionised water, calcium ions at 50 ppm concentration increased the intensity of sulfooxy species band at (1151, 1119 cm$^{-1}$). In process water calcium in conjunction with dissolved carbon dioxide precipitated calcium carbonate on the surface of the pyrite at (871, 1368 to 1461 cm$^{-1}$) with highest intensity at 300 ppm of calcium. Sulphate ions in deionised water generally have no effects on surface species of pyrite. In process water sulfooxy species are at higher intensity and no effect is noticed with increase in sulphate concentration. The pyrite surface is mostly composed of ferric sulphate in process water containing several reduced sulfooxy species and there is no marked influence of additional sulphate concentration in process water.
Xanthate adsorbs on pyrite to form mono-coordinate ferric and ferrous xanthate (1199, 1060-1043 cm\(^{-1}\)) and dixanthogen (1239 and 1021 cm\(^{-1}\)) in deionised water. The surface xanthate compounds bands seen in process water are diminished. Calcium ions increased the intensity of sulfoxy species band at 1119 to 1172 cm\(^{-1}\) and a low intensity of carbonate band at 848 cm\(^{-1}\) at 300 ppm calcium concentration. Xanthate adsorption on pyrite is also increased in the presence of calcium at (1155 and 1124 cm\(^{-1}\)) in deionised water. In process water the intensity of the iron xanthate band at 1143 cm\(^{-1}\) reduces and the sulfoxy and carbonate species bands are removed probably through formation of soluble complex between calcium, sulfoxy and carbonate species. Sulphate ions increase oxidised ferric sulphate at 1000 ppm sulphate concentration while the carbonate is marginally removed from the surface in deionised water and both are entirely removed in process water. Xanthate adsorption is not significantly affected by sulphate ions.

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References


