Recycling of process water in sulphide flotation: 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, diffuse reflectance FTIR spectroscopy and XPS measurements using pure galena mineral 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 lower recoveries of galena in the presence of calcium and sulphate ions using potassium amyl xanthate as collector. Calcium ions increase zeta-potential of galena while sulphate ions have no effect. FTIR and XPS studies revealed the presence of surface oxidised sulfoxy, hydroxyl and carbonate species on galena at pH 10.5 in deionised and process water, which surface species affected xanthate adsorption. Bench scale flotation using two different complex sulphide ores showed that galena recovery is better in process water than tap water at room temperature. Flotation results also indicated decrease of galena recovery at temperatures lower than 22°C in either tap water or process water.

Keywords: Galena; Flotation; Zeta-potential; FTIR; XPS.

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). The usual procedure in the flotation stage of complex sulphide ore is floating Cu and Pb in the first stage while Zn is floated in the second stage (Liu and Zhang, 2000). Pb flotation is usually affected by a number of factors which includes 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) electrochemical effects, 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). Calcium and sulphate ions are two very common components in the process water from flotation of sulphide minerals. The origins of calcium and sulphate species in process water are the ore and flotation reagents (Broman, 1980). Previous studies dealt with the effect of calcium and sulphate ions on environmentally important organic and inorganic anions and metal cations 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 formation of dixanthogen, flotation recovery and grade.

Previous work has shown that calcium ions promote flotation of galena (Liu and Zhang, 2000). In this study the influence of process water components; Ca^{2+} and SO_4^{2-} independently and combined were investigated on galena flotation using pure mineral and complex sulphide ore.

EXPERIMENTAL

Materials and reagents

The pure galena mineral used in this study was procured from Gregory, Bottley & Lloyd Ltd., United Kingdom and it contains 73.69% Pb, 6% S, 1.38% Fe, 1.26% Zn and 0.2% Cu. The mineral was crushed, ground and classified into different size fractions. A size fraction of $-150+38\ \mu\text{m}$ was used in the Hallimond single mineral flotation tests and $-5\ \mu\text{m}$ size fraction was used in zeta-potential measurement, FTIR and XPS studies. 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 steel mill to obtain $K_{80} \leq 65\ \mu\text{m}$ size particles, which is the same feed size in plant operation flotation.

Potassium amyl xanthate (KAX) and Danafloat were used as collectors, Dowfroth 250 (polypropylene oxide methanol) was used as frother, dextrin (Boulton et al., 2001; López Valdivieso et al., 2004), sodium hydrogen sulphite (NaHSO_3) (Khmeleva et al., 2003; Shen et al., 2001), and zinc sulphate (ZnSO_4) (Cao and Liu, 2006) were used as pyrite and sphalerite

depressants in flotation. 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, and 186 mg/l Ca²⁺ and 153 mg/l SO₄²⁻ ions concentrations were collected during Renström and Kristineberg ores concentration by flotation respectively. An analysis of Boliden process water for chemical species showed that calcium, sulphate and iron are the major species (Table 1).

Table 1. Chemical species and their concentration range in Boliden process water.

Concentration range of chemical species in process water				
Species		Concentrations		Unit
		From	To	
Sulphate	SO ₄	200	1500	mg/l
Calcium	Ca	100	500	mg/l
Iron	Fe	0.1	1300	mg/l
COD (Cr)		<30	130	mg/l
Nitrogen	N	0.1	10	mg/l
Phosphorus	P	<0.050	0.7	mg/l
Magnesium	Mg	4.3	53	mg/l
Manganese	Mn	4.4	8000	µg/l
Zinc	Zn	12	3900	µg/l
Aluminium	Al	59	59000	µg/l
Cadmium	Cd	0.12	5.2	µg/l
Cobalt	Co	4	540	µg/l
Copper	Cu	2.7	20000	µg/l
Mercury	Hg	<0.1	<0.13	µg/l
Conductivity at 25°C		96	160	ms/m

Hallimond flotation tests

The tests were conducted with 1 g of mineral conditioned in a 100 ml standard volumetric flask and subsequently transferred into a 100 ml Hallimond tube flotation cell; this is followed by flotation under magnetic stirring. A collector concentration of 20 mg/l and a frother dosage of 50 µg/l were used unless otherwise specified.

Zeta-potential measurements

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 is recalculated to zeta-potential value. In each measurement; about 10 mg of $-5\ \mu\text{m}$ 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 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 measurements were carried out at the flotation pH 10.5 unless otherwise specified.

FTIR (DRIFT) spectroscopy measurements

The instrument used was Bruker FTIR spectrometer model IFS 66v/s. The samples were prepared similarly as in zeta-potential and 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.

XPS measurements

The samples subjected to XPS measurement were the same as the FTIR samples. The measurement was carried out with the aid of a Kratos Axis Ultra electron spectrometer using mono AlK α operated at 150W X-ray source and a low-energy electron flood gun for charge compensation. The spectrometer is equipped with nitrogen pre-cooling chamber to prevent evaporation of volatile components in the sample. The measurement procedure and data acquisition was as described by Sandstrom et al.(Sandström et al., 2005).

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 a steel mill with 8 Kg grinding medium followed by flotation in a 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 collectors in a three stage sequential lead 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°C and at 11°C and 4°C. Total flotation time was 4.5 min. The three float products in each test are combined for the chemical analysis.

RESULTS AND DISCUSSIONS

Hallimond flotation studies

The data presented are average of three results. 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 from pH 3 to pH 6 and above which it rises. However the recovery between pH 7 and 9 is the same around 50%. In addition the recovery of galena in process water is generally lower than in deionised water.

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

Fig. 2 presents the effect of Ca^{2+} and SO_4^{2-} ions at different concentrations on recovery of pure galena in both deionised and process water. There is no significant effect of Ca^{2+} ions in deionised water; however there is a slight increase in recovery in process water from 50 mg/l to 400 mg/l and a sharp decrease at 500 mg/l. Presence of SO_4^{2-} ions in deionised water

decrease the flotation of galena on the average. The mineral is generally more depressed in process water than in deionised water.

Fig. 2: Effect of calcium (Top) and sulphate (Bottom) ions on galena flotation in both deionised and process water.

The lower recovery in process water 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 ($\text{Ca}^{2+}\text{-SO}_3^{2-}$) (Houot and Duhamet, 1992), dissolved iron (Kant et al., 1994; Peng et al., 2003b) in the process water which could form hydrophilic layers of iron oxidation species on the surface of the mineral, these species can play a major role in the depression of galena flotation. It is also an indication that high concentration of SO_4^{2-} ions may have some depressing effect on galena 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.

Zeta-potential studies

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. 3.

Fig. 3: 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.

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 iso-electric point (iep) lies at about pH 2. This is in agreement with the reported iep values of galena ranging from pH 2 to 4 (Healy and Moignard, 1976), depending on its conditioning time in water and whether the surface is clean or composed of oxidised sulfoxy anions. In general the magnitude of negative zeta-potential is lesser in process water than in deionised water. It 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).

Fig. 4: Zeta-potential of galena at different calcium ions concentration and with a fixed concentration of sulphate ions at pH 10.5.

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.4. The zeta-potential

increases (becomes less negative) with increase in calcium ions concentration due to their adsorption and the presence of sulphate ions is seen to increase the negative charge marginally. Calcium ions forming complex with sulphate ions either in bulk or on surface could be the reason for the increased negative charge. The effect of sulphate ions concentration in the absence and presence of calcium ions on zeta-potentials is shown in Fig. 5. Since the sulphate ions have no significant effect on adsorption, the decrease in zeta-potential could be due to the increase of ionic strength. 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. 5: Zeta-potential of galena at different sulphate ions concentration and with a fixed concentration of calcium ions at pH 10.5.

The zeta-potential at different concentrations of KAX in deionised and process waters, and in the presence of fixed concentrations of calcium (300 mg/l) and sulphate (700 mg/l) is shown in Fig. 6. 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.6: Zeta-potential of galena at different concentration of KAX in deionised and process water and in the presence of calcium, sulphate, zinc sulphate, sodium hydrogen sulphite, and dextrin at pH 10.5.

The increase in the zeta-potential in process water compared to in deionised water was due to the adsorption of metal cations that exist in process water. Calcium ions exist as Ca^{2+} ions up to pH 11 and their adsorption similarly decreases the magnitude of negative charge which is seen in the results of Figs. 3 and 4. This is an indication that adsorption of negatively charged collector on galena particles may be enhanced (Fuerstenau and Pradip, 2005; Vergouw et al., 1998; Zhang et al., 1997). The usual pH of flotation in practice is 10.5 and at this pH, the hydrolysis of calcium ions forms calcium hydroxyl species (CaOH^+) and these species are

established to be more susceptible to adsorption. Overall, the effect of calcium ions is significantly higher than the sulphate ions.

Diffuse reflectance FTIR spectroscopy studies

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 pure mineral was deliberately treated in hydrogen peroxide at different times to distinguish the extent of their surface oxidation during sample preparation. The spectra of the pure sample and the ones conditioned with H_2O_2 at different times are presented in Fig. 7. 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} are not really noticed in the spectra.

Fig. 7: Spectra of pure and H_2O_2 treated galena.

Absorption bands characteristic of C–O vibrations in lead carbonate are seen at about 679, 838, 1408 and 1425 cm^{-1} . The intensity of sulphate bands increased with increasing time of H_2O_2 treatment with no or little effect on carbonate bands. From a comparison of the intensities of S–O vibrations, the pure mineral sample is observed to be partially oxidized.

Infrared spectra of galena conditioned at pH 3, 7 and 10.5 in deionised and processed water show that the extent of surface oxidation is pH and process water dependent (Fig. 8). The sulphate and carbonate bands intensities are low at pH 3, increased at pH 7 and pH 10.5 in deionised water whereas in process water at pH 10.5, high intensity lead carbonate bands (680, 838, 1051, 1425 cm^{-1}) and calcium carbonate bands (875, 1425 cm^{-1}) are observed besides lead sulphate bands (1050, 1159 cm^{-1}).

Fig. 8. Spectra of galena conditioned at pH 3, 7 and 10.5 in deionised water (Top) and process water (Bottom).

Fig. 9. Difference DRIFT spectra of galena treated with calcium and sulphate ions in the presence of 5×10^{-5} M xanthate after subtracting the mineral spectrum in deionised water (Top) and process water (Bottom) at pH 10.5.

The difference spectra (spectra after subtracting the mineral treated at pH 10.5 spectrum from the xanthate treated spectra) of galena after treatment in 5×10^{-5} M xanthate concentration and in the presence of calcium and sulphate in deionised and process water at pH 10.5 are shown in Fig. 9. The xanthate band in deionised water showed three bands associated with adsorbed xanthate components at 913, 1011, and 1087 cm^{-1} . The band at 1087 cm^{-1} is related to the C-O-C and S-C-S symmetric stretching vibration band while the 1011 cm^{-1} is associated with the S-C-S group. Comparing the corresponding bands in lead amylxanthate (1:2) compound, these bands are shifted from 1220 cm^{-1} to a lower value of 1087 cm^{-1} and from 1022 to 1011 cm^{-1} . These bands can be assigned to mono-coordinated form of lead xanthate.

In the presence of calcium the intensity of surface lead sulphate, hydroxide and carbonate bands are seen to decrease and the spectra also displayed negative bands. Xanthate adsorption on galena is also reduced in the presence of calcium as shown by the decreased intensity of xanthate bands (1087 and 1011 cm^{-1}). Similar spectra but in process water show that the surface oxidized compounds, in particular lead carbonate, is removed. In process water and in the presence of 5×10^{-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. The presence of sulphate ions shows that the oxidised lead sulphate and carbonate is marginally removed from the surface in both deionised and process water. Xanthate adsorption band is also seen to reduce in the presence of sulphate in both waters.

Galena exhibit a fundamental vibration below 200 cm^{-1} , therefore 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_2O_2 oxidant substantiate that these

bands are characteristic of oxidized species present on the sample. They are subsequently confirmed to be sulphate and carbonate species.

Sulphate and carbonate bands intensities are low at pH 3, increased at pH 7 and then marginally decreased at pH 10.5 (Fig. 9). 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. 4). 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 observed in Hallimond tube flotation tests. The positive and negative lead sulphate and lead carbonate bands (Fig. 10) illustrates different level of surface oxidation compounds in the xanthate treated galena spectra compared to mineral spectrum that was subtracted. The successive decrease in surface oxidised compounds bands in the presence of calcium and sulphate could be due to a result of sulfoxy and carbonates species forming soluble complexes with the calcium and sulphate and dissolved into the bulk of the solution.

Xanthate adsorbs on galena to form mono-coordinate lead amylxanthate (1087 and 1011 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 sulfoxy species bands decreased illustrating an ion-exchange adsorption mechanism since there is no change in zeta-potential up on xanthate adsorption (Fig. 6). 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}). The calcium carbonate observation in XPS at 290 eV as well as reduced $\text{S}2\text{p}$ intensity observation at 162 eV binding energies substantiates these results.

X-ray photoelectron spectroscopy (XPS) studies

Pure galena samples used in XPS measurement were from the same samples used in FTIR measurements. Spectra of galena surface components in this study were recorded at similar binding energies found in literatures and databases (Chernyshova and Andreev, 1997; Kartio et al., 1997; Laajalehto et al., 1993; Nowak and Laajalehto, 2000; Nowak et al., 2000; Page and Hazell, 1989; Pillai et al., 1983; Sui et al., 2000). The XPS results are summarized in Table 2.

The XPS results of galena treated in deionised water show that the surface contains more of oxide species (CO_3^{2-} ; Pb-O; Pb-OH) and lower Pb-S compared to the sample conditioned in process water. In process water, the surface contains relatively high Pb-OH, a little lesser CO_3^{2-} and significantly lower Pb-O species. The marginally lower recoveries of galena in process water than in deionised water in Hallimond flotation is difficult to correlate directly with the surface species. However, the bench-scale flotation results (Table 3) correspond well with the XPS results with lower surface oxidation species in process water and better recoveries. The results also show the presence of calcium and carbonate species in process water indicating calcium carbonate precipitate layers on the surface.

In the presence of xanthate, there is a significant reduction of Pb-O species with a corresponding adsorption of xanthate species in deionised water while xanthate adsorption is less in process water in addition to significant amount of calcium and CO_3^{2-} species. Thus the surface calcium carbonate in process water is inhibiting the xanthate adsorption.

Table 2. XPS binding energies and atomic concentrations on galena surfaces at different conditions (DW and PW - deionised and process water)

Atomic concentration in % on PbS surfaces from XPS measurement												
Line	BE, eV	DW pH 10.5	PW pH10.5	DW 300ppm Ca	PW 300ppm Ca	DW 5.10 ⁻⁵ MKAX	PW 5.10 ⁻⁵ MKAX	DW 300CaKAX	PW 300CaKAX	DW 1000SO ₄ KAX	PW 1000SO ₄ KAX	Species
C 1s	285.0	8.8	17.99	12.87	14.06	12.76	18.22	14.28	14.45	14.46	16.79	C-(C,H)
	286.7	10.78	5.07	4.58	4.54	6.38	4.7	5.86	5.97	3.08	4.7	
	287.9			1.18	1.7	0.94	1.79	1.02	1.29	1.55	1.09	COOH
	289.3	8.85	7.26	7.14	8.85	5.78	8.25	6.12	4.88	4.58	4.59	CO ₃ ²⁻
O 1s	529.8	25.77	1.77	27.39	1.1	1.07	1.9	0.97	2.7	1.05	1.41	Pb-O ?
	531.7	17.17	28.88	15.87	41.7	28.09	36.97	31.12	30.22	32.78	30.09	Pb-OH, SO ₄ , etc
	533.0	1.7	12.31		3.17	15.38	4.02	9.37	9.76	9.92	7.9	organic, SiO ₂
Sb 3d 5/2	531.0		0.58	0.7	0.47	0.7	0.33	0.8	0.75	0.95	0.8	Sb ₂ O ₅
K 2p 3/2	293.6	0.54	0.56	0.49	0.46	0.58	0.37	0.55	0.44	0.68	0.66	
Pb 4f 7/2	137.8	2.27	5.84	6.47	4.67	6.78	5	8.19	7.9	7.43	7.13	PbS
	138.3	2.45	9.26	11.37	5.51	10.02	4.77	8.47	8.92	10.04	10.54	Pb(II)
	139.2	9.17										
	140.4	1.75										
	160.9											
S 2p 3/2	162.1	2.22	5.44	5.95	4.18	6.32	4.5	6.89	7.08	6.98	7.33	PbS S ²⁻
	163.2	0.84	1.78	1.29	5.51	1.29	0.94	1.71	1.69	1.5	1.98	poly-S? S ₂ ²⁻ ?
	160.9	5.47				0.78	0.24	0.39	0.67	0.94	0.84	KAX? poly-S?
		1.26									1.38	S(0)?
	168.3	0.95	2.38	1.86	1.62	2.25	1.38	1.98	2.64	2.91	2.76	SO ₄ ²⁻
Ca 2p 3/2	348.5	~1	~1	~1	6.51	~1	6.29	1.21	~1	~1	~1	
		99.99	99.12	97.16	104.05	99.12	99.67	98.93	99.36	98.85	99.99	

In deionised and process waters, a significant reduction of carbonate species bands seen in FTIR (Fig.9), is also observed in XPS results with a decrease in carbonate species when galena is treated with xanthate in the presence of calcium and sulphate independently.

Bench-scale flotation studies

Each flotation test was carried out thrice and the data presented in Table 3 is the average result of the three flotation tests. The two ores used in the bench scale studies were from Renström and Kristineberg mines; Renström ore grades 1% Pb, while Kristineberg ore grades 0.1% Pb. Flotation was carried out using tap and process water at 22, 11 and 4°C temperatures to cover the seasonal temperature changes in process plant from winter to spring and summer through autumn in the north of Sweden and simulated tap water at 22°C temperature. In Renström ore the recovery is more in process water than tap water and it decreases as temperature decreased, while there is no significant change in the grade. There is no clear difference in the results of Kristineberg ore besides at 22°C where the recovery is more in process water. Addition of Ca^{2+} and SO_4^{2-} ions singly and combined in the water has little influence on both the recovery and grade of lead.

Table 3: Recovery and grade of lead from bench scale flotation using both tap water and process water at 22, 10 and 5°C temperatures.

Pulp liquid (species added)	Renström ore		Kristineberg ore	
	Recovery, %	Grade, %	Recovery, %	Grade, %
22°C				
Ca ions	88	4.9	82	0.5
Sulphate ions	89	5.2	85	0.6
Ca+Sulphate ions	87	4.6	83	0.8
Tap water	83	5.6	81	0.5
Process water	89	5.0	86	0.5
11°C				
Tap water	75	4.5	83	0.6
Process water	75	4.1	77	0.8

4°C				
Tap water	76	3.7	82	0.6
Process water	74	5.5	85	0.9

Balance of calcium and sulphate species in pulp solution

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 4. The concentrations of Ca^{2+} and SO_4^{2-} ions in the tap water are 22.5 and 7.4 mg/l respectively while in process water are 128 and 63 mg/l respectively.

The lower concentration of calcium in solution after flotation presented in Table 4 indicate their adsorption on the mineral surfaces and/or precipitated as calcium carbonate as seen in zeta-potential, FTIR and XPS studies, and the excess of SO_4^{2-} must have been contributed from the dissolved sulphur composition of the mineral. Similar but not exact balance was observed with Kristineberg ore.

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.

Pulp liquid	Tap water		Process water	
	22 °C			
	SO ₄ ²⁻ mg/l	Ca ²⁺ mg/l	SO ₄ ²⁻ mg/l	Ca ²⁺ mg/l
Initial	373	472	455	456
Final	375	370	511	446
Difference	2	-102	56	-10
	11°C			
Initial	306	267	303	231
Final	281	155	364	200
Difference	-25	-112	61	-31
	4°C			
Initial	249	220	344	239
Final	224	121	366	239
Difference	-25	-99	21	0

The reduction in recovery as temperature decreases are most likely due to reduced kinetics 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 Ca^{2+} and other metal ions that enhances collector adsorption to KAX (an anionic collector) as seen in zeta-potential studies (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 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. Depleted calcium ions and excess sulphate ions in the pulp liquid after flotation closely corroborate adsorption of calcium on minerals as noticed in zeta-potential studies and as well caused by the calcium precipitation revealed in DRIFT and XPS 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.

CONCLUSIONS

Calcium ions reduce galena recovery in Hallimond flotation using process water while it has no significant effect in deionised water. Sulphate ions show overall reduction of galena recovery in both deionised and process waters.

The zeta-potential of galena is negative in the entire pH region, where the magnitude of negative charge is significantly higher in deionised water than in process water and water

containing calcium ions, illustrating the adsorption of calcium and other metal ions that exist in process water.

The DRIFT spectrum of galena pure sample showed that the surface is partially oxidised depicting surface hydroxyl-, sulfoxo and carbonate species bands, the composition of which is pH dependent. Xanthate adsorption on galena is reduced in process water but improved with the addition of calcium ions in the process water and sulphate ions in both waters. In the presence of calcium and sulphate ions, the decrease or disappearance of surface oxidised compounds could be due to the formation of soluble complexes with carbonate and lead surface species respectively.

Galena recoveries decrease as flotation temperature decreases in bench-scale test in tap water. Recoveries both increased and decreased when process water was used in bench-scale flotation. There is adsorption of calcium ions on the mineral and dissolution and release of sulphate ions in solution.

Based on the findings so far the process water has no detrimental effect on galena flotation, hence can be reused in the flotation of galena but with frequent assessment of the components in the water.

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