

# Malachite and heterogenite behavior during the locked-cycle recycling of process water in flotation of copper-cobalt oxide ores



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## ABSTRACT

The behavior of malachite and heterogenite was investigated during the process water recycling in flotation of copper-cobalt oxide ores from the deposit of Luiswishi located in Haut-Katanga province (DRC). A synthetic mill wastewater (SMWW) was utilized as feed water alone and in mixture with water recovered from the flotation tails in view to achieve at the laboratory scale the locked-cycle recycling of the industrial mill wastewater (IMWW). To simulate the chemical species presence in the pulp water and their effects on the flotation of malachite and heterogenite, calcium, magnesium and bicarbonate ions were added to the feed water and the recoveries of copper and cobalt followed during the roughing flotation stage. The concentrate XRD and SEM analyses together with the floated minerals microanalyses by EDX spectroscopy, leaching tests of mono-minerals followed by the Pourbaix diagrams construction and DRIFT spectroscopic analyses, have enabled identifying changes in the surface properties of malachite and heterogenite and describing their behaviors. It was concluded that the locked-cycle recycling of process water is inducing the build-up of chemical species in the pulp, which favors the exaggerated dissolution and hydration of malachite and heterogenite interfering on the recovery of copper (40%) and cobalt (58%) with a significant drop in their concentrate grades (7.3% Cu and 2.7% Co). The deterioration of the concentrate characteristics results also from the gangue minerals entrainment. A better description of the valuable minerals behavior in the SMWW presence could enable designing strategies in view enhancing their floatability during the locked-cycle recycling of water.

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## 1. Introduction

Water reuse has become an established practice in many regions of the world (Bixioa et al. 2006; Miller, 2006). Even in regions that are not confronted to water scarcity, it has gained academic and practical interest because it is related to the quality of human life and environment (Biçak et al., 2012; Bixioa et al. 2006; Chen et al., 2009). In response to the global increase in the world population, Gupta et al. (2012) stated that wastewater treatment and recycling are the only alternatives for getting fresh water and preventing its scarcity in the days to come. The same authors stressed on the necessity to develop the low-cost and rapid wastewater treatment techniques for water reuse. In the arid regions of the world such as Australia, Chile and Israel, etc. water-saving practices are encouraged because they are seen as an essential part of a sustainable tomorrow (Bosse et al., 2007; Exall et al., 2006; Dolnicara et al., 2012; Hochstrat et al., 2008; Mudd, 2008; Nobel and Allen, 2000; Norgate and Lovel, 2004; Orona et al., 2007; Oudshoorn,

1997; Queensland Government, 1999). Among the benefits to be derived from water recycling, one finds the sustainable use of water resources, the ecosystems safeguarding together with the minimization of the pollution that is threatening interior water bodies in many countries (Fatta and Kythreotou, 2005; McIntyre, 2006; Miller, 2006; Nedved and Jansz, 2006; Nobel and Allen, 2000; Slatter et al., 2009; World Bank Group, 1999). Plenty of research reports on water reuse during flotation of sulfide ores place an emphasis on its advantages and drawbacks (Abramov, 2005; Ikumapayi et al. (2012a,b); Jing Xu et al., 2012; Molina et al., 2013; Rao and Finch, 1989, Slatter et al., 2009). During the minerals dressing, water recycling enables minimizing the consumption in fresh water and reagents which practice has ultimately resulted in the abatement of the pollutants concentrations in water bodies used as spillways for industrial wastewaters (Batisteli and Peres, 2008; Slatter et al., 2009). It should be noted, however, that the recycled water induces changes in the pulp physicochemical properties resulting in perturbations on the valuable minerals flotation (Abramov, 2005; Ikumapayi et al. (2012a,b); Jing Xu et al., 2012; Levay et al., 2001; Molina et al., 2013; Ng'andu, 2001; Rao and Finch, 1989; Slatter et al., 2009; Shengo et al., 2015). Indeed, the recycled water decreases the reagents efficiency due to generation of higher levels of contaminants in

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the pulp water, the build-up of matters in suspension, adverse side reactions as well as the bacteria-induced oxidation reactions of sulfide minerals subjected to flotation (Liu et al., 2013; Slatter et al., 2009). Furthermore, the recycled water chemical species are acknowledged to bring about unwanted changes in the pulp pH and redox potential resulting in the minerals surface properties alteration (Levy et al., 2001; Liu et al., 2013; Slatter et al., 2009).

It is important bearing in mind that effects from process water recycling on flotation of oxide minerals have not yet been widely investigated compared to sulfide minerals (Bulatovic, 2007; Chen et al., 2009; Gupta, 2003; Ikumapayi et al. (2012a,b); Shengo et al., 2014). Besides, advantages can be derived from water recycling in minerals dressing by flotation namely in terms of the process wastewaters management and water resources conservation because it enables minimizing the amount of fresh water consumed by industrial processes as well as the lowering of the reagents consumption via the recovery of the unconsumed reagents retained in wastewaters. Unfortunately, the recycling of process wastewater is not a widespread practice at copper ores concentrators operated in Haut-Katanga, which is a mining region confronted since many decades to water pollution related to the mismanagement of flotation effluents (Chadwick, 2008; Kanku, 2007; Kitenge, 2008). The present research work is interested in the locked-cycle recycling of process water during flotation of copper-cobalt oxide ores from the Luiswishi deposit located in Haut-Katanga. It has investigated the behavior of malachite and heterogenite in the SMWW presence. The adopted methodological approach primarily comprises the preparation of a SMWW with the composition resembling that of the IMWW (Shengo et al., 2015) and its use as feed water alone and in mixture with the recycled water during flotation of copper-cobalt oxide ores. Secondly, it comprises the achievement of XRD and SEM analyses of the roughing flotation concentrate in order to determine its mineralogical characteristics. Additionally, malachite was successively conditioned with NaHS and KAX in the presence of calcium, magnesium and bicarbonate ions prior to the DRIFT spectroscopic analyses along with leaching tests of malachite and heterogenite in the presence of bicarbonate ions in order to construct the Pourbaix diagrams and to describe phenomena influencing the valuable minerals behavior during the process water recycling. Specifically, the interest in the achievement of the above-mentioned experiments was to simulate the build-up of chemical species in the pulp through the addition of calcium, magnesium and bicarbonate ions to the feed water and to investigate their effects on flotation of malachite and heterogenite. It is expected that the understanding of phenomena, which control the valuable minerals behavior in the SMWW presence, could enable designing strategies in view enhancing their floatability during the locked-cycle recycling of process water in flotation of copper-cobalt oxide ores from the deposit of Luiswishi.

## 2. Material and methods

### 2.1. The IMWW chemical composition

The mill wastewater concerned by the present research was recovered from flotation effluents sampled inside the New Concentrator in

**Table 1**  
Chemical composition of the industrial and the synthetic mill wastewaters.

| Chemical compound         | IMWW <sup>a</sup> | SMWW    |
|---------------------------|-------------------|---------|
| Calcium sulfate (mg/L)    | 72.20             | 72.41   |
| Magnesium sulfate (mg/L)  | 79.20             | 79.15   |
| Potassium chloride (mg/L) | 66.86             | 66.36   |
| Sodium bicarbonate (mg/L) | 629.70            | 629.73  |
| Sodium chloride (mg/L)    | 195.26            | 199.76  |
| Sodium sulfate (mg/L)     | 1039.50           | 1039.50 |

<sup>a</sup> Electric conductivity = 2641  $\mu\text{S}/\text{cm}$ ; pH = 7.92; total hardness = 12 °F, permanent hardness = 0 °F; Langelier index = 0.16, CO<sub>2</sub> = 4.2 mg/L.

Kipushi (NCK). Its chemical characteristics are given in Table 1 (Shengo et al., 2015).

### 2.2. Chemical analysis of the ore and flotation products

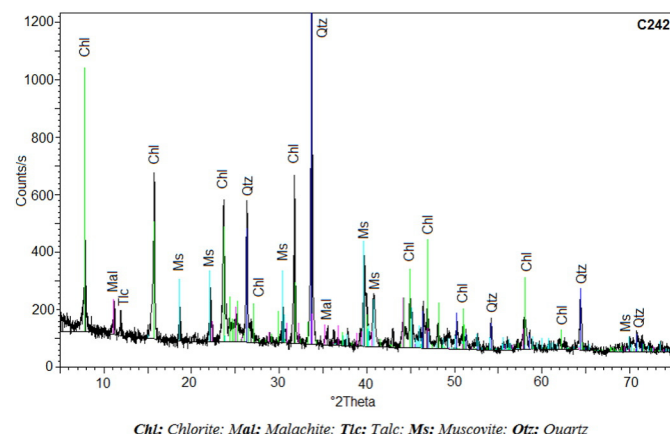
The ore subjected to flotation in the present research comes from the Luiswishi deposit located in the Haut-Katanga province (DRC). It contains copper (2.85%) and cobalt (0.89%) essentially as malachite and heterogenite. Froth and tailings recovered during flotation tests were separately collected, dried in a Memmert steam room at 105 °C and sampled by quartering before being spectrophotometrically assayed for copper and cobalt. Concerning the concentrate mineralogical analysis, it was conducted by means of a PANALYTICAL PW 3710 diffractometer using the FeK $\alpha$  radiations ( $\lambda = 1.9373 \text{ \AA}$ ). A ground subsample of the concentrate was converted into a powder by means of an agate mortar and pestle before being scanned between 5 and 75° 2 $\theta$  at speed of 0.02° 2 $\theta$  per second. The XRD pattern (Fig. 1) peaks assignment was done using the *Panalytical X'pert* programs and the ICDD WebPDF4+ database.

A second subsample of the ground concentrate was mixed with *Araldite* (an epoxy resin) to fabricate a thin layer through the polishing by means of abrasive papers with the silicon carbide grains of varied size (P 400, P 600) – 3 M as well as the ESCIL (France) abrasive disks GR 2400 (800/2400) and GR. 4000 (1200/4000) respectively. The concentrate thin layer preparation was completed by a re-polishing of using a diamonded suspension (1PS – 1MC, ESCIL) with the size particles kept a 1  $\mu\text{m}$  in absolute methanol as solvent. Afterward, an area of interest of the polished thin layer was selected, metalized, enclosed with a silver bridge prior to be carbonized inside a *Bolzlers MED. 010* Evaporator. Finally, the prepared thin layer was subjected to analyses by means of a PHILIPS FEI XL30 ESEM-FEG scanning electron microscope (SEM) using the backscattered electrons (BSE) detector (Fig. 2).

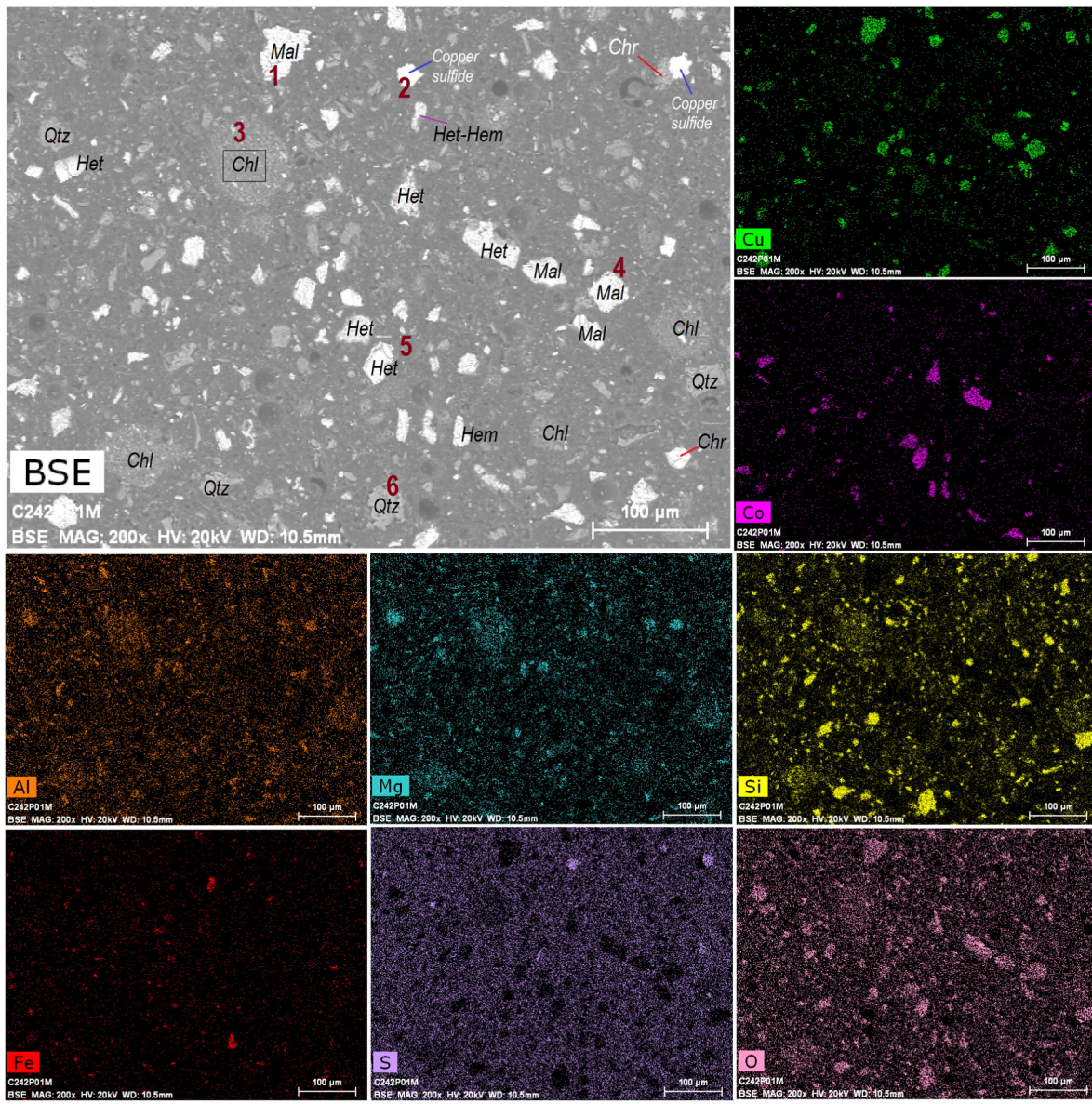
The primary electrons' beam of the SEM was scanned in a raster pattern across the carbonized area (mapping) of the thin layer with the aim to determine the spatial distribution of constituents (Cu, Co, Si, Mg, Al, Fe, S and O). With the electrons' beam width of 10.5 mm and the voltage of 20 kV, the thin layer analyses have enabled obtaining SEM images with the magnification of 200. Besides, chemical microanalyses achieved by means of the EDX spectroscopy have confirmed the nature of minerals initially identified in the concentrate based on the analysis of SEM images (Figs. 3a–f).

### 2.3. Locked-cycle recycling of the SMWW

Before the achievement of flotation tests with the locked-cycle recycling of water, the SMWW was prepared at laboratory using the analytical grade chemicals provided by VWR Prolabo Chemicals in order to replicate the chemical composition (Table 1) of the IMWW sampled at



**Fig. 1.** XRD pattern of the concentrate given by flotation of ores with the SMWW.



*Mal*: Malachite; *Het*: Heterogenite; *Chl*: Chlorite; *Chr*: Chrysocolla; *Hem*: Hematite; *Qtz*: Quartz ;1 up to 6: Identified minerals

**Fig. 2.** Scan pattern of the concentrate given by flotation of ores with the SMWW.

the effluents discharge point inside the NCK. On the other hand, the industrially ground ores (0.5 kg) from the deposit of Luiswishi were conditioned in pulp for 3 min with  $D_{250}$  and sodium silicate respectively as frother and slime depressant before the roughing flotation (15 min) conducted using the SMWW (7.0 L) as feed water (Fig. 4).

Flotation tails were allowed to settle with the aim to recover the mill wastewater (3.5 L) for reuse (see C at Fig. 4). The recovered water was added to 3.5 L of the SMWW to reconstruct the feed water and simulate the mill wastewater locked-cycle recycling during flotation of copper-cobalt oxide ores conducted using a Denver-D12 pneumo-mechanical machine with the impeller speed kept at 800 rpm and implementing the following reagents regime:

*Talc flotation* (3 min):

- 120 g/t D 250 (100%) as frother;
- 200 g/t  $\text{Na}_2\text{SiO}_3$  (30%) as slimes depressant.

*Roughing flotation* (15 min):

- Sulfidizer: 756–1512 g/t, 108–216 g/t, 108–216 g/t, 108–216 g/t and 108–216 g/t NaHS (9%);
- Collector: 90–180–360 g/t, 15–60–120 g/t, 15–60–120 g/t, 15–60–120 g/t and 15–60–120 g/t KAX (2.5–5–10%);
- Frother: 48 g/t D250 (100%).

#### 2.4. Effects of the build-up of chemical species in pulp on malachite and heterogenite flotation

The valuable minerals behavior was studied based on variations in the recoveries of copper and cobalt during the flotation of the pulp from the wet grinding of 1 kg copper-cobalt oxide ore (see A and B at Fig. 4) using deionized water (DW) doped with chemical species observed in the IMWW ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$ ). In this case, the roughing flotation of copper-cobalt oxide ore was conducted during 30 min while doubling the dosages of NaHS and KAX. Additionally, the same ore was subjected to wet

grinding with DW doped either with calcium and magnesium ions or with magnesium and bicarbonate ions and floated with the recoveries of copper and cobalt followed versus the amount of KAX added to

the pulp and without water recycling (Fig. 4). The results from these experiments are depicted at Figs. 5a and b and given in Tables 4, 5 and 6 as well.

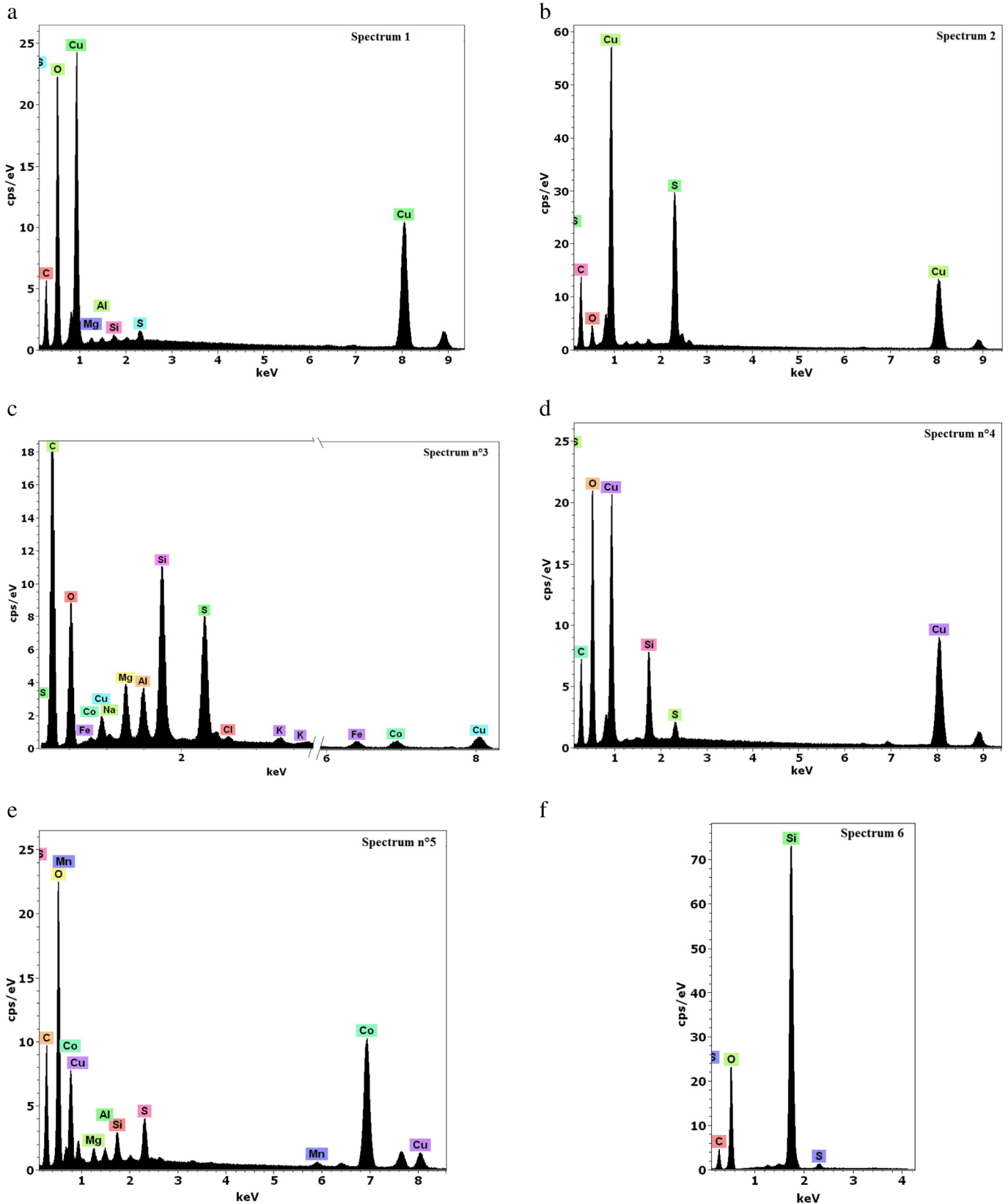
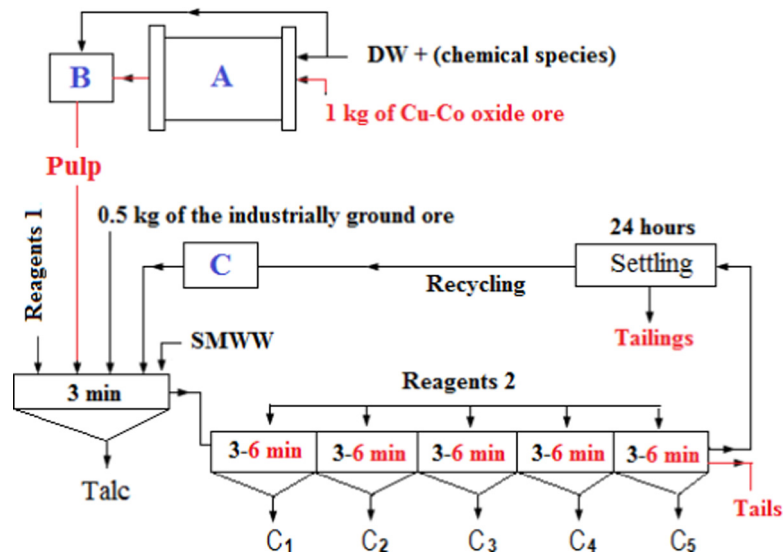


Fig. 3. a. Spectra of a malachite grain containing the gangue minerals. b. Spectra of a copper sulfidized grain in the concentrate. c. Spectra of the concentrate area rich in chlorites and tiny grains of malachite and heterogenite. d. Spectra of a malachite grain containing siliceous matters. e. Spectra a heterogenite grain. f. Spectra of a quartz grain.



**A:** Ball Mill (7 kg of steel balls, 123 rpm, 8 minutes)

**B:** Pulp with specific gravity adjusted at 1200 g/L

**C:** 3.5 L of the mill wastewater recovered from the flotation tails settling.

**Reagents 1:**  $D_{250}$  and  $Na_2SiO_3$

**Reagents 2:** NaHS and KAX

**C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub>:** concentrates skimmed at 3 or 6 minutes intervals.

**Fig. 4.** Flowsheet for Cu-Co ore flotation in the presence of chemical species (B) and the locked-cycle recycling (C) of the SMWW. A: Ball mill (7 kg of steel balls, 123 rpm, 8 min) B: Pulp with specific gravity adjusted at 1200 g/L C: 3.5 L of the mill wastewater recovered from the flotation tails settling. Reagents 1:  $D_{250}$  and  $Na_2SiO_3$ . Reagents 2: NaHS and KAX. C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub>: concentrates skimmed at 3 or 6 min intervals.

### 2.5. Conditioning of malachite with NaHS and KAX under the influence of $Ca^{2+}$ , $Mg^{2+}$ and $HCO_3^-$

The conditioning of malachite with NaHS and KAX was conducted with the aim to investigate the mineral surface properties alteration in relationship with the mill wastewater chemical species. It has enabled also to comprehend how they are interfering on the sulfidization process and the collector efficiency, which phenomena result in very poor recoveries with respect to copper. Thus, 1 g of malachite (42.7% Cu) was suspended during 3 min by stirring (250 rpm) in 100 mL of DW containing 1.5 g/L of calcium, 1.0 g/L of magnesium and 10 g/L of bicarbonate ions respectively prior to its conditioning with NaHS (1 mL - 0.36%) and KAX (1 mL - 0.1%) during 3 min. Afterward, the suspended malachite was recovered by filtration using an ashless WHATMAN - (589/2) filter paper and dried at room temperature. An aliquot (2 mg) was added to 150 mg of high-grade spectrographic KBr to fabricate pellets that were subjected to the DRIFT spectroscopic analyses (4000–400  $cm^{-1}$ ) using a BRUKER EQUINOX 55 FTIR spectrophotometer. The results from the concerned analyses are depicted at Figs. 6, 7 and 9.

### 2.6. Leaching tests of malachite and heterogenite in the presence of bicarbonate ions

These leaching tests were conducted with the aim to identify changes arising in the valuable minerals surface or behavior during the mill wastewater recycling in flotation of copper-cobalt oxide ores from the Luiswishi deposit. Thus, 1 g of malachite or heterogenite was subjected to dry grinding (40–63  $\mu m$ ) using an agate mortar and pestle and the obtained matter stirred at constant speed (250 rpm) during 3 min in

100 mL of DW containing 10 g/L of bicarbonate ions. The suspended matter was allowed to settle in view to recover the aqueous phase intended for the assaying of copper and cobalt (see Table 7). The data gathered during the leaching tests of minerals have enabled to construct the Pourbaix diagrams of the system Cu (Co-Cu)-C-H<sub>2</sub>O at 25 °C (see Figs. 8a and b) using the OUTOTEC HSC CHEMISTRY software v.7.0.

## 3. Results and discussions

### 3.1. Flotation of ores with the SMWW

The results from flotation of copper-cobalt oxide ores using the SMWW (see Fig. 4) are given in Table 2.

A perusal of the reference flotation results (63% Co and 77% Cu) conducted with DW enables noticing the decrease in the recoveries and grades of copper and cobalt. This phenomenon is supporting the statement according which the flotation efficiency is greatly influenced by variations in the feed water quality. Besides, one finds in the concentrate more cobalt (59%) than copper (43%) revealing a great sensitivity of malachite towards chemical species introduced in the pulp water. Indeed, the flotation of malachite is more hindered compared to that of heterogenite dropping by 44% the recovery of copper versus 7% for cobalt respectively.

The decrease in the recoveries and grades of copper and cobalt is possibly due either to poor floatability of malachite and heterogenite in the SMWW chemical species presence or the unwanted activation of minerals from the gangue. The same phenomenon can also occur due the gangue minerals mechanical entrapment in the concentrate. The latter assumption is supported by the high intensities of peaks related to the gangue minerals (Talc, quartz, chlorite, mica and muscovite)

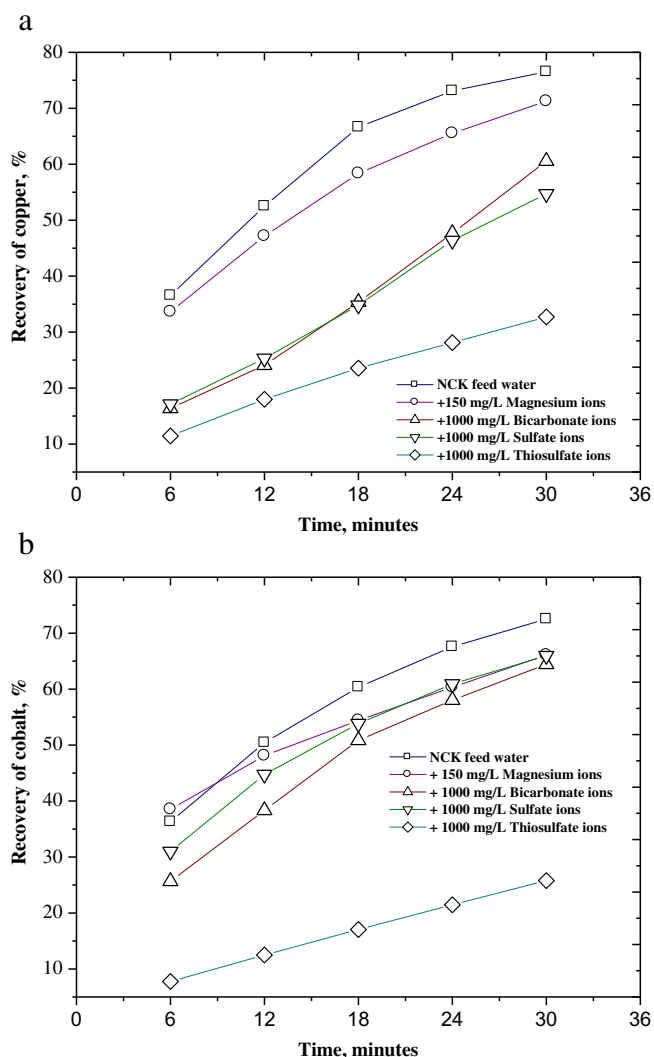


Fig. 5. a. Influence of the chemical species build-up in the pulp on flotation of copper. b. Influence of the chemical species build-up in the pulp on flotation of cobalt.

observed in the concentrate XRD pattern (Fig. 1). It is also supported by the increased presence of Al, Mg, Si and Fe in the concentrate SEM images (Fig. 2) as well as the presence of chlorite, hematite and quartz among the floated minerals (Figs. 3a–f) confirmed by the results from EDX spectroscopic microanalyses. Based on what precedes, one can argue that flotation of copper-cobalt oxide ores from the deposit of Luiswishi, using the SMWW as feed water, favors the gangue minerals recovery in the concentrate at the expense of malachite and heterogenite, which are the bearing minerals of the copper and cobalt.

### 3.2. Locked-cycle recycling of the SMWW

The results given in Table 3 are in relationship with the locked-cycle recycling of the SMWW during flotation copper-cobalt oxide ores from the deposit of Luiswishi.

It could be seen from Table 3 that the locked-cycle recycling of the SMWW is deleterious to flotation of malachite because it has significantly dropped the recovery of copper in the concentrate. Apart from the poor recoveries of copper, which characterize the 3rd recycling cycle, owing to the high level of suspended matters in the feed water recovered from the flotation tails, the locked-cycle recycling of SMWW has globally resulted in the lowering of the recovery of copper (40%) in the concentrate. However, it is important noticing that the recovery of cobalt (58%) was less affected whatever the number of the SMWW

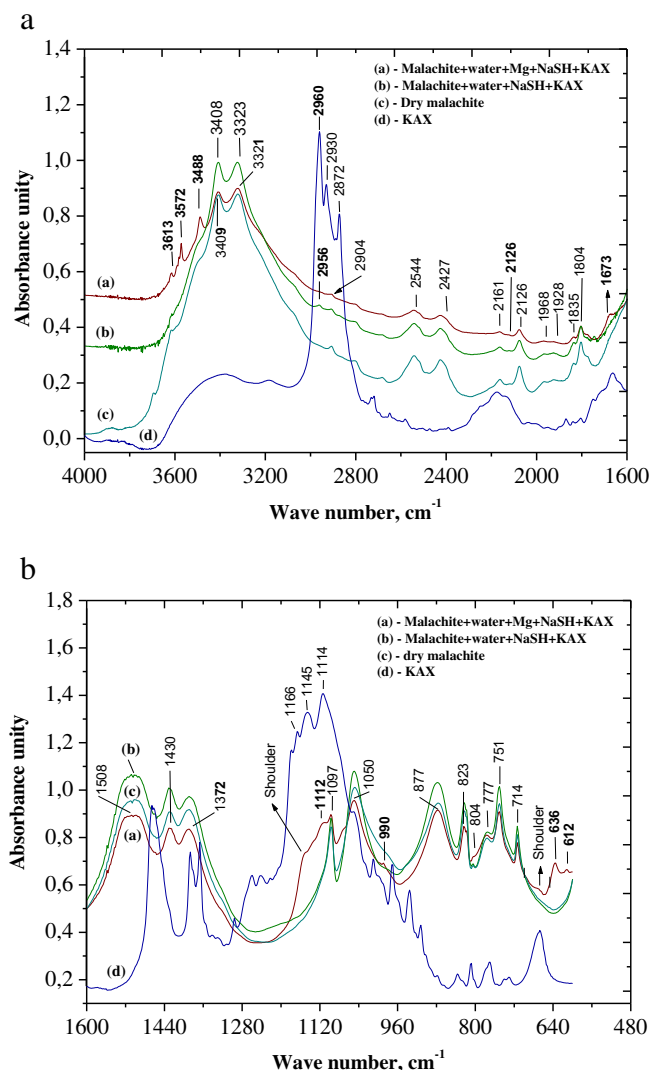


Fig. 6. a. Functions region of the spectrum of malachite conditioned with the reagents in the presence of Ca<sup>2+</sup>. b. Fingerprint region of the spectrum of malachite conditioned with reagents in the presence of Ca<sup>2+</sup>.

recycling. When one compares the obtained results to the ones from the reference flotation conducted with DW, cobalt appears once more to be less sensitive to changes in the feed water quality. The same phenomenon occurs when magnesium, bicarbonate, sulfate and thiosulfate ions are added one after another to the feed water (Figs. 5a and b). Based on what precedes, it can be stated that the locked-cycle recycling of the SMWW is resulting in the build-up of chemical species in the pulp worsening ultimately the flotation efficiency (Liu et al., 2013; Rao and Finch, 1989; Shengo and Mutiti, 2016; Slatter et al., 2009).

As can be seen from Figs. 5a and b, the presence of magnesium ions interferes on flotation of copper and cobalt as confirmed by the drop in their respective recoveries. This phenomenon could result from the adsorption of magnesium ions on the valuable mineral surfaces increasing their hydrophilicity. As for bicarbonate ions, their presence is increasing the disturbance brought about by magnesium ions on flotation of copper resulting in a synergic depressing effect towards malachite. However, it should be noticed that the presence of sulfate, magnesium and bicarbonate ions in the feed water is enhancing the recovery of cobalt without an improvement in direction of copper. The promoting effect, with respect to the flotation of cobalt, might result from the softening of the pulp water brought about by the precipitation of alkaline earth ions in the presence of sulfate and bicarbonate ions. Concerning thiosulfate ions, they dramatically hinder the flotation of malachite and

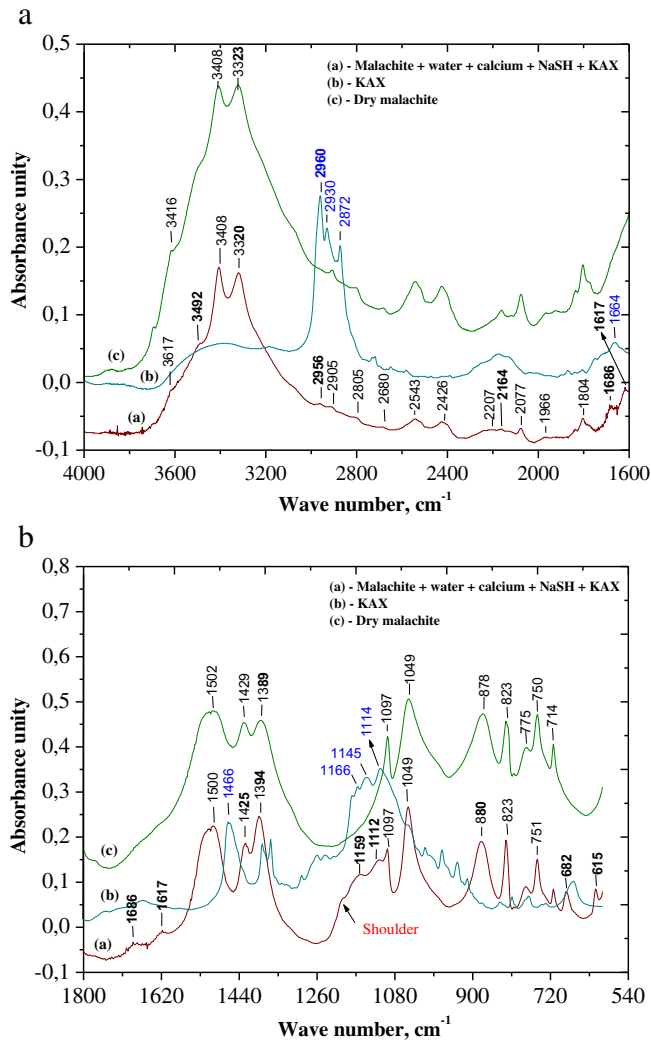


Fig. 7. a. Functions region of the spectrum of malachite conditioned with the reagents in the presence of  $Mg^{2+}$ . b. Fingerprint region of the spectrum of malachite conditioned with reagents in the presence of  $Mg^{2+}$ .

heterogenite as confirmed by significant the drop in the recoveries of copper (33%) and cobalt (26%) – Figs. 5a and b. Based on what precedes, it can be argued that the loss in efficiency experienced during flotation of copper-cobalt oxide ores using the SMWW as feed water results from the build-up of chemical species in the pulp. The concerned chemical species are exacerbating the surface properties alteration undergone by malachite and heterogenite. They are also interfering on their sulphidization and the collector adsorption processes leading ultimately to poor metallurgical results. To confirm these statements, a series of experiments was conducted with the aim to investigate the effects from calcium, magnesium and bicarbonate ions on flotation of copper and cobalt.

### 3.3. Copper and cobalt flotation in the presence of calcium and magnesium ions

The results in relationship with the study of the influence of calcium and magnesium ions on flotation of copper and cobalt are given in Table 4.

It is obvious that a concentrate with the highest grades of copper and cobalt is achieved when calcium and magnesium ions are added to the feed water to concentrations similar to those of the IMWW (Table 1). Under those conditions, one obtains a recovery of copper oscillating on average around 60% which value is low when compared to the result

from the reference flotation conducted with DW. As for the recovery of cobalt, it decreases when the amounts of calcium and magnesium ions increase in the feed water (50–100 mg/L  $Ca^{2+}$  and 37.5–75 mg/L  $Mg^{2+}$ ). The worsening in the flotation efficiency may result from the poor flotation of malachite and heterogenite due to the excess calcium and magnesium in the pulp or the unwanted activation of minerals from the gangue (Rao and Finch, 1989; Slatter et al., 2009). The poor flotation of the valuable minerals or their depression could also result from an increase in their natural hydrophilicity.

A perusal of the Table 5 shows that with feed water containing 150 mg/L of magnesium ions, the recovery of copper and cobalt significantly improves when more KAX is added to the pulp. This phenomenon is simply demonstrating that additional collector is needed for rendering the bearing minerals of copper and cobalt sufficiently hydrophobic and floatable in the presence of magnesium ions which naturally act as depressant. It can be assumed that calcium and magnesium ions increase the hydrophilicity of the floated minerals through adsorption onto their surface as suggested by Slatter et al. (2009). This assumption is supported by the data confirming changes in the mineral surface brought by the infrared spectra (DRIFT) of malachite conditioned with NaHS and KAX in the presence of calcium and magnesium ions respectively (Figs. 6 and 7).

In the region of the spectrum of malachite (Fig. 6a) reserved for functional groups (4000–3000  $cm^{-1}$ ), one observes a marked decrease in the area of bands (3408 and 3320  $cm^{-1}$ ) related to stretching vibrations of O—H bonds in the hydroxyl groups of malachite. In the same region of the spectrum, one observes also a new infrared band (3492  $cm^{-1}$ ) due to stretching vibrations performed by free O—H bonds revealing or suggesting the mineral hydroxylation. Moreover, the vibration bands of O—H bonds have decreased in intensity while one of them has undergone a shift to the lower wave numbers (3323 to 3320  $cm^{-1}$ ). Hence, it could be assumed that malachite has undergone dissolution and hydration via formation of the hydrogen bond's bridges in the presence of calcium ions. These phenomena suggest considering that alkaline earth ions have increased the hydrophilicity of malachite requesting to add more KAX to the pulp in view to improve the recovery of copper (Table 5). However, the collector adsorption has taken place as confirmed by the presence in the spectrum of an infrared band (2956  $cm^{-1}$ ) characteristic of stretching vibrations of C—H bonds in the methyl groups of KAX. In the region of the spectrum reserved for overtones of carbonates bands and in the fingerprint region (Fig. 6b), one finds new infrared bands (1686, 1617; 1159, 1112, 682 and 615  $cm^{-1}$ ) and a shoulder around 1215  $cm^{-1}$ . These bands could be regarded as proofs of changes in the surface properties of malachite. Besides, one finds among the aforementioned bands those related to stretching vibrations of S—O bonds of sulfates (Bensted, 1976). The band, which appears in the spectrum around 1680  $cm^{-1}$  can be assigned to vibration of O—H bonds in the adsorbed water molecules as well as in cupric hydroxide suggesting an hydroxylation of malachite. As for the poor flotation of malachite or its depression by magnesium ions, it is understandable based on the analysis of spectroscopic data brought by Fig. 7a and b.

One observes a shift to lower wave numbers (3323 to 3321  $cm^{-1}$ ) of an infrared band associated with stretching vibrations of O—H bonds of malachite (Fig. 7a). Apart from infrared bands (3409 and 3321  $cm^{-1}$ ) related to stretching vibrations of O—H bonds in the hydroxyl groups of malachite, one finds in the region of the spectrum reserved for the functional groups three other bands appearing at 3613, 3572 and 3488  $cm^{-1}$  respectively. The areas these bands are halved comparatively to those of the same bands in the spectrum of dry malachite. The abovementioned facts are confirming the hydration of malachite through a process encompassing a partial dissolution followed by formation of hydrogen bond's bridges on its surface where one finds also free O—H bonds. Even after hydration, the spectrum of malachite comprises an infrared band (2658  $cm^{-1}$ ) related to stretching vibrations of the C—H bonds in the methyl groups of KAX. This band confirms the

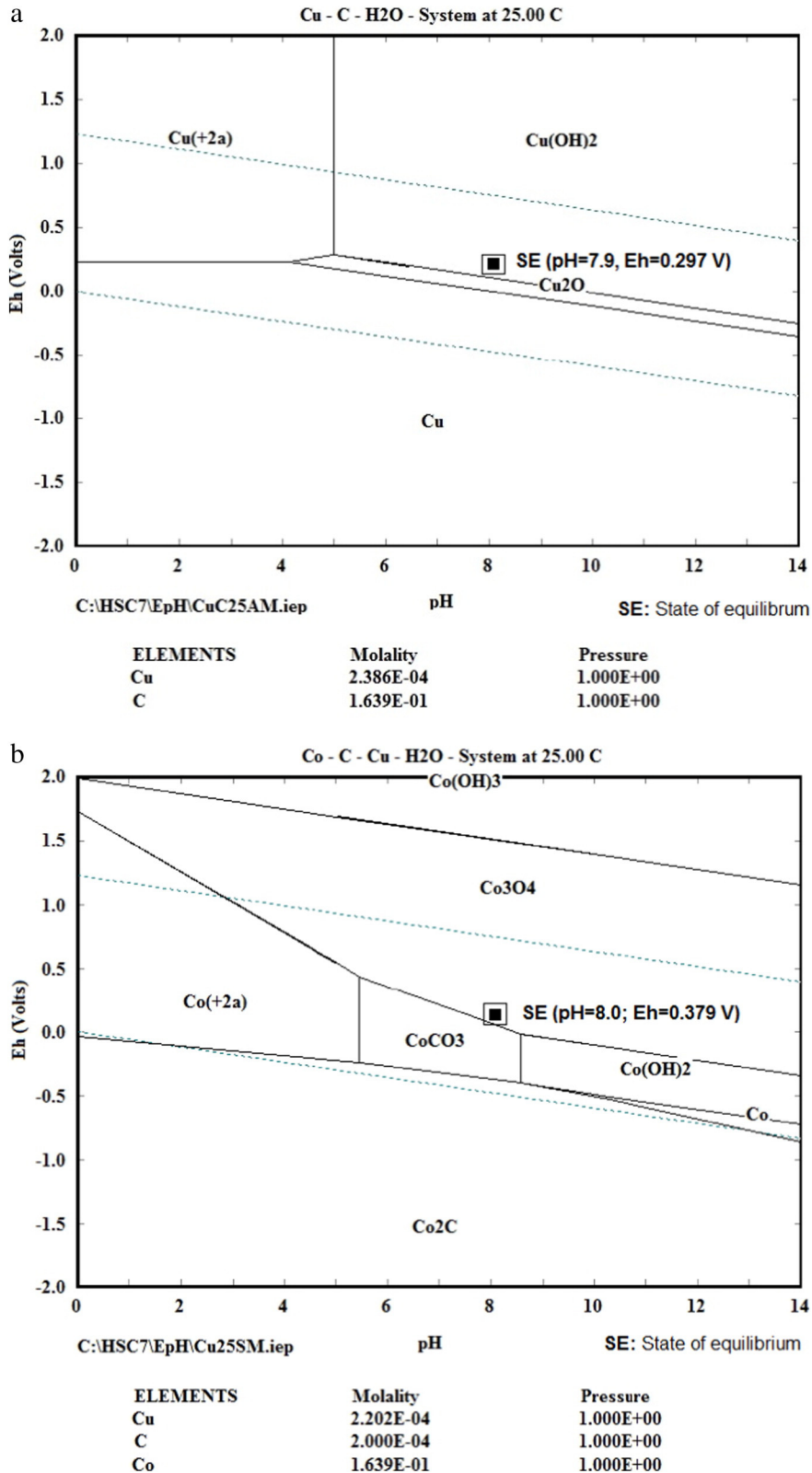


Fig. 8. a. Pourbaix diagram of the system Cu-C(HCO<sub>3</sub><sup>-</sup>)-H<sub>2</sub>O at 25 °C. b. Pourbaix diagram of the system Cu-Co-C(HCO<sub>3</sub><sup>-</sup>)-H<sub>2</sub>O at 25 °C.

collector adsorption on the mineral surface. Concerning the fingerprint region of the spectrum of malachite (Fig. 7b), it contains news infrared bands (1112, 990, 636 and 612 cm<sup>-1</sup>) and shoulders (around 1160 and 680 cm<sup>-1</sup>) apart from those representative of the functional groups. The bands that are observed at 990, 636 and 612 cm<sup>-1</sup> can be assigned respectively to the symmetric and asymmetric stretching and the

bending of S—O, O—S—O and S=O bonds in sulfate groups (Bensted, 1976; Krylova, 2007) probably brought by CaSO<sub>4</sub>·2H<sub>2</sub>O introduced in DW during the conditioning of malachite in the presence of calcium ions. As for the abovementioned shoulders, they may indicate the beginning of formation of bands usually observed between 1263 and 1022 cm<sup>-1</sup> in the spectrum of sulfates. These bands are related to the



**Table 2**  
Copper and cobalt flotation in the SMWW presence.

| Feed water        | Concentrate weight (g) | Grade (%) |      | Recovery (%) |       |
|-------------------|------------------------|-----------|------|--------------|-------|
|                   |                        | Cu        | Co   | Cu           | Co    |
| DW <sup>a</sup>   | 83.6                   | 14.46     | 3.03 | 76.73        | 63.43 |
| SMWW <sup>b</sup> | 73.3                   | 9.19      | 3.23 | 42.76        | 59.10 |

<sup>a</sup> Reference flotation conducted in the absence of the studied chemical species.

<sup>b</sup> Flotation conducted while simulating the studied chemical species presence and build-up in the pulp.

symmetric and asymmetric stretching of their S—O bonds (Bensted, 1976). In this region of the spectrum, there is an overlapping of bands related to stretching vibrations of bonds (C—O and C—S) in the KAX “head” with those due to vibrations of bonds in the sulfur bearing species. These bands might result from the mineral surface alteration or the adsorbed species.

### 3.4. Effects of bicarbonate ions on flotation of copper-cobalt oxide ores

The results related to the study of the effects from bicarbonate ions on flotation of ores are given in Table 6.

The depression of copper and cobalt increases with the amount of bicarbonate ions added to the feed water. Once again, the flotation of heterogenite seems to be less sensitive to the presence of chemical species and their build-up in the pulp water. Indeed, the cobalt recovery remains as high as 61% when the feed water content of bicarbonate ions is increased up to 500 mg/L. Moreover, an increase in the concentrate grade in cobalt is observed when the feed water content of bicarbonate ions is varied between 0 and 500 mg/L. However, the increase in the content of bicarbonate ions adversely raises the collector rate of consumption (Table 5). Consequently, more than 80% of copper and cobalt are recovered in the concentrate when the collector concentration was increased up to 10% (600 g/t) in spite of the depressing effect from bicarbonate ions (1000 mg/L). With the collector concentration of 2.5% (150 g/t), the recovery remains below 50% and 60% respectively for copper and cobalt. Thus, it can be assumed that bicarbonate ions increase the collector rate of consumption because they render more hydrophilic the valuable minerals. Besides, the build-up of bicarbonates ions is rendering the pulp water scaling or incrusting due to the rupture of the calco-carbonic equilibrium. Based, on what precedes, it can be assumed that the floated minerals depression may arise also due to precipitation of carbonates on their surfaces (Hamrouni and Dhahbi, 2002). Depression of the floated minerals according to the above-suggested pattern was ascertained based on the results from the leaching tests of malachite and heterogenite in the presence of bicarbonate ions (Table 7).

As can be seen from the results given in Table 7, it can be stated that bicarbonate ions favor the superficial dissolution of the valuable minerals considering that in their presence the amount of copper ions liberated by malachite when suspended in DW is multiplied by 58 times. The same phenomenon also occurs with respect to the dissolution of heterogenite because the concentrations of copper and cobalt ions in the aqueous phase are multiplied by 139 and 75 respectively in the

**Table 3**  
Influence of the locked-cycle recycling of the SMWW on flotation of copper and cobalt.

| Recycling cycle  | Concentrate weight (g) | Grade (%) |      | Recovery (%) |       |
|------------------|------------------------|-----------|------|--------------|-------|
|                  |                        | Cu        | Co   | Cu           | Co    |
| 1st              | 83.8                   | 7.46      | 2.86 | 39.72        | 60.01 |
| 2nd              | 83.8                   | 7.59      | 2.78 | 40.41        | 58.16 |
| 3th <sup>a</sup> | 88.0                   | 6.77      | 2.34 | 37.80        | 51.41 |
| 4th              | 89.0                   | 7.66      | 2.76 | 43.27        | 61.31 |
| 5th              | 89.6                   | 7.12      | 2.61 | 40.52        | 58.52 |
| Mean value       | 86.8                   | 7.32      | 2.67 | 40.35        | 57.88 |

<sup>a</sup> Low performances given by the flotation process due to a high level of matters in suspension in the feed water.

**Table 4**  
Copper and cobalt flotation in the presence of calcium and magnesium ions.

| Ca <sup>2+</sup> –Mg <sup>2+</sup> (mg/L) | Concentrate weight (g) | Grade (%) |      | Recovery (%) |       |
|---|------------------------|-----------|------|--------------|-------|
|   |                        | Cu        | Co   | Cu           | Co    |
| 0–0                                       | 83.6                   | 14.46     | 3.03 | 76.73        | 63.43 |
| 10–7.5                                    | 79.0                   | 12.90     | 2.77 | 64.47        | 54.61 |
| 20–15 <sup>a</sup>                        | 65.5                   | 14.54     | 3.17 | 60.46        | 51.96 |
| 50–37.5                                   | 77.8                   | 12.18     | 2.28 | 60.16        | 44.36 |
| 100–75                                    | 82.5                   | 11.59     | 1.90 | 60.37        | 39.13 |
| 200–150                                   | 89.4                   | 10.99     | 1.94 | 62.41        | 43.41 |

<sup>a</sup> Average contents of calcium and magnesium ions in the IMWW (Table 1).

presence of bicarbonates ions. Based on the Pourbaix diagrams of the systems Cu (Co–Cu)–C–H<sub>2</sub>O at 25 °C depicted at Fig. 8a and b, it can be stated that the natural hydrophilicity of malachite and heterogenite increases when bicarbonate ions are added to the feed water.

Indeed, copper and cobalt ions present in the aqueous phase are expected to remain in equilibrium with Cu(OH)<sub>2</sub> and CoCO<sub>3</sub>/Co(OH)<sub>2</sub> covering the surfaces of malachite and heterogenite owing to their increased dissolution in the presence of bicarbonate ions (Table 7). Therefore, it can be assumed that the presence of bicarbonate ions on the surface of malachite and heterogenite has increased their hydrophilicity requesting to add more NaHS and KAX to the pulp in view enhancing their floatability (Table 5). This assumption was validated by the spectroscopic data from the analysis of malachite conditioned with NaHS and KAX in the presence of bicarbonate ions (Fig. 9a and b).

The collector adsorption has taken place on malachite as proved by the presence in the spectrum (Fig. 9a) of infrared bands (2962 and 2792 cm<sup>-1</sup>) related to stretching vibrations of C—H bonds in the methyl groups of KAX (3000–1600 cm<sup>-1</sup>). The shoulders observed at 1240 and 1166 cm<sup>-1</sup> in the fingerprint region of the spectrum (Fig. 9b) confirm the adsorption of KAX on malachite both as dixanthogena and as xanthate. The infrared band seen in the spectrum at 3476 cm<sup>-1</sup> could be assigned to vibrations related to the free O—H bonds without the hydrogen bonds bridging. However, the bands observed around 3320 cm<sup>-1</sup> result from vibrations of the hydrogen bonded O—H bonds in the hydrated cupric hydroxide (Balintova et al., 2012; Rath et al., 2001). The above-mentioned phenomena are giving proofs of the studied mineral hydration. The band related to bending vibrations in the O—H (1382 cm<sup>-1</sup>) bonds appearing in the fingerprint region of the spectrum of malachite (Fig. 9b) are overlapped by the band associated with the asymmetric stretching of C—O bonds in the carbonate functional groups of the studied mineral. As for the shoulders observed around 3200 and 1640 cm<sup>-1</sup>, they might result from water adsorbed onto the surface of malachite. These shoulders and particularly the increase in width which affects the bands related to asymmetric stretching of C—O bands in the carbonate functional groups as well as the shift towards the lower wave numbers (1389 to 1384 cm<sup>-1</sup>) are supporting the assumption of an increase in the hydrophilicity of malachite related to the bicarbonate ions presence. Moreover, the increase in the bands width observed at 1516 and 1056 cm<sup>-1</sup> together with the raise in the intensity of one of the concerned infrared bands are supporting the assumption that malachite has undergone hydration. The later phenomenon has arisen due to formation of hydrogen bond

**Table 5**  
Recovery of copper and cobalt versus the collector dosage under the influence of magnesium and bicarbonate ions.

| KAX               |              | Recovery of copper and cobalt after flotation (30 min) |        |   |        |
|-------------------|--------------|--|--------|---|--------|
| Concentration (%) | Dosage (g/t) | 150 mg/L Mg <sup>2+</sup>                              |        | 1000 mg/L HCO <sub>3</sub> <sup>-</sup> |        |
|                   |              | Cu (%)   | Co (%) | Cu (%)                                  | Co (%) |
| 2.5               | 150          | 66.08  | 61.82  | 49.08                                   | 53.55  |
| 5                 | 300          | 68.99  | 66.08  | 67.55                                   | 77.02  |
| 10                | 600          | 73.99  | 70.73  | 81.05                                   | 83.44  |

**Table 6**  
Copper and cobalt flotation in the presence of bicarbonate ions.

| Bicarbonate ions (mg/L) | Concentrate weight (g) | Grade (%) |      | Recovery (%) |       |
|-------------------------|------------------------|-----------|------|--------------|-------|
|                         |                        | Cu        | Co   | Cu           | Co    |
| 0                       | 83.6                   | 14.46     | 3.03 | 76.73        | 63.43 |
| 100                     | 65.2                   | 15.68     | 3.48 | 64.93        | 56.65 |
| 250                     | 58.8                   | 15.15     | 4.14 | 58.07        | 60.89 |
| 500                     | 58.9                   | 13.01     | 4.13 | 48.67        | 60.75 |
| 750                     | 58.3                   | 11.02     | 3.96 | 40.78        | 57.73 |
| 1000                    | 65.8                   | 8.26      | 3.08 | 34.52        | 50.69 |

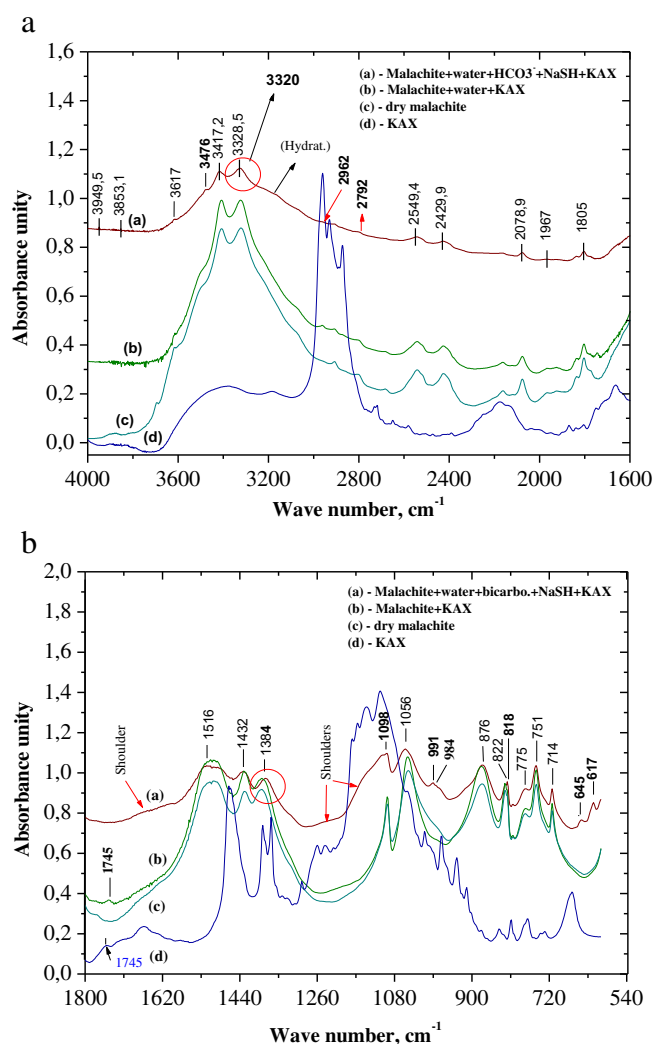
bridging on the carbonate and hydroxyl functional groups. Concerning new infrared bands (1493, 1098, 991, 984, 646 and 617  $\text{cm}^{-1}$ ) which are observed in the fingerprint region of the spectrum of malachite (Fig. 9b), they are in their majority related to stretching and bending vibrations typical of S—O bonds belonging to thiosalts. The concerned chemical species might consist either of products generated by oxidation of the unconsumed reagents namely NaHS and KAX or sulfate ions adsorbed on the mineral surface.

#### 4. Conclusion

The results from the experiments confirm that the locked-cycle recycling of the SMWW during flotation of copper-cobalt oxide ores from the deposit of Luiswishi is inducing the build-up of chemical species in the pulp water dropping dramatically the recoveries of copper and cobalt in the concentrate. The decrease in the flotation efficiency arises due to the synergic depressing effects from calcium, magnesium, bicarbonate ions towards the valuables minerals. Alkaline earth and bicarbonate ions increase the recovery of minerals from gangue in the concentrate at the expense of malachite and heterogenite which minerals undergo an increase in their natural hydrophilicity requesting to add more KAX to the pulp in view enhancing their floatability. The locked-cycle recycling of the SMWW can be implemented successfully during flotation of copper-cobalt oxide ores from the Luiswishi deposit at the condition that the pulp water concentrations of the studied chemical species do not surpass the following limits:  $\text{Ca}^{2+} \leq 20$  mg/L,  $\text{Mg}^{2+} \leq 15$  mg/L, and  $\text{HCO}_3^- < 100$  mg/L (values measured in the SMWW). Otherwise, the concerned chemical species perturb the flotation of malachite and heterogenite due to their exaggerated dissolution and hydration which favor the hydrophilic species adsorption namely thiosalts on their surface. The same chemical species interfere on the sulfidization process and collector adsorption mechanism because they increase their rates of consumption resulting ultimately in poor recoveries of copper and cobalt. The build-up of chemical species in the pulp water also provokes the gangue minerals mechanical entrainment decreasing the concentrate grade in copper and cobalt. Based on these findings, it can be stated that the good description of the valuable minerals behavior in the SMWW presence and the understanding of phenomena implicated in the poor recoveries of copper and cobalt can

**Table 7**  
Results from the leaching tests of malachite and heterogenite in the presence of bicarbonate ions.

| Time (seconds) | Malachite – 1 g in 100 mL    |   | Heterogenite – 1 g in 100 mL |              |                           |               |
|----------------|------------------------------|---|------------------------------|--------------|---------------------------|---------------|
|                | Distilled water<br>Cu (mg/L) | $\text{HCO}_3^-$<br>(10 g/L)<br>Cu (mg/L) | Distilled water              |              | $\text{HCO}_3^-$ (10 g/L) |               |
|                |                              |   | Cu (mg/L)                    | Co (mg/L)    | Cu (mg/L)                 | Co (mg/L)     |
| 30             | 0.560                        | 14.140                                    | 0.058                        | 0.000        | 14.290                    | 1.523         |
| 60             | 0.696                        | 20.000                                    | 0.067                        | 0.005        | 11.586                    | 10.371        |
| 90             | 0.401                        | 15.050                                    | 0.099                        | 0.000        | 12.522                    | 13.694        |
| 120            | 0.295                        | 13.380                                    | 0.107                        | 0.015        | 12.408                    | 11.294        |
| 150            | 0.290                        | 14.710                                    | 0.101                        | 0.032        | 11.632                    | 10.394        |
| 180            | <b>0.262</b>                 | <b>15.150</b>                             | <b>0.100</b>                 | <b>0.157</b> | <b>13.982</b>             | <b>11.789</b> |



**Fig. 9.** a. Functions region of the spectrum of malachite conditioned with the reagents in the presence of  $\text{HCO}_3^-$ . b. Fingerprint region of the spectrum of malachite conditioned with reagents in the presence of  $\text{HCO}_3^-$ .

enable to design the suitable strategies in view enhancing the floatability of malachite and heterogenite during the locked-cycle recycling of process water.

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