Effects of process water recycling during flotation of copper and cobalt oxidised ores from Luiswishi deposit in the Democratic Republic of Congo

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ABSTRACT

Laboratory flotation tests with copper–cobalt oxidized ore from the Luiswishi deposit in the Katanga province were done using process water being recycled to different degrees. Grade and recovery of copper and cobalt were followed by 10, 20 and 80% process to fresh water addition with the results from these conditions being compared to those without water recycling. When process water was recycled at 10%, 83.7% copper and 84.1% cobalt were recovered at the rougher stage bringing the cleaner stage to a concentrate with recovery of 53 and 60% for copper and cobalt, respectively. However, recycling process water, up to 20 and 80%, has reduced the recovery of copper in the final concentrate to 23 and 6%, respectively, and of cobalt to 46 and 27%, respectively. Monitoring of dissolved oxygen content, pulp pH and Es potential during flotation, coupled with thermodynamic estimation of the predominant chemical compounds in the system, has enabled to evaluate the effects on flotation from the undesirable compounds' formation during process water recycling. DRIFT spectroscopy was used to identify the nature of the chemical compounds formed on malachite and heterogenite surface during their sulphidisation in the presence of thiosulphate ions. Thiosulphate ions depending on their concentration could promote or hinder malachite and heterogenite flotation by inducing changes in pulp physicochemical parameters or by altering mineral surface properties.

Keywords: Oxide ores flotation; Process water recycling; Sulphidisation efficiency; Mineral surface alterations

1. Introduction

Mineral processing operations consume large amount of water, which in certain cases inevitably affects the availability of water resources in the concerned regions [1–5]. Flotation plant managers tend to encourage water saving technologies as shown in recent studies by Muzenda [2], Slatter et al. [6] and Liu et al. [7]. At the same time, recycling of process water in flotation has become an established practice

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at several concentrators, since many years [4,8–13]. During mineral ores processing by flotation, process water recycling can be realised either through internal or external schemes, both options being applicable in one and same concentrator [6,7,14]. Internal water recycling consists of reusing the process water from the dewatering units of the mill, such as concentrate thickeners and filters, while external water recycling implies reusing of both process water from the mill and the decanted water from the tailings ponds [2,4,6]. The recovered water can be either utilised inside the grinding circuits or added to the flotation feed water. Process water recycling can certainly reduce the impact of the mineral processing industry upon the consumption of water resources and local environment. It should be pointed out, however, that water recycling can, in some instances, induce hindering effects on flotation due to accumulation of suspended matter, dissolved salts as well as organic and inorganic compounds from the flotation reagents [4,7,10,11,15–19]. Xu et al. [10] postulated that process water could be successfully recycled after physical and chemical purification. In the same study, it is underlined that the existing advanced water treatment technologies could enable up to 75% water reuse during flotation of complex sulphide ores. Among the proposed solutions to flotation problems caused by water quality variation, Liu et al. [7] suggest strategies based on treatment of the recycled water on one hand and such focused on the improvement of flotation operation efficiency on the other. Conditioning of the recycled water with sodium salts containing phosphate anions, carbonates or silicates, for example, can help to mitigate the "hindering" effects from the impurities on metals recovery. This approach can also contribute to combating the problem of overconsumption of reagents, mostly collectors, increase the floatability of the valuable minerals, and reduce losses due to gangue activation [2,7,20]. Similar results could be achieved through modification in the sequence of reagents dosage or through the addition of specific reagents in the feed water, or through the approaches which could modify the surface properties of the minerals and improve their floatability [2,6,7]. In a recent paper, which was summarizing the research on water recycling effects on flotation, the importance of understanding the reasons for water quality fluctuation and the possibility for quantification of its adverse effects on process performance are highlighted [7]. Recycling process water in the flotation of copper oxide ores is virtually an unknown practice in the mineral rich province of Katanga in the Democratic Republic of Congo. Therefore, the present work aims to provide practically relevant information about the admissible level of process water recycling during the flotation of an oxidised copper–cobalt ore coming from an economically important deposit by focusing explicitly on the effects of thiosulphate ions' presence. Apart from that, an objective is to bring some light into some scarcely addressed issues like understanding the factors inhibiting flotation of copper–cobalt oxide ores.

2. Experimental materials and methods

2.1. Materials

2.1.1. Ore chemical and mineralogical characteristics

The studied ore originates from the Luiswishi deposit in the Katanga province of the Democratic Republic of Congo. Copper is present mainly as malachite, while the principal cobalt bearing mineral is heterogenite. Copper and cobalt are found as 3.15% and 0.90%, respectively. The XRD analysis indicates a gangue consisting mainly of chlorite, muscovite, mica, talc and quartz—Fig. 1.

The ROM ore was crushed by laboratory jaw and roll crushers and was screened using screen with 2 cm openings with recrushing of the oversized material. Further on, the ore was subjected to wet grinding for 8 min using a lab mill with 7 kg ball charge and speed of 123 rpm delivering a pulp of 75% passing 200 mesh.

2.1.2. Mono minerals

Mono mineral samples of malachite and heterogenite originating from the same deposit were used. These consist of handpicked mineralised phases cut by a geological hammer from large rock blocks of the ROM processed at the New Concentrator in Kipushi (NCK). The mean copper content in the malachite sample was found to be 42.7%, while that of cobalt in the heterogenite was −2.07%. The main mineralogical composition of the mono minerals is shown in Figs. 2 and 3.

The mono mineral samples were ground manually using an agate mortar before being dry screened to obtain granulometric fractions comprised between 40 and 63 µm.

2.2. Methods

2.2.1. Thermodynamic data calculation

The stability diagrams for the species likely to exist in the mineral systems or formed onto mineral surfaces in the presence of thiosulphate ions were drawn using the HSC Chemistry v.7 software.
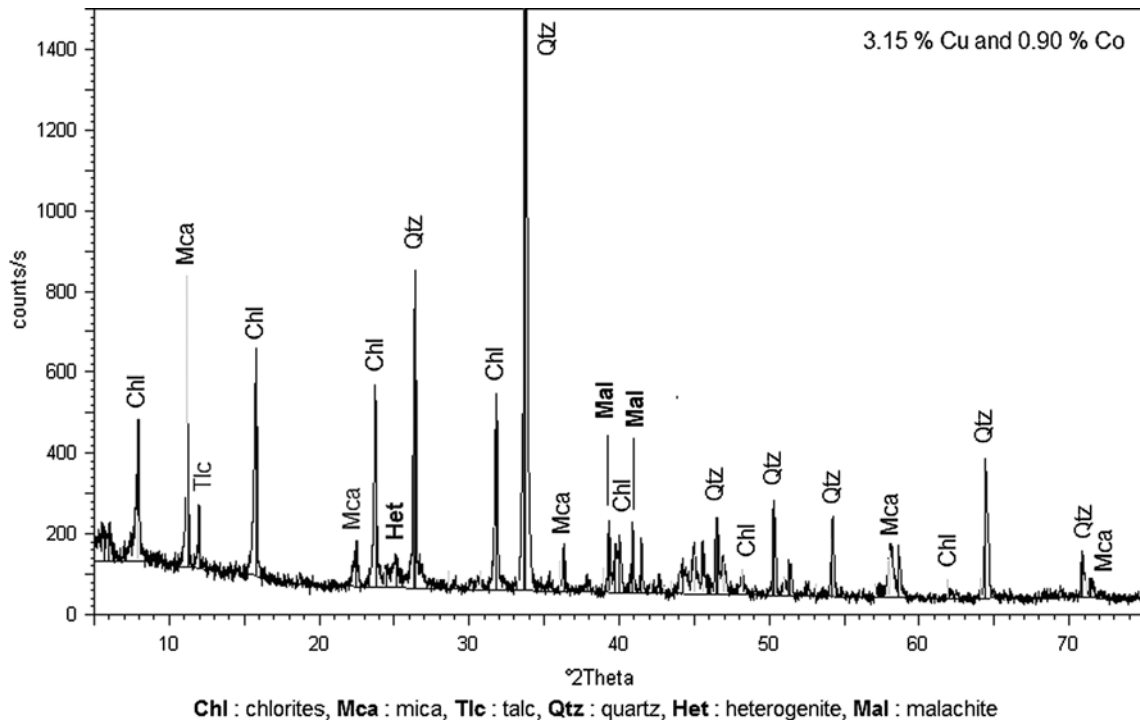
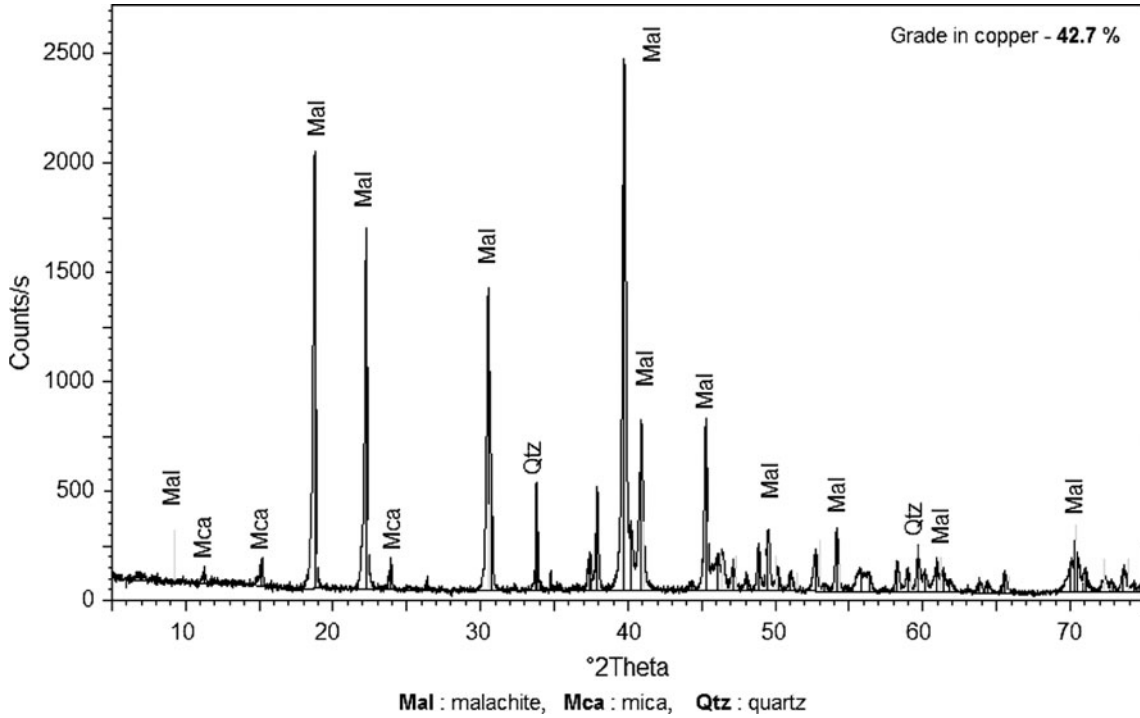Fig. 1. XRD pattern of the studied ore.
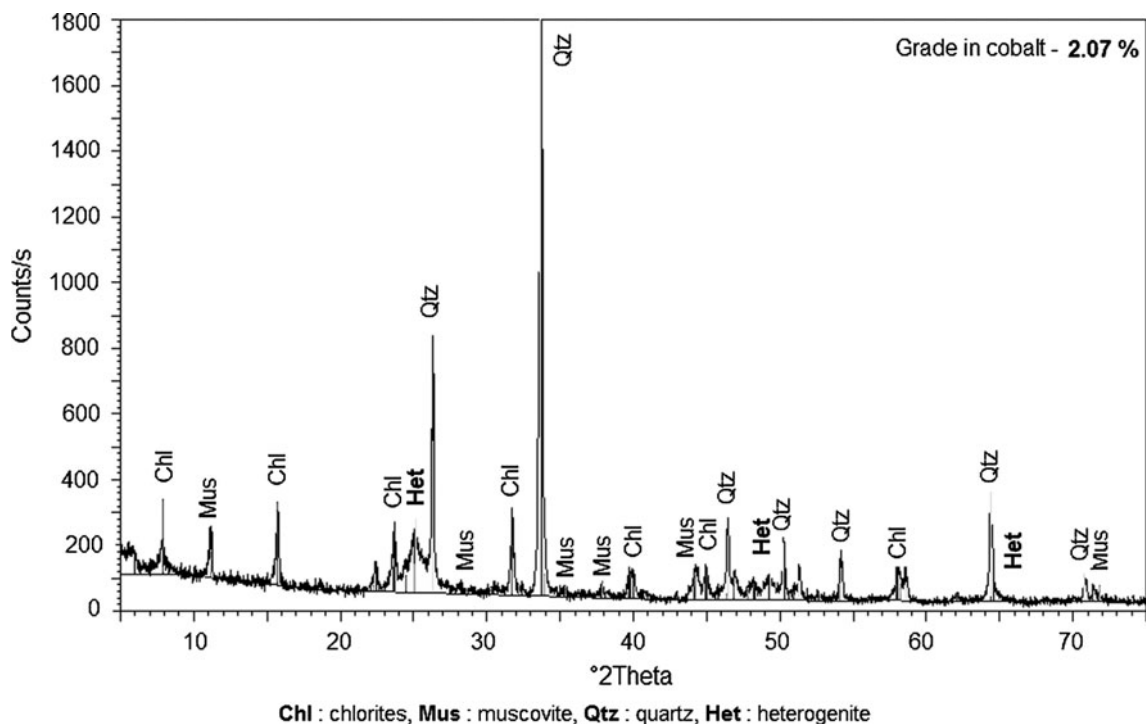

Fig. 2. XRD pattern of malachite.

Fig. 3. XRD pattern of heterogenite.

2.2.2. Analysis

Chemical analysis of the raw ore and flotation products together with mono minerals was done using an atomic absorption spectrophotometer (ANALYTIKJENA BU300 AAS), while the mineralogical one was through a PANALYTICAL PW-3710 diffractometer with Fe$K\alpha$ ($\lambda = 1.9373$ Å) radiation.

Process water was sampled both at the mill plant effluents' discharge point and recovered at the laboratory with volume of 300 mL for each case, which was then divided into two subsamples of 150 mL used for two separate analyses. An aliquot from the first subsample coming from the process water has been analysed for conductivity, pH and ion analysis by capillary electrophoresis (WATERS). An aliquot from the second subsample has been acidified with concentrated hydrochloric acid (36%) and assayed for heavy metals. For comparative purposes, the supernatant recovered during the lab tests after tailings settling has been subjected to the same analytical and manipulation procedure as the plant effluents. Water hardness and ionic composition were determined using RADIOMETER VIT90 and TIM845 automatic titrators.

DRIFT spectroscopic analysis (4,000–400 cm^{-1}) using a BRUKER EQUINOX 55 FTIR spectrometer was used to trace eventual changes in the surface properties of malachite when conditioned with NaHS and KAX in the presence of thiosulphate ions.

2.2.3. Reagents

Flotation reagents and their dosage levels were the same as those practiced in the plant, namely: sodium silicate (Na_2SiO_3) as gangue depressor, Dowfroth (D_{250}) as frother and an emulsion of gasoil (85% w/w) and tall oil (15% w/w) as a secondary collector. Ammonium sulphate ($(NH_4)_2SO_4$) was used as promoter, whereas citric acid ($C_6H_5O_7$) as pH regulator. The sulphidising reagent and the primary collector were, respectively, sodium hydrosulphide–NaHS and potassium amyl xanthate–KAX. The level of reagents dosage and their points of addition during flotation are depicted in Table 1.

Thiosulphate containing solution was obtained through dissolution of an analytical grade $Na_2S_2O_3 \cdot 5H_2O$ (Merck AG Darmstadt) in distilled water. The thus prepared stock solution was used either for doping the feed water in flotation or added in predetermined quantities to the aqueous suspensions of malachite and heterogenite mono minerals during their conditioning with NaHS and KAX.

Table 1
Reagent dosage rate with points of addition

| Stage	Reagents; mL (g/t)						
	NaSH-36%	KAX-10%	[a]D_{250}-100%	Na_2SiO_3-20%	[b]EGT	$C_6H_5O_7$-20%	$(NH_4)_2SO_4$-30%
Talc flotation	0-[0]	0-[0]	4-[60]	1.5-[300]	0-[0]	0-[0]	0-[0]
Rougher	18-[4,536]	8-[480]	3-[45]	0-[0]	0.15-[150]	4-[800]	1.3-[390]
1st Scavenger	3-[648]	2-[120]	4-[60]	0-[0]	0-[0]	0-[0]	0-[0]
Cleaner	8-[1,728]	2.5-[150]	0-[0]	0-[0]	0-[0]	0-[0]	0-[0]
1st Re-cleaner	4.5-[972]	0.5-[30]	0-[0]	0-[0]	0-[0]	0-[0]	0-[0]
2nd Re-cleaner	1-[216]	0.5-[30]	0-[0]	0-[0]	0-[0]	0-[0]	0-[0]
2nd Scavenger	0,7-[151]	0.5-[30]	0-[0]	0-[0]	0-[0]	0-[0]	0-[0]
Total consumption	35.2-[7,603]	14-[840]	11-[165]	1.5-[300]	0.15-[150]	4-[800]	1.3-[390]

[a]Expressed via number of drops.
[b]EGT: Emulsion of gasoil—85% and tall oil—15%.

2.2.4. Ore flotation

Flotation is a process for separating valuable minerals from finely ground ores in aqueous pulp based on the difference in their surface properties. The ROM ore used during the present study of process water recycling is treated at the NCK, where commercially grade copper and cobalt concentrates are obtained. Process water for the concentrator is sourced from two different sites: the Kipushi underground mine and Kamarenge Lake with a mixing ratio being varied around 0.78 in a view of maintaining the total hardness between 15 and 20°F. For the flotation lab-scale tests in the current study, two different process waters collected at the concentrator site were used: feed process water and process water sampled at the effluents' discharge point. In order to mimic closely the plant operation, the effect from the degree of process water recycling was studied using an exact lab scale replication of the flow sheet (Fig. 4) employed by the NCK.

Flotation was realized at natural pH using a Denver D12 pneumo-mechanical laboratory machine, with impeller speed kept at 1,000 rpm and flotation pulp with specific weight of 1,200 g/L, i.e. close to the one used at the plant. The rougher and first scavenger stages were done inside a 5-L cell to obtain a concentrate, which has been subsequently transferred inside a 2.5-L cell for cleaner, first recleaner, second recleaner and second scavenger stages. Industrial grade reagents and the plant feed water mixed with different proportions of recycled water were utilized throughout the experiments. To follow the effects from process water quality and thiosulphate ions' presence, 1 kg of ore has been subjected to wet grinding to prepare a pulp immediately transferred inside a flotation cell and conditioned for 3 min with Na_2SiO_3 (20%) at 200 g/t
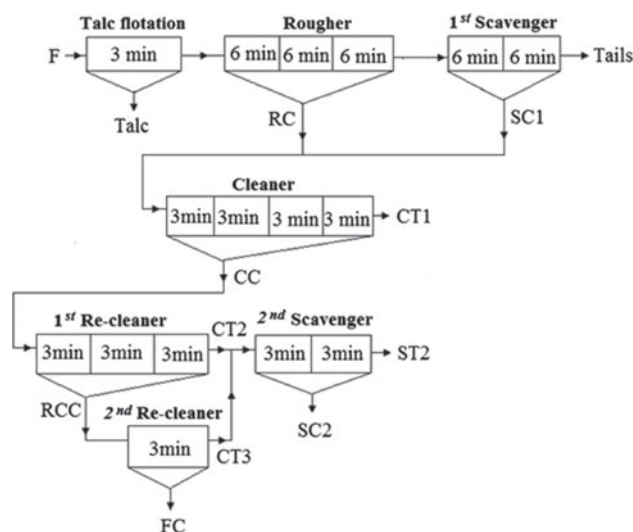
F: Feed
RC: Rougher concentrate
SC1: First scavenger concentrate added to RC
CC: Cleaner concentrate
CT1: Cleaner tails to be returned to first scavenger
RCC: First re-cleaner concentrate
CT2: First re-cleaner tails added to CT3
CT3: Second re-cleaner tails to be sent to second scavenger
FC: Final concentrate
SC2: Second scavenger concentrate to be sent to re-cleaner
ST2: Second scavenger tails to be returned to first scavenger

Fig. 4. Lab-scale replication of NCK flow sheet.

and D_{250} at 120 g/t, respectively, as slime depressor and frother. After talc flotation (3 min), the tailing fraction has been subjected to rougher-scavenger flotation (30 min) following the addition of sulphidising agent NaHS (18%) and KAX (5%) as collector, respectively, at 2,268 and 300 g/t. These two reagents were supplied in multistage addition mode as follows:

1,512–180 g/t, 216–30 g/t, 216–30 g/t, 216–30 g/t, 216–30 g/t and 112–30 g/t. The thiosulphate ions were supplied at dose levels of 1 and 2 g/L, which is higher than the concentration detected in the process water (about 100 mg/L). To supply thiosulphate ions at the selected dose levels during flotation of the ROM ore, 17.71 and 35.42 grams of analytical—grade $Na_2S_2O_3 \cdot 5H_2O$ have been dissolved in 8 L to be used as feed water. For the case when the content of thiosulphate ions in the industrial process water was supposed to be 100 mg/L, the amount added to the feed water has been increased 10- and 20-fold in order to easily trace their effects on the dissolved oxygen content of the pulp and on flotation performance.

2.2.5. Flotation pulp control

Es, pH and dissolved oxygen content were followed through a CONSORT C933 electrochemical analyser equipped with respective probes and controlled via D.I.S. software (v1.6.32), which enables data storage on a PC as shown in Fig. 5. For Es control, a Symphony combination Ag/Ag_2S electrode was used, pH was recorded with a SP10B general purpose electrode coupled with ATC (Pt 1000) electrode while dissolved oxygen content was registered by a SZ10T-ATC (Pt 1000) electrode. Es values present the electrochemical potential proportional to the amount of sulphide ions in solution, the latter being in equilibrium with hydrosulphide ions.

2.2.6. Mono minerals conditioning in the presence of thiosulphate ions

The effect of thiosulphate ions' presence on sulphidiser and collector action towards malachite and heterogenite has been investigated using 100 mL suspensions containing one-gram mono minerals (40–63 μm) stirred at 150 rpm during three minutes. Different aqueous suspensions were prepared: distilled water only, distilled water doped with 10 g/L thiosulphate ions and distilled water containing NaHS or KAX at predetermined concentrations.

The first series of tests were done with malachite or heterogenite immersed in distilled water in the presence or absence of thiosulphate ions. Each 30 s, an aliquot of 1 mL was withdrawn and the concentration of copper and cobalt released from minerals' dissolution was measured. In the second series of tests, the samples of malachite and heterogenite were subjected to sulphidisation during 3 min by adding 1 mL NaHS (0.05%), while following the Es potential. In the last
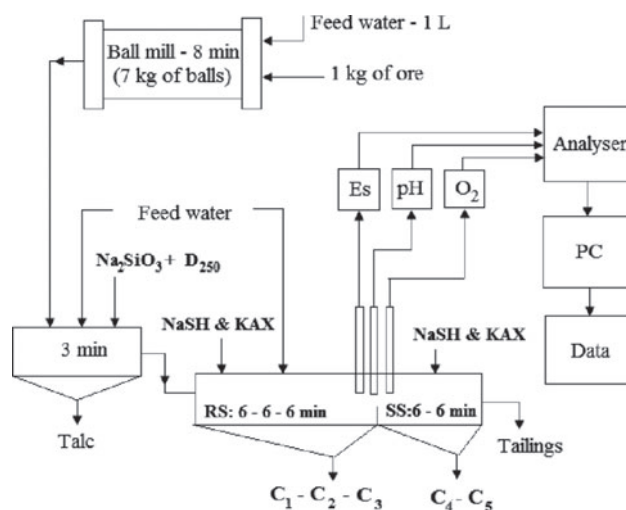
RS: Rougher stage (three concentrates skimmed at 6 min interval)
SS: Scavenger stage (two concentrates skimmed at 6 min interval)

Fig. 5. Reagent dosage and pulp survey sequence at rougher-scavenger stage.

series of tests, 1 g malachite (with granulometry below 32 μm) has been placed in 100 mL distilled water in the presence of thiosulphate ions (10 g/L) and subjected to 3 min sulphidisation in the presence of 1 mL NaHS (0.36%) followed by further agitation with 1 mL KAX (0.1%) for 3 min. After agitation elapsing, the suspended matter was allowed to settle and then filtered using an ashless filter paper (WHATMAN 589/2). The recovered solids from the reagent-conditioned malachite were dried at room temperature. Two milligrams from the thus conditioned particles were finally withdrawn and pressed with 150 mg KBr to produce pellets, which were delivered to DRIFT spectroscopy.

3. Results and discussion

3.1. Effect of process water recycling and composition of feed water on flotation

The grade and recovery of copper and cobalt at the various flotation stages of the flowsheet shown in Fig. 4 are presented in Table 2.

An immediate impression from the results is that recycling of process water adversely influences flotation performance. As the proportion of process to feed water increases, copper and cobalt grade and recovery in the concentrates from the cleaning stages are dropping, bringing significant part of copper and cobalt to report in flotation tailings. It can be therefore argued that the recycled water increases the solid matter

Table 2
Effect of process water recycling on Cu and Co flotation at different stages

Flotation stage	Process water addition to flotation feed water, %															
	0%				10%				20%				80%			
	Cu (%)		Co (%)		Cu (%)		Co (%)		Cu (%)		Co (%)		Cu (%)		Co (%)	
	Grade	Recovery	Grade	Recovery	Grade (%)	Recovery	Grade	Recovery	Grade	Recovery	Grade	Recovery	Grade	Recovery	Grade	Recovery
F	3.2		0.9		3.2		0.9		3.2		0.9		3.2		0.9	
Talc	2.7	1.8	0.8	2.0	2.6	2.0	0.8	2.0	2.9	5.0	0.8	5.1	2.9	4.2	0.8	3.8
RC + SC1	7.5	83.1	2.1	83.2	6.1	83.7	1.7	84.1	6.0	77.5	1.6	77.2	6.1	64.0	1.9	66.5
Tails	0.7	15.1	0.2	14.8	0.7	14.3	0.2	13.9	0.8	17.5	0.2	17.7	1.4	31.8	0.4	29.7
Tails + Talc	0.8	16.9	0.2	16.8	0.8	16.3	0.2	15.9	0.9	22.5	0.3	22.8	1.4	36.0	0.4	33.5
CC	16.3	74.8	4.5	75.4	12.4	73.5	3.8	72.6	11.9	59.4	3.5	65.1	7.3	24.4	4.3	47.9
CT1	1.6	8.3	0.4	7.7	1.8	10.2	0.6	11.5	2.3	18.2	0.4	12.2	5.5	39.6	0.8	18.6
RCC	26.4	69.2	7.8	72.0	25.4	67.0	7.1	69.9	20.3	50.5	6.4	59.2	8.9	9.8	9.7	35.6
SC2	3.2	5.6	0.5	3.5	3.3	6.5	0.4	2.7	3.6	8.9	0.6	5.8	6.5	14.6	1.6	12.3
ST2	14.5	16.4	2.6	10.8	13.7	14.5	2.8	10.1	19.8	27.6	2.6	13.6	6.9	3.5	5.7	9.9
FC	29.0	52.8	9.0	61.1	28.1	52.5	9.5	59.9	20.9	23.0	11.2	45.7	10.8	6.2	13.2	25.7

Notes: Bold values indicates the changes in the concentrate characteristics (grades and recoveries of Cu and Co) at different stages of the raw ore flotation due to variations in the feed water quality.

circulation inside the flotation circuit and does not allow efficient scavenging of tailings.

At 20% process to feed water ratio, the mean copper grade in the final concentrate is approaching 21% at 23% recovery. At the same conditions, cobalt reaches a grade of 11% and a recovery of 46%. It could be seen that high proportions of copper (18%) and cobalt (12%) are retained in the first cleaner tailings. The total copper and cobalt recoveries achieved at the rougher stage remain around 77% in contrast to 83–84% when process water was not recycled or when was recycled at 10% only. When process water was recycled to as little as 10%, one could note an increased copper and cobalt recovery both at the rougher (83.7% Cu and 84.1% Co) and at the cleaner stages (53% Cu and 60% Co) yielding a final concentrate with 28.1% copper and 9.5% cobalt grades—Table 2.

When the level of process to feed water ratio was increased to 80%, the recovery of copper and cobalt at the rougher stage has barely reached 64 and 66.5%, respectively. Under these conditions, the scavenging of the tailings is strongly influenced by 32% Cu and 30% Co being still lost. It could be therefore argued that recycling process water at 80% could drastically reduce the total recovery and grade of the concentrate at the cleaner stage. As stated by Slatter et al. [6], cleaner flotation stages are more prone to disturbances than the rougher ones when process water is recycled. The results in Table 2 are suggesting undoubtedly that copper grade and recoveries in the concentrate are dropping significantly with increased water recycling. Cobalt seems to be less affected owing to the fact that its grade in the concentrate has improved, however on the expense of recovery decrease. The worsening in metallurgical results for the studied ore when more than 10% process water is recycled could be provoked to a large extent by reagents' degradation and by loss in efficiency leading finally to reduced sulphidisation and collecting power and reagent overconsumption. The trend of Es potential vs. time shown in Fig. 6 reveals a rapid raise in Es during the first six minutes following NaHS and KAX introduction in the pulp, a phenomenon mostly due to increased consumption of sulphide and hydrosulphide ions when process water originating from plant effluent discharge stream was recycled. About 2 min after reagents addition, Es has risen from −408 to −292 mV before finally reaching −279 mV within the time frame, coinciding well with the completion of the primary rougher stage. However, when the pulp was prepared with the plant feed water, within the same time interval, the Es potential has varied from −791 up to −428 mV. These significant variations undergone by the Es potential are in relationship with the increased consumption of sulphide and hydrosulphide ions during sulphidisation of the valuable minerals and with the oxidation phenomena accompanying pulp aeration. Moreover, the Es potential has continued to rise until reaching about −280 mV at the end of flotation even when plant feed water is used without addition of recycled water.

Similar to Es, pulp pH follows significant variations in the course of flotation—Fig. 7. Contrary to the Es trend, however, one could observe a more pronounced pH shift for the process water than for the fresh one. According to studies done by Gush [21], the
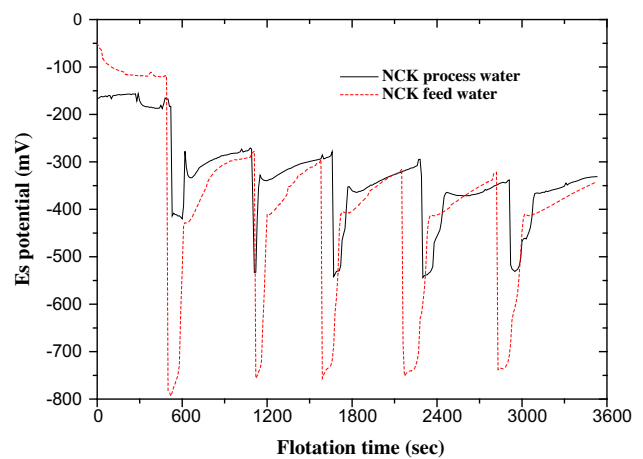

Fig. 6. Evolution of Es with time (dotted line–"fresh" feed water, continuous line–process water sampled at effluent discharge point).
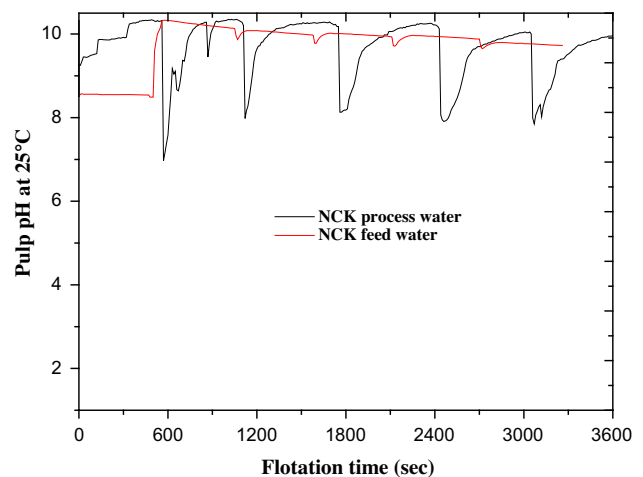

Fig. 7. Evolution of pulp pH with time (dotted line–"fresh" feed water, continuous line process water sampled at effluent discharge point).

Table 3
Grades and recoveries of copper and cobalt in the rougher concentrate vs. time and the feed water type

Time	NCK feed water					NCK process water				
		Grade (%)		Cumulative Recovery (%)			Grade (%)		Cumulative recovery (%)	
(min)	Yield (%)	Cu	Co	Cu	Co	Yield (%)	Cu	Co	Cu	Co
6	9.0	16.41	4.97	47.27	46.39	10.8	6.06	2.3	23.69	30.43
12	17.2	11.73	3.45	64.57	61.61	20.6	6.03	2.14	44.98	53.96
18	22.0	9.9	2.95	69.72	67.38	29.4	6.09	1.88	64.85	67.76
24	25.8	8.79	2.66	72.62	71.2	32.6	5.81	1.65	68.62	71.41
30	29.0	8.04	2.47	74.67	74.35	37.0	5.41	1.65	72.44	74.91

Table 4
Physicochemical characteristics of NCK flotation feed water, process water and "lab" process water

Parameter	Feed water[a]	Process water[b]	Lab process water[c]
pH	**6.93**	**7.89**	**7.42**
Langelier index	−0.86	0.16	−0.81
Water character	Aggressive	Scaling	Aggressive
Electric conductivity at 25℃ (μS/cm)	513.0	2,650	901.8
Total hardness (℉)	21.90	12.1	2.7
Permanent hardness (℉)	10.10	**0.0**	**0.0**
Temporary hardness (℉)	11.80	12.1	2.7
Ca^{2+} (mg/L)	50.06	22.0	9.5
Mg^{2+} (mg/L)	22.89	16.0	0.79
Na^+ (mg/L)	26.97	590.3	188.09

[a]NCK feed water sampled at mill site.
[b]NCK process water sampled at point of flotation effluent discharge at mill site (after seven days of settling).
[c]Supernatant recovered from the tailings during lab scale tests (with 98 mg/L $S_2O_3^{2-}$).

Table 5
Chemical composition of NCK flotation feed water, process water and "lab" process water
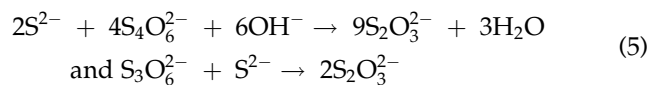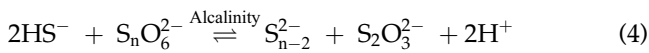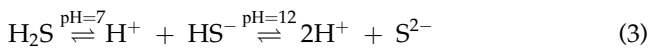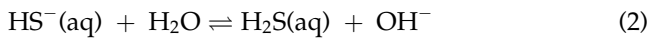
Compound	Feed water[a]	Process water[b]	Lab process water[c]
Calcium bicarbonate (mg/L)	21.89	–	–
Calcium nitrate (mg/L)	–	–	4.10
Calcium phosphate de (mg/L)	–	–	1.55
Calcium sulphate (mg/L)	151.80	74.88	26.55
Magnesium bicarbonate (mg/L)	137.58	–	–
Magnesium sulphate (mg/L)	–	78.85	3.61
Potassium chloride (mg/L)	6.71	60.39	–
Sodium bicarbonate (mg/L)	17.64	636.03	389.85
Sodium chloride (mg/L)	56.12	201.10	38.58
Sodium sulphate (mg/L)	–	1041.30	71.03

[a]NCK feed water sampled at mill site.
[b]NCK process water sampled at mill site from flotation effluents after seven days settling.
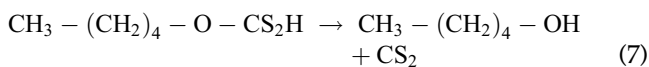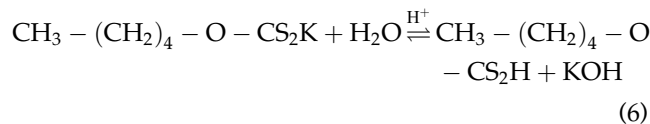[c]Supernatant recovered from freshly obtained tailings during flotation lab tests.

observed pH fluctuations could decrease drastically the recovery of the minerals due to adverse effects on reagents' stability bringing concomitant overconsumption. NaHS according to reaction 1 is easily water-soluble generating dissolved hydrosulphide species stable in the pH range of 7–12 as

demonstrated through reactions 2 and 3. The observed increase in Fig. 7 in pulp acidity when process water was recycled could induce conversion of the hydrosulphide species into hydrogen sulphide [21]. As a result, sulphide and hydrosulphide ions are consumed and pulp Es increases, an assumption supported by the results is shown in Fig. 6. The increased consumption of sulphidising agent indicated by the changes in pulp Es might also be due to the reactions of sulphide and hydrosulphide ions with the frequently encountered flotation process water polythionates, similar to the reactions 4 and 5 below [22]:

$$NaHS(s) \rightarrow Na^+(aq) + HS^-(aq) \tag{1}$$

$$HS^-(aq) + H_2O \rightleftharpoons H_2S(aq) + OH^- \tag{2}$$

$$H_2S \overset{pH=7}{\rightleftharpoons} H^+ + HS^- \overset{pH=12}{\rightleftharpoons} 2H^+ + S^{2-} \tag{3}$$

$$2HS^- + S_nO_6^{2-} \overset{Alcalinity}{\rightleftharpoons} S_{n-2}^{2-} + S_2O_3^{2-} + 2H^+ \tag{4}$$

$$2S^{2-} + 4S_4O_6^{2-} + 6OH^- \rightarrow 9S_2O_3^{2-} + 3H_2O$$
$$\text{and } S_3O_6^{2-} + S^{2-} \rightarrow 2S_2O_3^{2-} \tag{5}$$

Reactions 4 and 5 could be regarded as the alkalinity consuming ones, an assumption supported by the drop in pH is documented in Fig. 7. As suggested by Bulatovic [23], the increase in pulp acidity has a negative effect on the recovery of oxide minerals when xanthate-type collectors are used. This is because depletion of sulphide and hydrosulphide species in the aqueous phase is provoked, which subsequently affects the sulphidisation process. According to Bulatovic [23], the sulphidisation of malachite occurs at a relative constant rate within pH between 8 and 11. Moreover, an acidic environment hinders xanthate-collecting action by facilitating its chemical decomposition [17] as per reactions 6 and 7:

$$CH_3 - (CH_2)_4 - O - CS_2K + H_2O \overset{H^+}{\rightleftharpoons} CH_3 - (CH_2)_4 - O - CS_2H + KOH \tag{6}$$

$$CH_3 - (CH_2)_4 - O - CS_2H \rightarrow CH_3 - (CH_2)_4 - OH + CS_2 \tag{7}$$

The observed worsening of flotation results could be explained well from the above-mentioned observations

and also by having in mind that malachite usually floats very fast [24]. They also corroborate with the reduced efficiency of collector and sulphidiser provoked by the variation in water quality. To support this statement, a new series of tests have been done using plant feed water or process water only with the results been displayed in Table 3.

As could be seen from Table 3, the feed water quality has a strong influence upon the metallurgical results. When NCK process water was used, a significant drop in the recovery of copper and cobalt in the first 12 minutes of the rougher flotation was observed. When following copper and cobalt grade and recovery in the various concentrate fractions skimmed at different time intervals, one can notice that using process water affects to a less extent cobalt flotation than the copper one. As could be expected and as seen in Tables 4 and 5, the quality and the physicochemical characteristics of feed and process waters differ quite significantly.

Table 4 indicates that the fresh feed water used in flotation plant is slightly conductive with neutral pH and low permanent hardness. On the other side, mill process water when compared to the feed one is scaling, slightly alkaline, mild and conductive mainly due to the presence of sodium salts. The chemical composition of both waters shown in Table 5 is explicitly showing that the process water of our focus contains
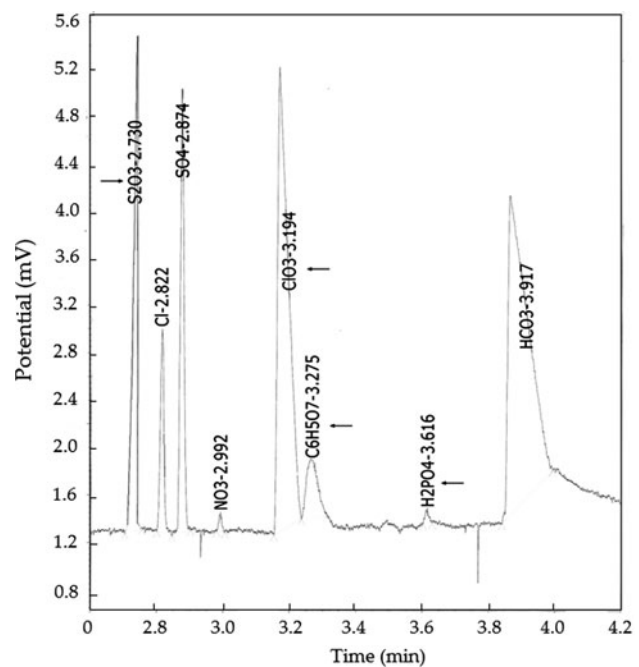

Fig. 8. Ionic composition of "lab" process water.

Table 6
Recovery of copper and cobalt at rougher flotation at different concentrations of thiosulphate and NaHS rates

Time (min)	0 mg/L $S_2O_3^{2-}$ 2,268 g/t NaSH		1 g/L $S_2O_3^{2-}$ 2,268 g/t NaSH		2 g/L $S_2O_3^{2-}$ 2,268 g/t NaSH		2 g/L $S_2O_3^{2-}$ 1,134 g/t NaSH	
	Cu (%)	Co (%)	Cu (%)	Co (%)	Cu (%)	Co (%)	Cu (%)	Co (%)
6	46.39	45.14	36.64	43.22	18.97	15.33	17.86	15.90
12	60.14	58.05	58.76	57.88	29.27	24.73	30.87	29.30
18	70.30	64.86	**72.14**	**67.32**	35.32	30.43	**41.75**	**39.28**
24	78.02	73.74	**78.30**	**76.90**	41.81	36.71	**47.83**	**44.86**
30	81.63	78.27	80.75	**79.92**	47.87	42.79	**54.24**	**51.21**

contaminants commonly met in flotation effluents [2]. It could be thus argued, that the poor flotation performance arises from the variations in water quality caused by the presence of contaminants altering the pulp chemical composition [2,7].

In contrast to the mill process water where calcium and magnesium are detected only in sulphate form, the NCK fresh feed water contains magnesium in bicarbonate form only. It contains nevertheless calcium both in bicarbonate and sulphate forms. The high electrical conductivity of the mill process water corroborates well in the presence of sodium and potassium in sulphate, chloride and bicarbonate forms. It should be noted, however, that the majority of the salts observed in flotation process waters are present also at low concentrations in the "simulated process" water used during the laboratory tests. However, regardless the existing similarities between both tested waters in terms of chemical characteristics, it could be assumed that the industrial process water has undergone certain chemical alterations during its conservation. This is supported by the fact that the capillary ion chromatography has indicated a presence of thiosulphates and citrates in the lab simulated process water—Fig. 8. Thiosulphate ions are usually formed inside flotation pulps following xanthate and hydrosulphide ions' oxidation by air or via oxidation reactions taking place at mineral surfaces [6,22,23]. The citrate ions from their side could come from decomposition of residual reagents.

It could be assumed that the thiosulphate ions detected in the recycled water and seen in Fig. 8 do interfere during flotation inducing drop in metallurgical results. To support this statement, thiosulphate ions were added to the "fresh" water and recovery of copper and cobalt was followed by the results from this trial, which has been displayed in Table 6.

The results depicted in Table 6 are showing that the presence of thiosulphate ions in the chosen concentration range could exercise either positive or negative impact on copper and cobalt recovery. Slightly better recovery of cobalt has been documented when thiosulphate ions have been added at 1 g/L in comparison when being absent. The recovery of copper has been almost identical for both the cases approaching 80% after 30 min flotation.

3.2. Effect of thiosulphate ions on mono minerals' dissolution and sulphidisation

The promoting effect of thiosulphate ions when supplied at 1 g/L depicted from the results in Table 6 could be attributed at first instance to the formation of Cu_2S/CuS compounds that facilitate collector adsorption. It could also be assumed that complexation and reduction of copper ions dissolved from the malachite and reporting in the aqueous phase take place, thus lowering the reagents overconsumption. A theoretical verification of this hypothesis could be drawn from the Pourbaix diagrams shown in Figs. 9 and 10, which are constructed using the concentrations of copper and cobalt measured at equilibrium during malachite leaching tests in the presence of thiosulphate ions.

The zone of thiosulphates to sulphates' conversion and the possibilities of formation of Cu_2S/CuS and Cu_2O on the malachite surface could be estimated from the Pourbaix diagrams in Fig. 9(a) and (b). It could be seen that Cu_2S/CuS and Cu_2O are likely to be stable along the existence of $Cu(OH)_2$. As far as heterogenite is concerned, it is expected that at equilibrium, cobalt ions will be present mainly as Co_3O_4 and $CoSO_4$. In the meantime, thiosulphate ions will be subjected to oxidation to polythionates and sulphates as shown in Fig. 10(a) and (b). In the presence of thiosulphate ions, Co_3O_4 undergoes dissolution through reduction of cobaltic to cobalteous ions. Based on the Pourbaix diagrams, we could derive the dissolution patterns of heterogenite starting from the release of copper and cobalt ions in the aqueous phase followed
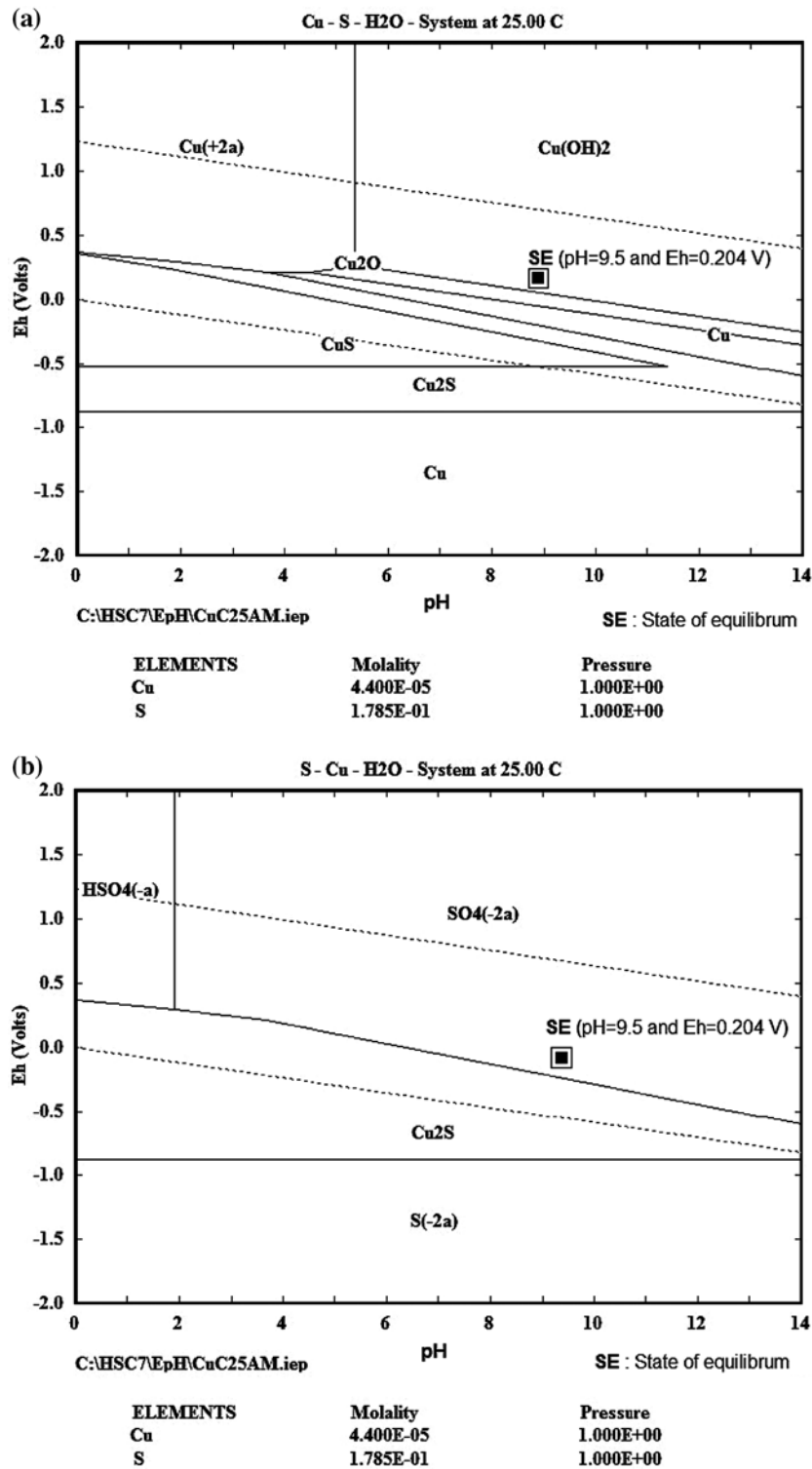
Fig. 9. Eh-pH diagram for the system Cu-S(thiosulphate)-H_2O (a) and S-Cu-H_2O (b) at 25℃ for malachite.

by their reduction/complexation by the thiosulphate ions as well as the formation of sulphides from the minerals being present [25,26]. The improved recovery of copper and cobalt in the presence of thiosulphate ions at 1 g/L might be also due to the reducing conditions created in the pulp from the increased dissolved
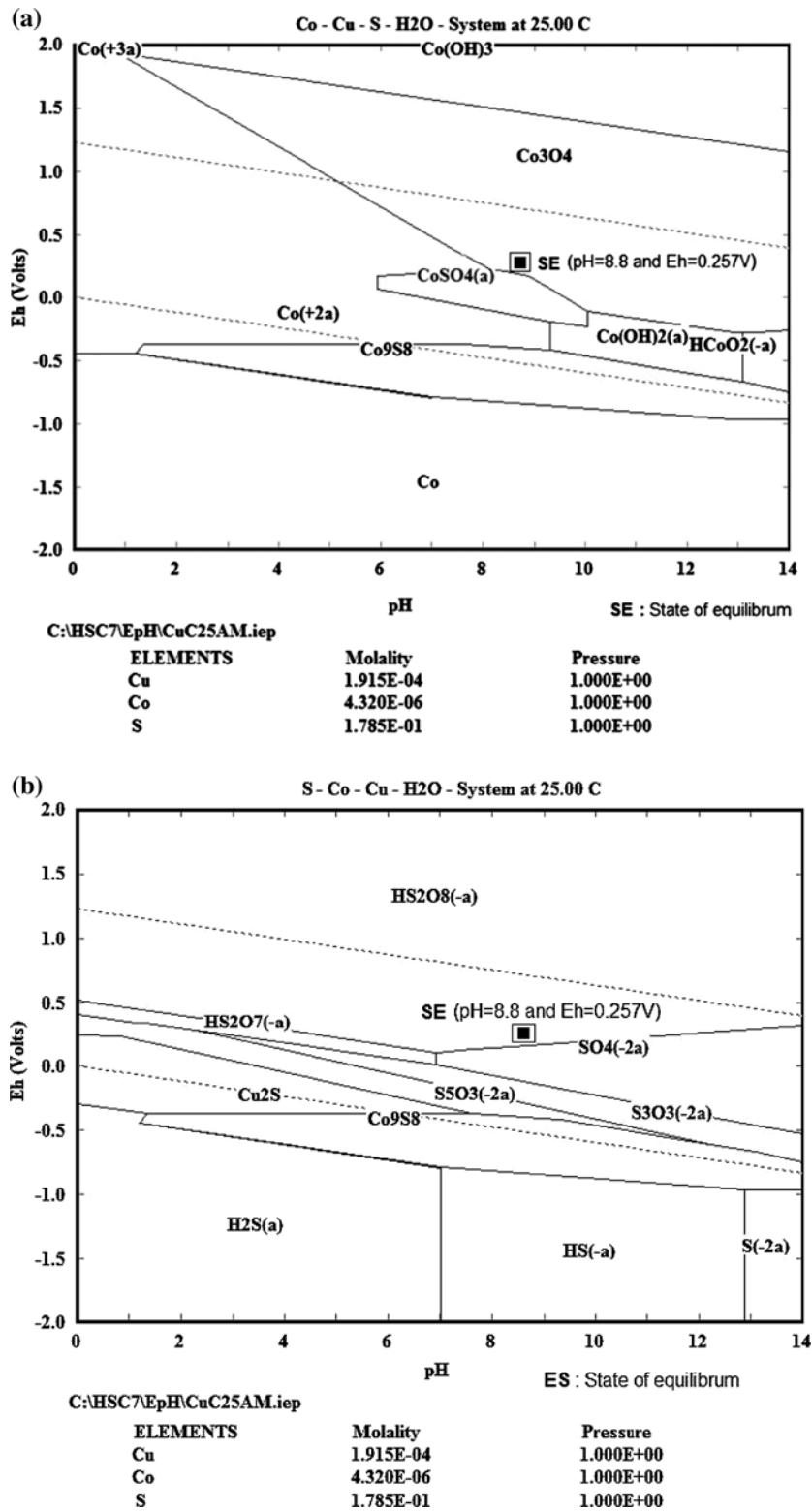
Fig. 10. Eh-pH diagram for the system Co-Cu-S(thiosulphate)-H$_2$O (a) and S-(Co-Cu)-H$_2$O (b) at 25°C for heterogenite.
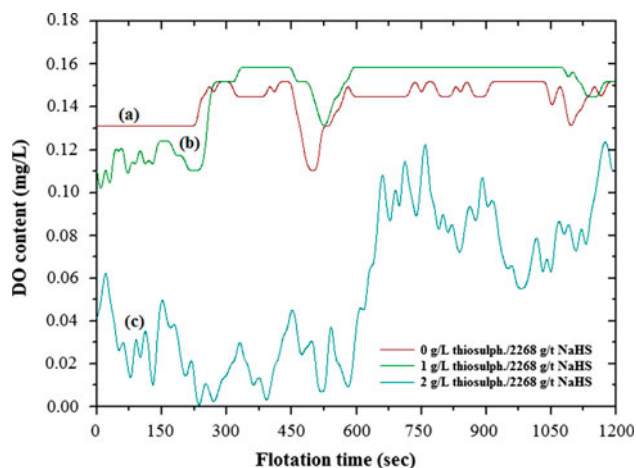
Fig. 11. Effect of thiosulphate concentration at constant sulphidizer dose on dissolved oxygen content: (a) is linked to the red curve (0 g/L); (b) to the green one (1 g/L); (c) to the blue curve (2 g/L).

oxygen consumption—Fig.11 curve b. Moreover, curve "c" implies that the decrease in dissolved oxygen content during the first 200 s and resulting from thiosulphates to sulphates' oxidation could enhance sulphidiser and collector availability and their efficiency [23,27,28].

Doubling the doses of thiosulphate ions, however, is leading to poor flotation results, dropping the recoveries to about 48% for copper and 43% for cobalt—Table 6, figures in bold. The data about dissolved oxygen content shown in Fig. 11 infer that the drop in copper and cobalt recovery could be due to the highly reducing conditions created inside the pulp and to deficiency in dissolved oxygen. The drop in dissolved oxygen content could be provoked by the oxidation of thiosulphate ions and could create conditions stimulating an excessive presence of sulphidiser and consequently, an environment lowering collector adsorption [23,29,30]. As can be seen in Table 7, the infrared bands associated with stretching of C–H bonds in the methyl groups belonging to the collector hydrocarbon chain (2,960, 2,930 and 2,873 cm^{-1}) do not appear inside the spectra, hence xanthate fails to adsorb.

Similarly, one does not observe the stretching characteristic signatures of xanthate molecules (1,182 cm^{-1}) inside the spectral bands corresponding to the C=S bonds. Additionally, the Es trend registered during the sulphidisation of malachite and heterogenite and reaching values below—400 mV in the presence of thiosulphates, Figs. 12a and 12b, indicates a slowdown of NaHS consumption leading possibly to an increased amount of available hydrosulphide and sulphide species in solution. When present

in high concentrations, these ions affect negatively copper and cobalt flotation since they compete with the xanthate ions for adsorption sites on mineral surface [21,29]. Their adsorption on sulphidised minerals can render the surface charge negative resulting in xanthate anions' repelling [30].

The failure of collector to adsorb onto mineral surfaces supports the possibility of hydrophilic species formation and mineral surfaces' alterations, hypothesis which could be derived as well from the Pourbaix diagrams—Figs. 9 and 10. The existence of hydrophilic coatings onto mineral surfaces is confirmed by the changes in the shape of infrared bands, by the shifts observed in their wave numbers and by the decrease in the band intensities, when malachite is conditioned in the presence of thiosulphate ions—Table 7. Moreover, in the spectral region reserved to the bands associated with the functional groups (4,000–1,300 cm^{-1}), one could trace evidences of malachite dissolution. This assumption is supported by the marked decrease in the areas beneath the infrared bands associated with stretching vibrations of O–H bonds in the hydroxylated complexes. Dissolution of malachite is noticeable also through the disappearance of overtones of the infrared bands related to vibrations of C–O bonds in the carbonate groups. The decrease in infrared bands' intensity in the absorbance patterns throughout the whole spectrum, shown in Table 7, reveals a deficiency in malachite hydrophobisation resulting in an increased hydration due to formation of hydrogen bond bridges [31] on the O–H bonds. This is confirmed by the shift towards lower wave numbers (from 3,324 to 3,321 cm^{-1}) undergone by the infrared bands. The trend observed in the characteristic bands of malachite and the appearance of new bands (1,655, 1,161, 1,119[$v3$], 990[$v1$], 684 and 615 cm^{-1}) in the 1,300–400 cm^{-1} spectroscopic fingerprint region reveal also alterations in its surface properties, namely through malachite dissolution and formation of new chemical species like thiosalts. The latter presence could be deduced from the appearance of bands related to stretching and bending vibration characteristics of S–O bonds [32]. These species could be also colloidal precipitates from copper ions' complexation at the surface of malachite or reoxidation products from an already sulphidised mineral. It is known that covellite (CuS) and chalcosite (Cu$_2$S) could be easily oxidised by air during sample drying or when soaked in aqueous phase as per the reactions below [33]:

$$S_2O_3^{2-} + \frac{3}{2}O_2 \rightarrow 2SO_3^{2-} \tag{8}$$

Table 7
IR spectra of malachite conditioned with NaHS and KAX in the presence of thiosulphate ions

Spectral regions		Malachite	Absorbance	KAX	Malachite conditioned with NaHS and KAX, 10 g/L $S_2O_3^{2-}$	Absorbance
Functional groups region (4,000–1,300 cm^{-1})	Hydroxylated complexes (4,000–3,000 cm^{-1})	3,880	0.04		3,853	0.136
					3,614	0.189
		3,416	0.861			
		3,408	0.876		3,408 (a,c)	0.368
				3,377		
		3,323	**0.879**		[4]3,32**1** (a,c)	0.362
				3,187		
	Carbonates bands' overtones (3,000–1,600 cm^{-1})			[1]2,960	No band	
				[1]2,930	No band	
		2,908	0.332	[1]2,872	No band	
		2,806	0.280		Vanishing of the band	
		2,684	0.220		Vanishing of the band	
		1802	0.347		1805	0.147
					1,686	**0.167**
					1,654	**0.166**
		1,502	0.960		[4]1,500 (a,c)	0.425
				1,466		
		1,429	0.908		[4]1,4**25** (a,c)	0.387
		1,389	0.918	1,387	[5]1,3**94** (a,c)	0.446
				1,356		
Spectroscopic fingerprint region (1,300–400 cm^{-1})	Carbonates and oxides			1,296		
				[2]1,260		
				[2]1,242		
				[3]1,166	**1,161**	**0.317**
				1,145		
				1,114	**1,119**	**0.349**
		1,097	0.845		1,097 (a,c)	0.374
		1,049	1.000		1,049 (a,c)	0.467
				1,010	**990** (sh)	**0.277**
		878	0.916		[5]881 (a,b,c)	0.390
		823	0.913		[5]824 (sp,a,c)	0.393
		776	0.796		777 (a,c)	0.290
		750	0.943		750 (a,c)	0.351
		714	0.812		714 (a,c)	0.285
					685	**0.279**
					615	**0.285**

Notes: 1—IR bands associated to C–H bonds vibrations in the methyl groups of KAX; 2—IR band associated to vibrations of bonds (C=S) in dixanthogena; 3—IR band associated to vibrations of bonds (C–O) in xanthate; 4—Red shift or shift towards the lowest frequencies (wave numbers); 5—Violet shift or shift towards the highest frequencies (wave numbers); (a)—Decrease in the band area; (b)—Broadening or bond weakening; (c)—Increase in band intensity; (sh)—Shoulder; (sp)—Sharp; Figures in bold—New infrared bands.

$$2SO_3^{2-} + 2S^{\circ} \rightarrow 2S_2O_3^{2-} \qquad (9)$$

It should be nevertheless noted, that the recovery of copper and cobalt has been slightly improved when thiosulphate ions were added to the feed water at 2 g/L, and when the concentration of sulphidiser has been halved. As can be seen from Table 6, more than

54% of copper and 51% of cobalt were recovered in the concentrate at the rougher stage. Halving the amount of hydrosulphide ions has led to increase in dissolved oxygen content—Fig. 11, thus creating a more favourable environment for collector adsorption [21,23,29]. It could therefore be assumed that the depletion of dissolved oxygen content observed in the pulp during flotation of the studied ore is both due to
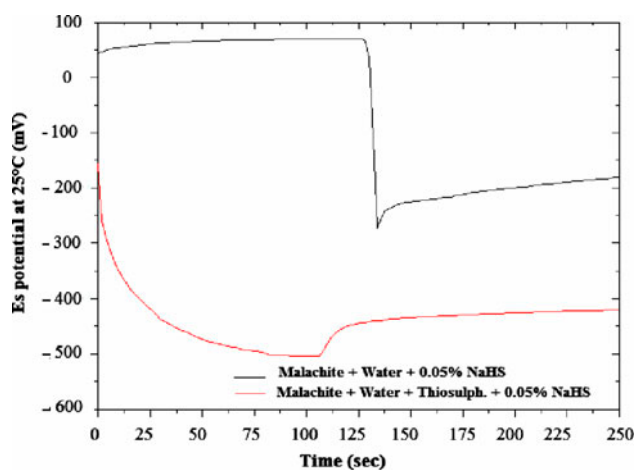
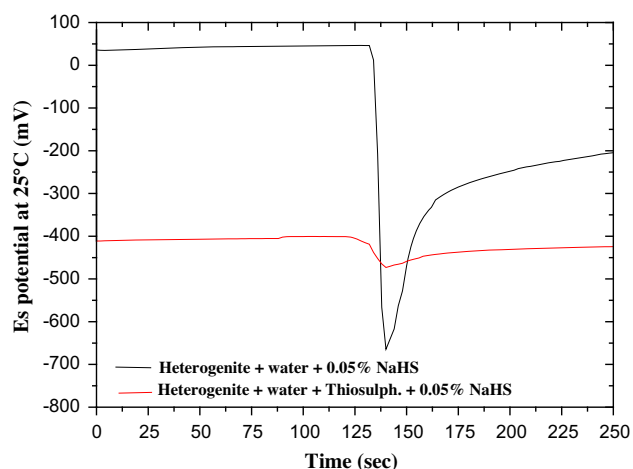Fig. 12a. Evolution of Es with time during sulphidisation of malachite.

Fig. 12b. Evolution of Es with time during sulphidisation of heterogenite.

sulphidiser oxidation phenomena and the scavenging action of the thiosulphate ions when present in the feed water [21].

4. Conclusions

Process water recycling induces marked changes in water quality, which may result in variation of metallurgical results. Recycling process to feed water under 10% does not influence negatively the flotation of Luiswishi copper and cobalt oxidised ore. Recycling of process water to more than 10% is inducing irreversible alterations in the pulp chemical characteristics. In such a way, physicochemical parameters such as Es, pH and dissolved oxygen content are affected

leading to poor flotation of cobalt and copper minerals and to gangue minerals reporting into the concentrate. The worsening in flotation could be mainly attributed to disturbances in the sulphidisation stage and to the losses in collector efficiency. Additionally, the drop in pulp pH promotes reagents' degradation and overconsumption. When thiosulphate ions are present in concentration ranges 1 to 2 g/L, the above-mentioned disturbances are mainly due to depletion of dissolved oxygen content of the pulp and to the reduced consumption of sulphidiser, bringing an excess of hydrosulphide ions and consequently a reduced collector adsorption. The worsening in the flotation results is also due to alterations in minerals' surfaces via dissolution and formation of hydrophilic species, traced through appearance of new infrared bands and through changes in intensity, shape and wave number in the spectral fingerprint of malachite. Thiosulphate ions present at different concentrations in the feed water could either improve or hinder the flotation of the minerals under study. The obtained results are strongly suggesting that every attempt for process water recycling has to be realized with careful consideration of the effects, which the chemical characteristics of the recycled water might induce on flotation.

References

[1] J.C. Jennett, B.G. Wixson, Geochemistry, mining and the environment, Miner. Environ. 5 (2005) 36–53.
[2] E. Muzenda, An investigation into effect of water quality on flotation performance, World Acad. Sci. Eng. Technol. 69 (2010) 237–241.
[3] T.E. Norgate, R.R. Lovel, Water use in metal production: A life cycle perspective, Report DMR-2505, CSIRO Minerals, September (2004) 15–16.
[4] S.R. Rao, J.A. Finch, A review of water re-use in flotation, Miner. Eng. 2 (1989) 65–85.
[5] H. Wotruba, Water, Energy and Masses, Notes from the workshop "Sustainability in Mineral Processing", International Mineral Processing Congress, Beijing, September, 2008, pp. 1–2.
[6] K.A. Slatter, N.D. Plint, M. Cole, V. Dilsook, D. De Vaux, N. Palm, B. Oostendorp, Water management in Anglo Platinum process operations: Effects of water

quality on process operations, Abstracts of the International Mine Water Conference organized by Cilla Taylor Conferences, 19th—23rd October 2009, Pretoria (South Africa), 46–55.

[7] W. Liu, C.J. Moran, S. Vink, A review of the effect of water quality on flotation, Miner. Eng. 53 (2013) 91–100.

[8] M.A. Bosse, H. Schneider, J.L. Cortina, Treatment and reutilization of liquid effluents of copper mining in desert zones, Water Sustainability and Integrated Water Resource Management, The Preliminary Program for 2007 Annual Meeting, (accessed 20.03.2015). Available from: <https://aiche.confex.com/aiche/2007/preliminaryprogram/abstract_101082.htm>.

[9] Economics Consulting Services, Water and the Western Australian Minerals and Energy Industry: Certainty of Supply for Future Growth, Report prepared for The Chamber of Minerals and Energy of Western Australia, Australian Government, Department of Industry, Tourism and Resources, Perth, (2004) 1–46.

[10] J. Xu, R. Liu, W. Sun, Y. Hu, J. Dai, Effect of mineral processing wastewater on electrochemistry of galena, J. Environ. Sci. Eng., A 1 (2012) 279–285.

[11] D.E. Ng'andu, The effect of underground mine water on performance of the Mufulira flotation process, J. S. Afr. Inst. Min. Metall. (2001) 367–380.

[12] R. Schneeweiss, S. Müller, Conservation of scarce water resources at Rössing Uranium Mining, 2009, last consulted on 20.03.2015. Available form: <http://www.iied.org/pubs/pdfs/G02461.pdf>.

[13] F. Stapelfeldt, R.M. Fernandes Lima, Recycling of process water containing amines in the reverse flotation of iron ores, Proceedings of the International Mine Water Association Symposium (IMWA), Belo Horizonte, Brazil, 2001, pp. 1–10.

[14] Queensland Government, Industry Water Recycling Background Study, Prepared on behalf of Queensland Water Recycling Strategy by Kinhill Pty Ltd, Department of Natural Resources, Brisbane, 1999, pp. 1–29.

[15] F.K. Ikumapayi, B. Johansson, K.H. Rao, Recycling process water in sulphide flotation, Part B: Effect of H_2O_2 and process water components on sphalerite flotation from complex sulfide, Miner. Metall. Process 29(4) (2012) 192–198.

[16] G. Levay, R.St.C. Smart, W.M. Skinner, The impact of water quality on flotation performance, J. S. Afr. Inst. Min. Metall. (2001) 69–76.

[17] G.C. Molina, C.H. Cayo, M.A.S. Rodrigues, A.M. Bernardes, Sodium isopropyl xanthate degradation by advanced oxidation processes, Miner. Eng. 45 (2013) 88–93.

[18] J. Rubio, M.L. Souza, R.W. Smith, Overview of flotation as a wastewater treatment technique, Miner. Eng. 15 (2002) 139–155.

[19] R.W. Smith, M. Miettinen, Microorganisms in flotation and flocculation: Future technology or laboratory curiosity? Miner. Eng. 19 (2006) 548–553.

[20] AA. Abramov, Russian perspective on indicator of sustainability for flotation processing of minerals, in: R.C. Villas Boas, D. Shields, S. Solar, P. Anciaux,

G. Ônal (Eds.), A Review on Indicators of Sustainability for the Minerals Extraction Industries, CETEM/MCT/CNPq/CYTED/IMPC, Rio de Janeiro, 2005, pp. 209–226.

[21] J.D.C. Gush, Flotation of oxide minerals by sulphidization—The development of a sulphidization control system for laboratory testwork, J. S. Afr. Inst. Min. Metall. 105 (2005) 193–198.

[22] N. Kuyucak, D. Yaschyshyn, Managing thiosalts in mill effluents, studies conducted at Kidd metallurgical site, International Conference on Mining and the Environment IV, Sudbury, 2007, pp. 1–16.

[23] S.M. Bulatovic, Handbook of Flotation Reagents, Chemistry, Theory and Practice: Flotation of Sulfide Ores, Elsevier Science & Technology Books, 2007, pp. 1–448.

[24] T.P. Phetla, E. Muzenda, A multistage sulphidisation flotation procedure for a low-grade malachite copper ore, World Acad. Sci. Eng. Technol. 69 (2010) 255–261.

[25] J.M. González-Lara, A. Roca, M. Cruells, F. Patiño, The oxidation of thiosulfates with copper sulfate. Application to an industrial fixing bath, Hydrometallurgy 95 (2009) 8–14.

[26] S. Zhang, Oxidation of refractory gold concentrates and simultaneous dissolution of gold in aerated alkaline solutions, Murdoch University, Western Australia, Thesis presented for the degree of Doctor of Philosophy, 2004, pp. 158–160.

[27] J. Bessière, A. El Housni, J.J. Prédali, Dielectric study of activation and deactivation of malachite by sulfide ions, Int. J. Miner. Process. 33 (1991) 165–183.

[28] M. Reyes, F. Patiño, F.J. Tavera, R. Escudero, I. Rivera, M. Pérez, Kinetics and recovery of xanthate-copper compounds by ion flotation techniques, J. Mex. Chem. Soc. 53(1) (2009) 15–22.

[29] J. Drzymala, Mineral Processing, Foundations of Theory and Practice of Minerallurgy, first English ed., Wroclaw University of Technology, Wroclaw, 2007, pp. 1–510.

[30] B.A. Wills, T. Napier-Munn, Mineral processing technology, An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, seventh ed., Elsevier Science, 2006, p. 279.

[31] R.L. Frost, P.A. Williams, W. Martens, P. Leverett, J.T. Kloprogge, Raman spectroscopy of basic copper(II) and some complex copper(II) sulfate minerals: Implications for hydrogen bonding, Am. Mineral. 89 (7) (2004) 1130–1137.

[32] G. Lefèvre, In situ Fourier-transform infrared spectroscopy studies of inorganic ions adsorption on metal oxides and hydroxides, Adv. Colloid Interface. Sci. 107 (2004) 109–123.

[33] L.A. Barskii, V.V. Rybas, M.A. Fat'yanova, G.P. Ponomarev, Influence of sulfur-containing ions on selective flotation of copper–nickel ores, IPKON, Academy of Sciences of the USSR, Moscow, Translated from Fiziko-Tekhnicheskie Problemy Razrabotki Poleznykh Iskopaenykg, 4 (1986) 99–106.