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# An Evaluation of Hydroxamate Collectors for Malachite Flotation

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## Abstract

Copper oxide minerals, such as malachite, do not often respond well to traditional copper sulphide collectors, and require alternative flotation schemes. Hydroxamic acid collectors have been suggested as a means to directly float malachite, however, there is limited information on the effect of reagent structure on the performance of these collectors. This paper investigates the effect of five alkyl hydroxamates and two aromatic hydroxamates on the flotation of a synthetic ore composed of malachite and quartz. Zeta potential measurements were used to aid in understanding reagent adsorption onto the surface of the two minerals. The collectors were then evaluated using bench scale flotation results. While zeta potential measurements suggested that all the collectors investigated selectively adsorb onto the surface of malachite, only benzohydroxamic acid and C<sub>8</sub> alkyl hydroxamates were effective collectors in the flotation of malachite. Benzohydroxamic acid was the most selective, however, significantly lower dosages of C<sub>8</sub> alkyl hydroxamates were required to obtain similar malachite recoveries, with minimal increases in quartz recovery. Benzo and octylhydroxamic acid were further examined for the flotation of fine (-38 μm) particles. For fine particle flotation experiments the effect of temperature was also investigated as a means to improve the flotation performance.

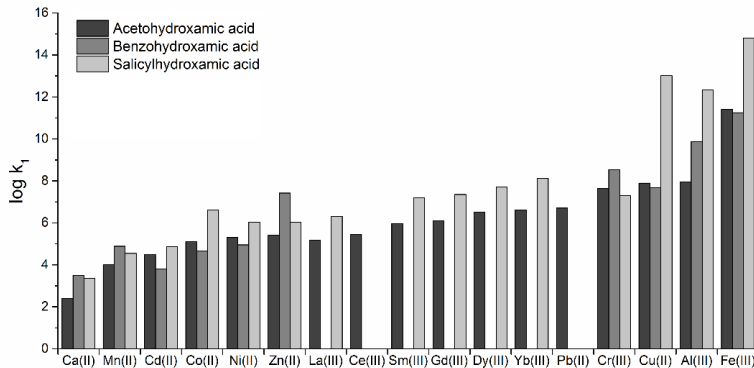
Keywords: Hydroxamates; Malachite; Flotation; Surface Chemistry

## 1. Introduction

The majority of copper is extracted from copper sulphide minerals, however, copper oxide minerals do account for a significant portion of copper production [1]. There are numerous different copper oxide minerals, and in general, more than one is present in a deposit. These minerals are commonly found close to the earth's surface, as they are often the product of the weathering of copper sulphide minerals. One of the more common copper oxide minerals is malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ) [2]. As with most copper oxide minerals, malachite does not respond well to traditional copper sulphide collectors, such as xanthates, and alternative flotation schemes are required [2]. The traditional method of copper oxide flotation involves sulphidising the mineral surface prior to the addition of a copper sulphide collector [2]. The effectiveness of sulphidisation is, however, highly dependant on the dosage of the sulphidising agent. The high degree of dosage control required in plant situations often leads to a poor flotation performance [3-5]. As an alternative to sulphidisation, multiple different oxhydril collectors have been evaluated for the direct recovery of malachite, such as fatty acids [2, 6], amines [2], phosphonic acids [7], phosphinic acids [7] and hydroxamic acids [2, 4, 5, 8, 9]. While all these collectors have been shown to be effective at recovering malachite, they often offer poor selectivity over gangue minerals, especially relative to the selectivity of xanthates in copper sulphide flotation. Hydroxamic acids, however, have been shown to effectively and selectively recover malachite [2, 4, 9]

Hydroxamic acids are a group chelating collectors, capable of forming complexes with specific metal cations at the surface of minerals. The stability constants of hydroxamate-metal complexes vary depending on the metal cation. Figure 1 shows the stability constants for metal complexes with acetohydroxamic acid (AHA), salicylhydroxamic acid (SHA), and benzohydroxamic acid (BHA). The most stable complexes are formed with  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Pb}^{2+}$ , followed by rare earth metal cations; and the weakest complexes are formed with alkaline-earth metal cations [10-13]. Several studies have suggested that the larger the difference in stability constant of the complexes formed with surface cations the greater the selectivity [14, 15]. Other authors, however, believe the selectivity of hydroxamic acid collectors is more closely related to adsorption kinetics [16]. It has been suggested that hydroxamic acid collectors may interact with metal cations in the mineral lattice in two ways: chemisorption and surface reactions [17]. Chemisorption involves coordinate and covalent bonding with the surface metal cation fixed in the mineral lattice. Surface reactions involve the hydrolysis of lattice cations, the formation of hydroxyl-complexes in solution, followed by re-adsorption at the mineral surface; providing sites for hydroxamic acid adsorption. It has been suggested that the kinetics of hydroxamic acid

adsorption through surface reactions are much faster than those through chemisorption, and therefore the selectivity of the collector is strongly related to mineral solubility [16]. More soluble minerals will exhibit faster adsorption kinetics compared to less soluble ones. Another important factor to consider in hydroxamic acid flotation is bulk precipitation, which occurs when the collector reacts with dissolved metal cations in the bulk solution forming undesirable precipitates.



**Figure 1 Stability constants for metal complexes with AHA, SHA and BHA. Adapted from [10-13]**

The use of hydroxamic acids and their salts (collectively referred to as hydroxamates throughout this paper) have been investigated in the flotation of a wide variety of minerals. Table 1 indicates the minerals (grouped by the lattice metal for which the mineral is generally extracted) for which hydroxamate collectors have been shown to be effective, along with the structure of the hydrophobic group of the hydroxamates investigated. Although the use of hydroxamates as flotation collectors has received extensive research, there is limited information available on the effect of hydroxamate structure on flotation. Some work has been conducted investigating the effect of the hydrocarbon chain length of alkyl hydroxamates [18, 19]; suggesting that an improved flotation performance can be achieved with a longer hydrocarbon chain. Others, however, have noted a reduced flotation performance with hydroxamates which have carbon chains higher than C<sub>9</sub> [20]. While the vast majority of the work to date investigating the flotation of minerals with hydroxamate collectors focuses on the use of alkyl hydroxamates, Xia, Hart [21] compared the use of three different aromatic hydroxamates (BHA, SHA and a naphthoyl hydroxamate) in the flotation of a rare earth ore. The authors found that all three collectors were effective at recovering rare earth minerals; however, depending on the rare earth cation present in the mineral lattice each collector resulted in a different flotation response. Later a more extensive study on the same ore was performed, investigating 3 aromatic hydroxamates (BHA,

SHA and tert-butyl benzo hydroxamate), a cyclic alkyl hydroxamate (cyclohexylhydroxamate) and an alkyl hydroxamate [octylhydroxamic acid (OHA)] [22]. It is important to note that there is currently no commercial process for manufacturing tert-butyl benzo hydroxamate; however, all other hydroxamate collectors which were investigated are manufactured commercially. Similar results were obtained to the previous study, however, in this case the authors also indicated that lower dosages of OHA were required to obtain similar recoveries to the other collectors investigated [22]. Similarly, Xia, Hart [23] compared the use of two aromatic hydroxamates (BHA and tert-butyl benzo hydroxamate) to alkyl and cyclic alkyl hydroxamates (OHA and cyclohexylhydroxamate) in the flotation of ilmenite and wolframite. The greatest recovery of ilmenite was obtained with tert-butyl benzo hydroxamate, with recoveries decreasing according to OHA>cyclohexyl hydroxamate>BHA. While tert-butyl benzo hydroxamate was not examined for wolframite flotation, the results differed from ilmenite flotation, with cyclohexyl hydroxamate resulting in the best flotation performance (followed by OHA and then BHA). The authors concluded that while hydroxamate structure plays a significant role on flotation, the selectivity and recovery performance of specific hydroxamate collectors varies depending on the mineral.

With limited information on the effect of reagent structure on the performance of hydroxamate collectors, this paper investigates the effect of five alkyl hydroxamates and two aromatic hydroxamates on a synthetic ore made of malachite and quartz. Zeta potential measurements were used to aid in understanding reagent adsorption to the surface of malachite and quartz. The collectors were then evaluated using bench scale flotation results. Collectors showing the best results were further examined for the flotation of fine (-38  $\mu\text{m}$ ) particles. For fine particle flotation experiments the effect of temperature was also investigated as a means to improve the flotation performance.

**Table 1 Minerals for which hydroxamate collectors have been shown effective**

Lattice Metal	Mineral	Mineral Type	Hydroxamate Hydrophobic Group	Reference
Rare Earth Elements	Bastnäsite	Carbonate	Alkyl	[24, 25]
	Monazite	Phosphate	Aromatic	[26, 27]
Copper	Chrysocolla	Silicate	Alkyl	[14, 24, 28, 29]
	Malachite	Carbonate	Alkyl	[3, 30]
Tin	Cassiterite	Oxide	Alkyl	[5, 8]
			Aromatic	[18]
Niobium	Fersmite	Oxide	Alkyl	[31, 32]
	Pyrochlore	Oxide	Cyclic Alkyl	[33]
Iron	Hematite	Oxide	Aromatic	[33]
			Alkyl	[34]
Manganese	Hubernite	Oxide	Alkyl	[35-37]
	Pyrolusite	Oxide	Alkyl	[10]
	Rhodochrosite	Carbonate	Alkyl	[38]
	Rhodonite	Silicate	Alkyl	[39, 40]
Titanium	Ilmenite	Oxide	Alkyl	[19]
			Cyclic Alkyl	[23, 28]
			Aromatic	[23]
Tungsten	Rutile	Oxide	Alkyl	[14, 28, 29, 41]
			Aromatic	[42]
Tungsten	Sheelite	Tungstate	Aromatic	[43]
			Alkyl	[23, 44, 45]
			Cyclic Alkyl	[23]
Zinc	Sphalerite	Sulphide	Aromatic	[23, 46]
			Alkyl	[47]
Zirconium	Zircon	Silicate	Alkyl	[14, 28, 29]

## 2. Experimental

### 2.1 Materials

Malachite and quartz used for this work were purchased from AMR Mineral and Metal Inc. (Canada) and Daubois (Canada) respectively. Both samples were determined to be pure by X-ray diffraction.

The malachite sample was initially broken into approximately 2-3 cm pieces using a hammer and chisel. The sample was then stage pulverized to produce a -150 +38  $\mu\text{m}$  and -38  $\mu\text{m}$  size fractions for flotation experiments. Quartz was sieved to produce samples with the same size distributions. For zeta potential measurements, -38  $\mu\text{m}$  samples of malachite and quartz were ground wet using a Pulverisette 6

planetary monomill (Fritsch, Germany) to produce very fine particle sizes (malachite  $d_{50} = 3.3 \mu\text{m}$ ,  $d_{80} = 7.0 \mu\text{m}$ ; quartz  $d_{50} = 3.8 \mu\text{m}$ ,  $d_{80} = 6.1 \mu\text{m}$ ). Particle size (equivalent spherical diameter) was determined using a LA-920 particle analyser (Horiba, Japan).

The hydroxamate collectors used in this investigation are shown in Table 2. All collectors were prepared by dissolving the respective solids in deionized water, whereas tetradecylhydroxamic acid (THA) was dissolved in ethanol at a 1:20 mass ratio of THA:ethanol. Hydrochloric acid and sodium hydroxide, used for pH modifications in both zeta potential and flotation experiments, were purchased from Fisher Scientific. For flotation experiments F150 (obtained from Flottec, USA) was used as frother. All reagents were used as provided.

**Table 2 Hydroxamate collectors used in zeta potential and flotation experiments**

Hydroxamate	Abbreviation	Hydrophobic Group	Manufacturer
Benzo	BHA	Benzene ring	Sigma Aldrich (USA)
Salicyl	SHA	Hydroxy-benzene ring	Alfa Aesar (USA)
Aceto	AHA	C <sub>2</sub>	Alfa Aesar (USA)
K-Butyl	PBH	C <sub>4</sub>	Synthesized
Octyl	OHA	C <sub>8</sub>	Synthesized
K-Octyl	POH	C <sub>8</sub>	Synthesized
Tetradecyl	THA	C <sub>14</sub>	Synthesized

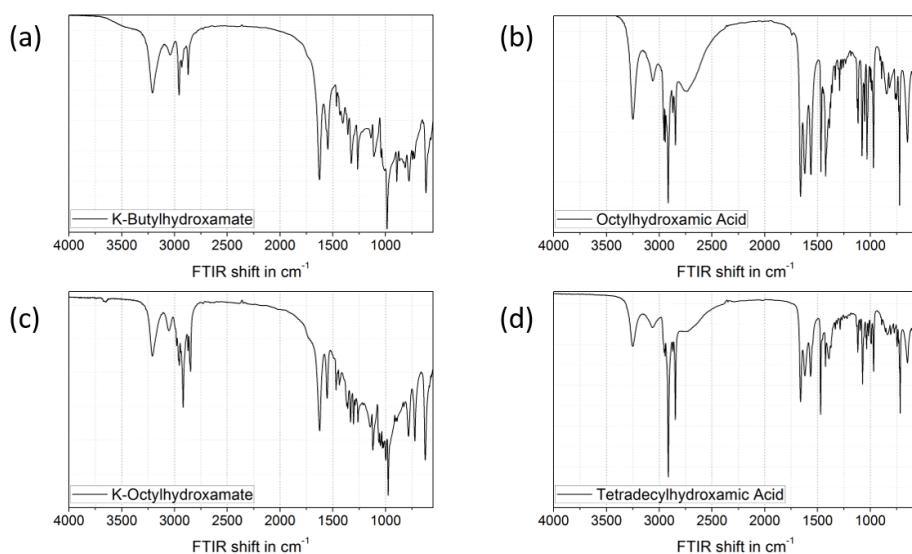
## 2.2 Synthesis of Alkyl Hydroxamate Collectors

The procedures for synthesis of alkyl hydroxamates follow the descriptions in [48] for benzohydroxamic acid, only that the ester reagent ethyl benzoate is replaced by methyl butyrate, methyl octanoate and methyl myristate for synthesis of the butyl hydroxamate, octyl hydroxamate and tetradecyl hydroxamate, respectively. The reactions involved have been discovered and described by Lossen in 1872 [49] and are therefore referred to as "Lossen reactions". All chemicals mentioned below are ACS reagent quality and have been acquired from Sigma Aldrich. For the synthesis of potassium octyl hydroxamate (POH) a solution of 46.7 g (0.67 mol) hydroxyl amine hydrochloride in 240 ml (189.6 g) methanol at 65°C is prepared and slowly cooled to 30°C and added to another solution of 56.1 g (1 mol) potassium hydroxide in 140 ml (110.6 g) methanol which is also cooled to 30°C prior to mixing both solutions. The mixture is placed in an ice bath for 5 min for precipitation of potassium chloride. Subsequently 52.7 g (0.33 mol) of methyl octanoate are added under rigorous stirring. The mixture is then quickly filtered and the filter cake is washed with methanol. The filtrate is put in an Erlenmeyer flask quickly and shut to reduce contact with air. The potassium octyl hydroxamate crystallizes within 48 h in the flask and won by filtration, filtration, washing with ethanol and drying in ambient conditions. Approximately 35 g of hydroxamate salt is synthesized in this way. For the potassium butyl hydroxamate instead of methyl octanoate 0.33 mol (33.7 g) of methyl butyrate are used and for crystallization the methanol content is reduced by evaporation at 70°C. For potassium tetradecyl hydroxamate instead of methyl octanoate 0.33 mol (80 g) of methyl myristate are used and due to strong crystallization the double amount of methanol is used. For synthesis of the hydroxamic acid 0.2 mol of hydroxamate salt

Kommentar [cm1]: Martin

are dissolved in 1.25 mol acetic acid at elevated temperatures until a clear solution is formed. the hydroxamic acid crystallizes at reduced temperatures in an ice bath in the shape of white crystals which are filtered, washed with deionized water and dried. For further purification the hydroxamic acid is dissolved in hot ethyl acetate (4.5 times the amount of the acid). Remaining solids are filtered, the filtrate is cooled down, the hydroxamic acid crystals are filtered and washed with toluene and air dried.

In this way KBH, KOH, OHA and THA have been synthesized and qualitatively analyzed with ATR-FTIR (Tensor 27 from Bruker, Germany equipped with the ATR module MIRacle from PIKE Technologies, USA using a ZnSe reflection crystal). The results are presented in fig. 2.



**Figure 2 ATR-FTIR transmittance results for (a) PBH (b) OHA (c) POH (d) THA**

The signatures correspond very well to the once presented in IR studies on hydroxamic acids and hydroxamates, supporting the findings in [50, 51] and furthermore there is no signatures which correspond to the educts used as reagents in the synthesis procedure. Specific vibrational bands can be assigned using specifically tables 2 and 3 in [51].

### 2.3 Zeta Potential Measurements

Zeta potential measurements are used in flotation research as a technique to understand the surface characteristics of mineral particles and their interactions with reagents. Interested readers should consult Riley [52] for an excellent introduction to the concept of zeta potentials and Fuerstenau and Pradip [53] for an introduction to their application to flotation. A NanoBrook ZetaPlus electrophoretic analyser (Brookhaven Instruments, USA) was used in this work. A detailed explanation of the procedure followed can be found in Jordens, Marion [26]. The pH range investigated was from pH 4 to 10 (with measurements taken in steps of 1 pH units), as at pH values below 4 malachite was fully dissolved in



solution, and above pH 10 is approaching the limitations of the analyser. Particle sizes, measured surface areas [determined by the N<sub>2</sub> Brunauer–Emmett–Teller (BET) technique, using a TriStar Surface Area and Porosity Analyzer (Micromeritics, USA)], and hydroxamate dosages are shown in Table 3 for malachite and quartz.

**Table 3 Hydroxamate dosages used for malachite and quartz zeta potential measurements**

Mineral	Particle Size (d <sub>50</sub> ) (µm)	BET Surface Area (m <sup>2</sup> /g)	Hydroxamate dosage	
			(mol/m <sup>2</sup> )	(mol/ton)
Malachite	3.3	11.2	1.5 x 10 <sup>-4</sup>	1.7 x 10 <sup>3</sup>
Quartz	4.0	5.3	3.2 x 10 <sup>-4</sup>	1.7 x 10 <sup>3</sup>

## 2.4 Flotation

Flotation experiments were conducted on a synthetic malachite ore prepared by mixing 10 g malachite with 90 g quartz. All flotation tests were carried out using a 1.5 L Denver flotation cell operating at 1200 rpm with an air flow rate of 5.6 L/min. For each test, a fresh batch of ore was mixed with tap water in the flotation cell, with the water level adjusted to a set height. The ore was conditioned for 1 min following the addition of collector and pH adjustment. All flotation tests were carried out with 2 drops of F150 added to the cell. Following the conditioning step, the air was turned on and froth was collected after 0.5, 1, 2, 5 and 12 min to produce 5 concentrates. After each concentrate, the pH was readjusted to the desired value and the water level was readjusted to the set height. In all cases flotation experiments were performed in triplicate.

Initial flotation experiments were conducted on synthetic ore samples with a size distribution of -150 +38 µm (d<sub>50</sub> = 115 µm, d<sub>80</sub> = 134 µm). BHA was used as a baseline collector to determine the best pH for flotation. The collector dosage was kept constant with the dosage used in zeta potential measurements, on a basis of mol of collector per m<sup>2</sup> of malachite (1.5 x 10<sup>-4</sup> mol/m<sup>2</sup><sub>malachite</sub>, 3.65 mol/ton<sub>ore</sub>). Following this investigation, the pH was kept constant and each collector was tested. Collector concentrations were kept constant on a basis of mol/ton. Concentrates were analysed using a Frantz Isodynamic Separator (Frantz, USA) to magnetically separate malachite from quartz.

Due to the complexity of some ore bodies, requiring fine grinding to liberate valuable minerals, further investigation into the flotation of fine particles was performed using the hydroxamate collectors which showed the most promising results. Flotation experiments were conducted on -38 µm samples (d<sub>50</sub> = 18 µm, d<sub>80</sub> = 30 µm), to investigate the effect of particle size on flotation performance. For fine particle flotation experiments the effect of temperature was also investigated as a means to improve the

**Kommentar [RM(-12):** it is for zeta potential studies not useful to use mol/ton as a measure for the reagent concentration but rather mol/l, at least you need to mention on the particle concentrations used

**Kommentar [RM(-13):** can this be transferred to an actual amount?

**Kommentar [RM(-14):** is there a study that used a similar approach, because as a reviewer I would ask why it was done in this way ... I mean, it does make sense, however, it is not typically seen

flotation performance. Heated flotation tests were conducted by placing the flotation cell in a hot water bath, heated using a HS30 hotplate (Torrey Pines Scientific, USA) equipped with PID temperature control to keep the temperature of the slurry inside the flotation cell at a constant 60 °C ( $\pm 5$  °C). Water added to the cell throughout the test was added as hot tap water to avoid large fluctuations in temperature. As the particles were too fine for effective separation using the Frantz Isodynamic Separator, samples produced from fine particle flotation experiments were analysed using an AA240FS Fast Sequential Atomic Absorption Spectrometer (Varian, USA). Prior to analysis, representative 0.2 g samples were taken from concentrates and tailings. Standard sampling processes described by Gy [54] were followed and three samples were taken from each test to limit the sampling error. Samples were digested in 15 ml hydrochloric acid and diluted 100 times. The resulting solutions were examined for copper content. An average of the three assays was used to determine the copper content. The copper concentration from each sample was then compared to the copper concentration of a pure malachite sample to determine malachite content.

### 3. Results and Discussion

#### 3.1 Zeta Potential Measurements

The zeta potential results of malachite and quartz in the presence and absence of collectors are shown in Figures 3-5. The electrophoretic zeta potential data has been presented as a fitted trendline (third order polynomial), with calculated confidence intervals about the trendline. An explanation of the approach used to calculate the confidence intervals can be found in Marion, Jordens [55]. Figure 3 displays the zeta potential trend for the two minerals without collectors. The data for quartz displays a negative trend across the pH range investigated, corresponding well to previous work [56-59]. The malachite studied has an isoelectric point (IEP) at pH 7.8, which is consistent with work by Le Normand, Salman [5] (IEP 7.9) and Li, Zhong [7] (IEP 8.3); however, other authors have reported an IEP much closer to pH 9 [6, 60]. The shift to a higher pH may be due to insufficient conditioning prior to taking measurements. Le Normand, Salman [5] suggested that since dissolved CO<sub>2</sub> can produce potential determining ions for malachite, insufficient conditioning would not allow the suspension to reach an equilibrium with the atmospheric CO<sub>2</sub> resulting in the IEP to shift to a higher pH value. Another possible explanation for the differences in IEP may be due to differences in solids concentration used in each study. Mineral dissolution and the resultant differences in potential determining ion content in the bulk is likely to have a significant effect on the zeta potential trend of malachite. Other authors have shown that an increase in solids content, when measuring the zeta potential of bastnäsite [26] and muscovite

**Kommentar [RM(-15):** you should additionally discuss the following points which would demand an explanation (if I were the reviewer):

1. what is the reason for the maximum of the malachite curve? (answer would be referring to the dissolution behaviour)
2. why is this maximum diminished by the action of the collectors? (answer would be that the dissolved copper ions form complexes with the hydroxamic species!?)
3. (see next comment)

[61], resulted in a shift in IEP to a higher pH. Figures 4 and 5 show the results for malachite and quartz in the presence of the seven different hydroxamate collectors. It can be seen from Figure 4 that the addition of all of the collectors has a significant effect on the zeta potential of malachite, suggesting adsorption to the mineral surface. Figure 5 shows that the reagents have little effect on the zeta potential of quartz, suggesting that the hydroxamate collectors are not adsorbing onto the surface of quartz and selective flotation of malachite would be possible. While there is a minor shift in zeta potential trend obtained for quartz in some cases, which may suggest collector adsorption, it is likely a result of electrical double layer compression due to the high collector concentrations added to the suspension; as previous investigations in literature have suggested there is little to no interaction of hydroxamate collectors with quartz [26, 62].

**Kommentar [RM(-16):** why are you not discussing differences with the different collectors?

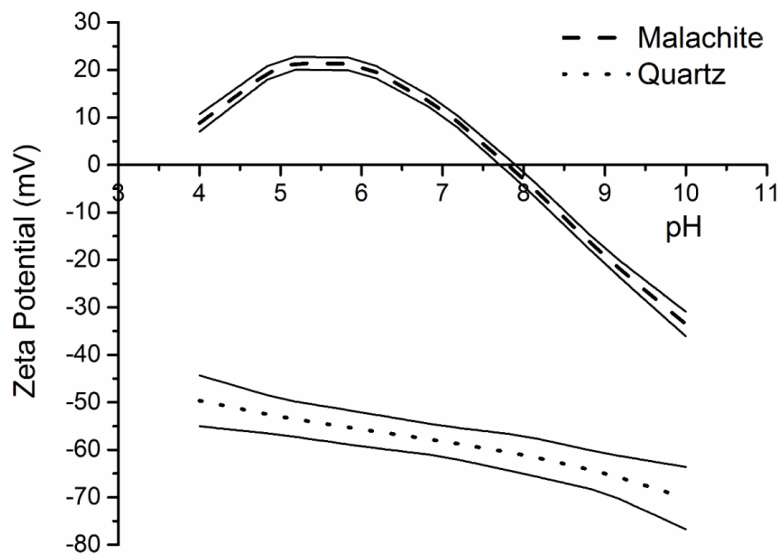


Figure 3 Zeta potential trend of malachite and quartz in  $10^{-3}$  mol/L KCl (Error intervals shown are 95 % confidence intervals)

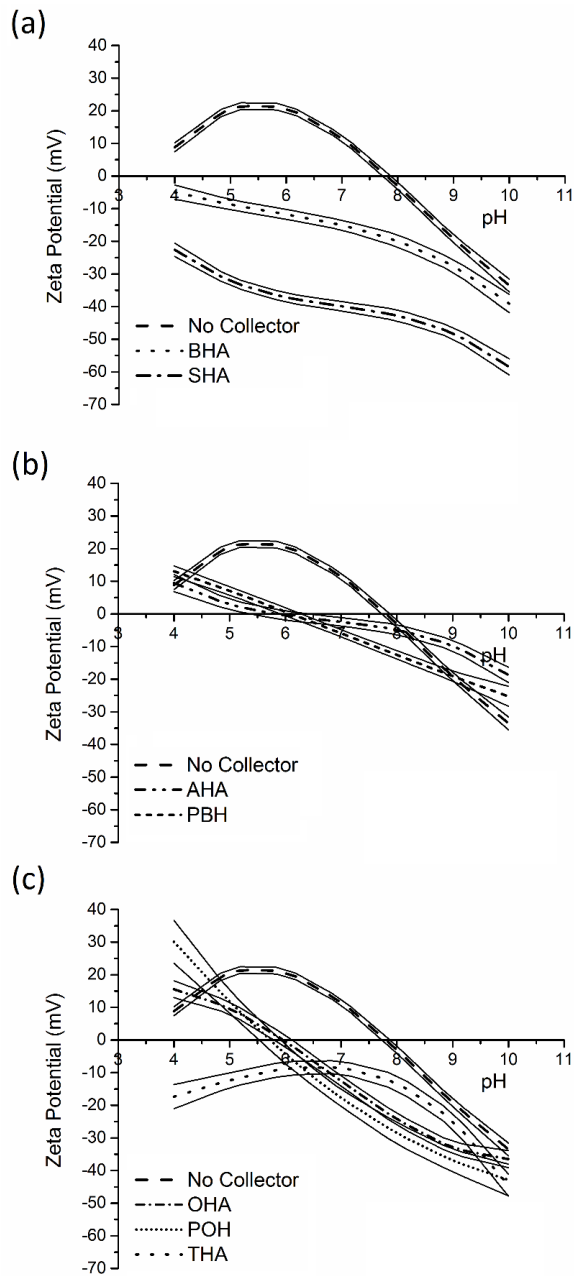


Figure 4 Zeta potential trend of malachite in the presence and absence of (a) aromatic, (b) short chain alkyl ( $C_2$  and  $C_4$ ) and (c) long chain alkyl ( $C_8$  and  $C_{14}$ ) hydroxamates at a concentration of  $1.7 \times 10^{-3}$  mol/ton (Error intervals shown are 95 % confidence intervals)

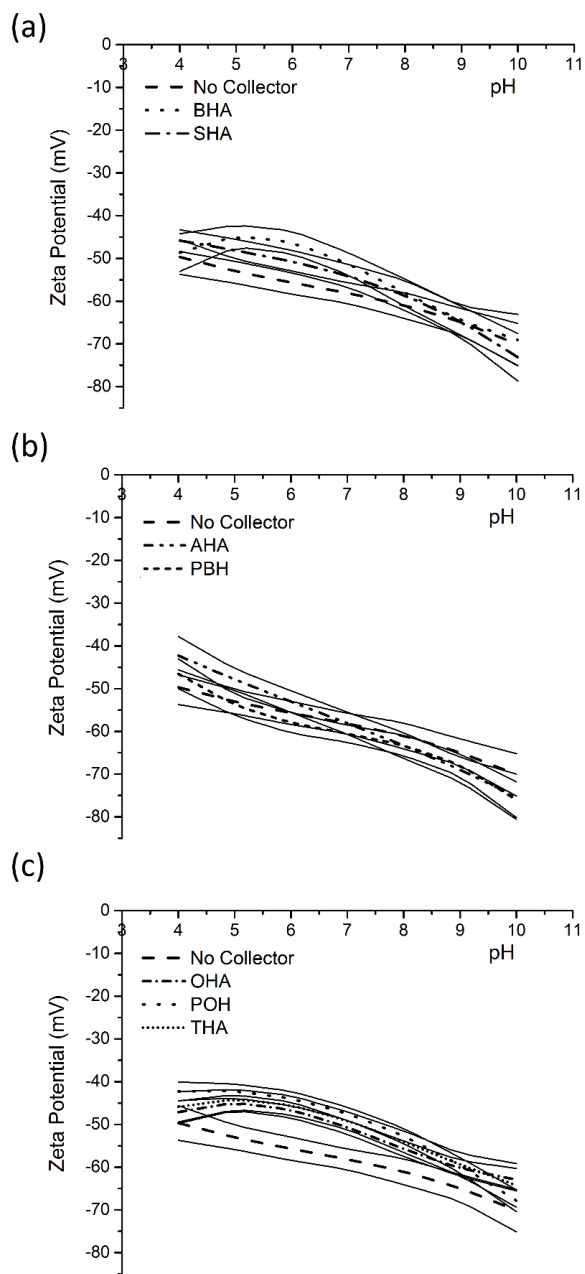


Figure 5 Zeta potential trend of quartz in the presence and absence of (a) aromatic, (b) short chain alkyl ( $C_2$  and  $C_4$ ) and (c) long chain alkyl ( $C_8$  and  $C_{14}$ ) hydroxamates at a concentration of  $1.7 \times 10^3$  mol/ton (Error intervals shown are 95 % confidence intervals)

## 3.2 Froth Flotation

### 3.2.1 Effect of pH

In order to properly evaluate the flotation performance of the different collectors at various conditions, both the recovery and rate of recovery of malachite and quartz must be considered. To determine the effect of pH using BHA as collector, the recovery data obtained from flotation experiments at each condition were fit to a first-order rate model of the form [63]:

$$R = R_{\max}(1 - e^{-kt}) \quad (1)$$

Where R is the recovery (%) at time t (min),  $R_{\max}$  is the maximum possible flotation recovery and k is the flotation rate constant ( $\text{min}^{-1}$ ). Statistical software, Stata13 (StataCorp, USA), was used to perform non-linear regressions, outputting  $R_{\max}$  and k for each condition (shown in Table 4). Recovery vs. time plots (Figure 6) were generated by substituting  $R_{\max}$  and k back into Equation 1. Examining Figure 6 and the k and  $R_{\max}$  values obtained for each condition (detailed in Table 4) it can be seen that the best flotation results were obtained at pH 8; with a decrease in malachite recovery and flotation rate kinetics obtained at both pH 6 and 9. An increase in quartz recovery was also observed at pH 6. For semi soluble minerals, such as malachite, it has been suggested that hydroxamate-mineral interactions occur mainly through surface reactions and bulk precipitation [17]. Therefore, the aqueous speciation of malachite plays a crucial role in collector adsorption. Le Normand, Salman [5] provide an excellent explanation for the observed reduction in flotation performance at pH 6. The authors suggest that below pH 6,  $\text{Cu}^{2+}$  is the predominant ion in solution, which results in the precipitation of cupric hydroxamate; depleting the collector species available for malachite flotation. In this case, an increase in quartz recovery was also observed, most likely due to cupric hydroxamate adsorbing/precipitating on the surface of quartz, thus causing it to float. The hydroxamate collector may also be directly adsorbing on to the surface of quartz at pH 6; which may explain the observed shift in the zeta potential of malachite when in the presence of benzohydroxamic acid at this pH (Figure 5a, Section 3.1). The similar recoveries observed at pH 6 and 9, however, are contradictory to the work by Le Normand, Salman [5], who reported that the best recovery of malachite with a POH collector occurred at pH 9 (pH 8 was not investigated). The authors do however suggest that  $\text{CuOH}^+$  and  $\text{HCO}_3^-$  ions are beneficial to malachite flotation. The concentration of both ions are higher at pH 8 than 9, which may be an explanation to the improved flotation performance at pH 8. In other mineral systems an increased concentration of metal hydroxyl species has been suggested to result in an improved flotation performance [16]; suggesting that  $\text{CuOH}^+$  ions may have a larger effect than  $\text{HCO}_3^-$  ions on malachite flotation. Another explanation for the poor flotation performance at pH 9

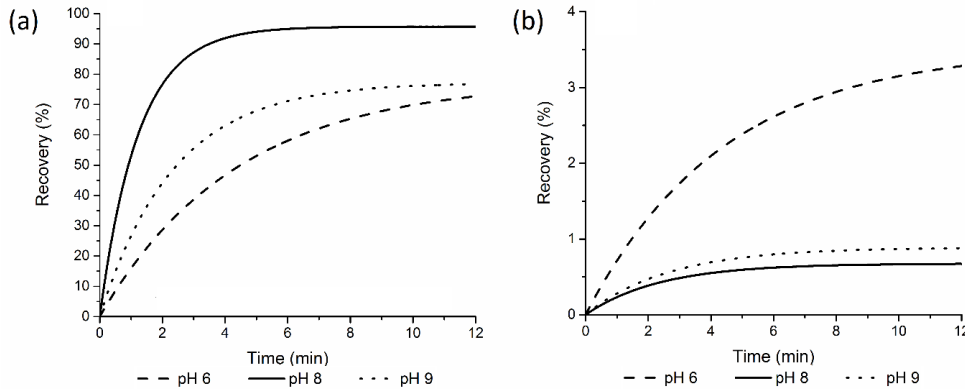
**Kommentar [RM(-17):** there is no mentioning on any froth effects, which could explain differences in the selectivity as well ... are there differences in the froth behaviours with respect to the different collectors used?

**Kommentar [RM(-18):** where are the variations of your results visible? (see comment below)

**Kommentar [RM(-19):** above you mention that you perform flotation in triplicates but you don't mention on the accuracy of the data in fig. 6 and table 4. How big are the variations here?

**Kommentar [RM(-110):** this causality I don't understand, what would then be the mechanism of collector adsorption on quartz?

may be due to the electrostatic repulsion of the negatively charged mineral surface (Figure 3, Section 3.1) and collector.



**Figure 6 (a) Malachite and (b) quartz recovery at pH 6, 8 and 9, using BHA as collector. Recovery vs. time curves were generated from the first-order flotation rate model**

**Table 4 Output of non-linear regression fitting to first-order rate equation for malachite and quartz using BHA at pH 6, 8 and 9**

pH	Malachite				Quartz			
	k (min <sup>-1</sup> )	R <sub>max</sub> (%)	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	k (min <sup>-1</sup> )	R <sub>max</sub> (%)	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>
6	0.23	77.6	0.97	0.97	0.23	3.51	0.99	0.99
8	0.81	95.7	0.99	0.99	0.42	0.68	0.87	0.86
9	0.42	77.2	0.99	0.99	0.38	0.89	0.96	0.95

### 3.2.2 Effect of Hydroxamate Structure

The mass recovery obtained using all seven hydroxamate collectors at pH 8 can be observed in Figure 7. The results show that short chain (C<sub>2</sub> and C<sub>4</sub>) alkyl hydroxamates and SHA resulted in very low mass recoveries. While zeta potential measurements suggest that these collectors selectively adsorb onto the surface of malachite, an increase in collector dosage is likely required for these collectors to be effective. Since OHA and POH recovered nearly all the mass at the initial concentration investigated (3.65 mol/ton), the dosage was reduced to 0.13 mol/ton to obtain mass recoveries much closer to the concentration of malachite in the flotation feed. The recovery of quartz using these two collectors may suggest that the observed shift in zeta potential (Figure 4c, Section 3.1) could be due to collector adsorption onto the mineral surface. THA was initially examined at 0.13 mol/ton, as the reduced

collector dosage provided reasonably good results when using the two C<sub>8</sub> alkyl hydroxamate collectors. However, low mass recoveries were obtained and the collector dosage was increased to 0.21 mol/ton.

Malachite and quartz recovery data, for flotation with the different hydroxamate collectors (concentrates produced using SHA, AHA and PBH were not examined due to low mass recoveries), were fitted to the first-order rate kinetic model (Equation 1, Section 3.2.1). The  $k$  and  $R_{max}$  values obtained for each condition can be seen in Table 5 and the recovery vs. time curves generated can be seen in Figure 8. Comparing the results, it can be seen that flotation with BHA resulted in the greatest recovery of malachite and lowest recovery of quartz. However, similar malachite recoveries and a significant increase in flotation rate constant were observed with significantly lower dosages of OHA and POH. Both collectors, however, resulted in similar increases in quartz recovery when compared to flotation with BHA. The lower dosages required with the two C<sub>8</sub> alkyl hydroxamates is consistent with work by Hart, Dimov [22], who observed a similar trend when comparing OHA to aromatic and cyclic alkyl hydroxamates for the flotation of a rare earth ore.

As a change in collector results in changes in both  $R_{max}$  and  $k$  for both minerals comparing the selectivity of BHA to the two C<sub>8</sub> alkyl hydroxamates becomes challenging. One way of comparing total flotation response is by using the modified rate constant introduced by Xu [64]; defined as the product of  $R_{max}$  and  $k$ :

$$K_m = R_{max} \times k \quad (2)$$

Based on this modified rate constant, a selectivity index (or relative rate constant) between malachite and quartz can be defined as the ratio of their modified rate constants [64]:

$$SI \left( \text{malachite} / \text{quartz} \right) = \frac{K_m \text{ of malachite}}{K_m \text{ of quartz}} \quad (3)$$

Modified rate constants and selectivity indices can be seen in Table 5. The selectivity indices obtained under each condition suggest that BHA is the most selective collector, however, the drastic decrease in collector concentration required when using OHA or POH may outweigh these improvements in selectivity. The results also indicate that there is little difference in flotation performance when using the C<sub>8</sub> alkyl hydroxamate in its acid or salt form, suggesting that the use of hydroxamic acids vs hydroxamate salts does not affect flotation. THA resulted in poor malachite recoveries; corresponding well to previous work, which has suggested that a reduced flotation performance is obtained when using alkyl hydroxamates with a carbon chain longer than C<sub>9</sub> [20].



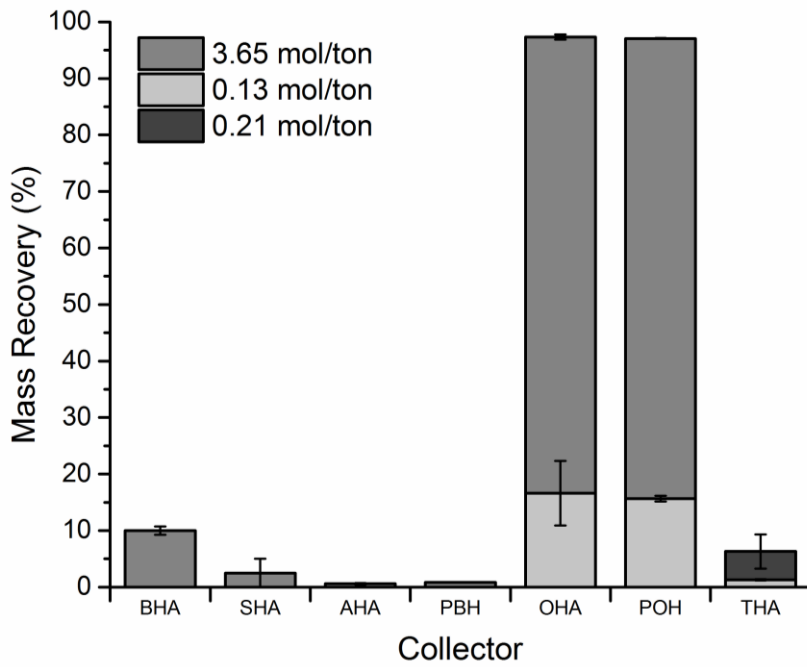


Figure 7 Mass recoveries obtained using the 7 different hydroxamate collectors. Error bars are 95 % confidence intervals

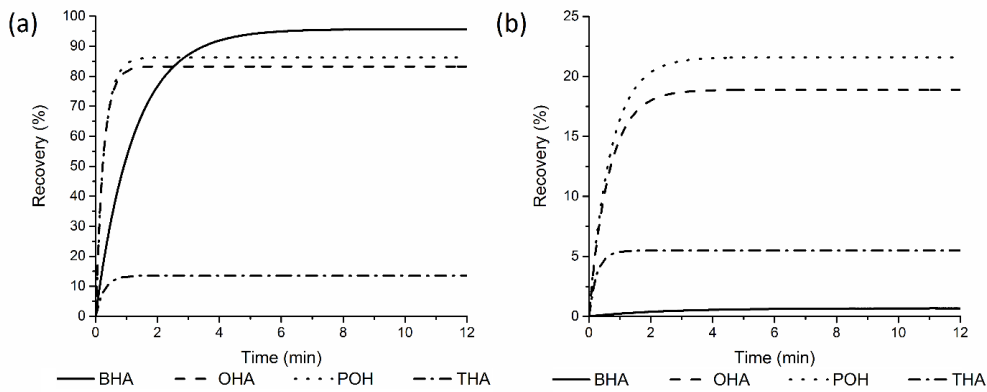


Figure 8 (a) Malachite and (b) quartz recovery with BHA, OHA, POH and THA at pH 8. Recovery vs. time curves were generated from the first-order flotation rate model

**Table 5 Output of non-linear regression fitting to first-order rate equation for malachite and quartz using BHA, OHA, POH, THA**

Collector	Malachite					Quartz					SI <sub>(malachite/quartz)</sub>
	k (min <sup>-1</sup> )	R <sub>max</sub> (%)	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	K <sub>M</sub>	k (min <sup>-1</sup> )	R <sub>max</sub> (%)	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	K <sub>M</sub>	
BHA	0.81	95.7	0.99	0.99	77	0.42	0.7	0.87	0.86	0.3	272
OHA	3.98	83.3	0.99	0.99	332	1.53	18.8	0.96	0.95	29	12
POH	3.91	86.3	0.99	0.99	316	1.42	21.6	0.93	0.92	31	10
THA	3.67	13.5	0.90	0.89	50	3.91	5.5	0.91	0.90	21	2

### 3.2.3 Effect of Particle Size

The effect of particle size on flotation was examined using BHA and OHA as collectors. All other hydroxamate collectors demonstrated a poor flotation performance and therefore were not tested further. POH was not examined as the hydroxamate salt offered little difference in flotation response to OHA. The results obtained from fitting the recovery data obtained after floating the synthetic feed (sized at -38 μm) with both collectors to the first-order rate model (Equation 1, Section 3.2.1) are shown in Table 6 and the recovery vs time plots can be seen in Figure 9 and 10 for BHA and OHA respectively. The results indicate a decrease in malachite recovery and flotation kinetics when compared to coarse particle flotation tests for both collectors; as well as a significant increase in quartz recovery for flotation using BHA. It is well established that the flotation of fine particles often results in a reduction in flotation performance. This reduction in performance is explained by multiple different physical and chemical sub-processes such as: the increased consumption and non-selective adsorption of reagents as a result of higher surface energies and surface areas [65-68]; the increased recovery by non-selective entrainment [66-69]; and a decrease in flotation kinetics and recovery due to a decreased probability of collision between particles and bubbles [66, 67, 70-74].

As a means to improve the flotation response when floating fine particles, the effect of elevated temperatures on flotation was examined. It has been suggested that flotation at elevated temperatures with hydroxamate collectors leads to a more selective and enhanced adsorption of the collector at the mineral surface; resulting in improvements in both grade and recovery [75]. The results from flotation experiments conducted at 60 °C are shown in Table 6 and Figures 9 and 10. Significant improvements in flotation are observed with BHA. While there are no improvements in total malachite recovery, the rate of malachite recovery is significantly improved and quartz recovery has decreased. These improvements are likely a result of the increased solubility of malachite at elevated temperatures resulting in faster adsorption kinetics. Flotation using OHA at elevated temperatures resulted in mixed results. Slight

improvements in selectivity were observed due to reductions in both the recovery and rate of recovery of quartz, however, a decrease in malachite recovery was also observed. While more work is required to determine why malachite flotation is reduced when using OHA, one explanation may be that the increased malachite solubility results in a more elevated concentration of  $\text{Cu}^{2+}$  ions in solution, and this coupled with the rapid reaction kinetics of OHA results in an increase of the bulk precipitation of copper-hydroxamate species reducing the concentration of collector available for malachite flotation. As the concentration of OHA (0.21 mol/ton) is significantly lower than that of BHA (3.65 mol/ton) the consumption of collector by bulk precipitation may have a much more significant effect on flotation.

Comparing the flotation rate constants obtained for the two minerals at each condition (Table 6), the flotation rate constant for malachite is significantly higher than that of quartz, indicating the possibility of selectively separating malachite from quartz by exploiting differences in flotation kinetics. By plotting the cumulative recovery of quartz as a function of cumulative malachite recovery (Figure 11), an optimal flotation time can be determined. When using BHA as collector, flotation for longer than 5 min results in limited improvements in malachite recovery and when floating fine particles significant increases in quartz recovery. At elevated temperatures flotation for 2 min is sufficient to maximize malachite recovery while limiting quartz recovery. When using OHA, flotation kinetics are much faster and the majority of the malachite is recovered after 1 min for coarse particles and 2 min for fine particles, with longer flotation times resulting in significant increases in quartz recovery. The grade and recovery of malachite at optimal flotation times for each condition are compared to those obtained after 12 min of flotation in Table 7. It can be seen that significant improvements in grade, with limited reductions in recovery can be obtained by taking into account the rate of recovery of each mineral.

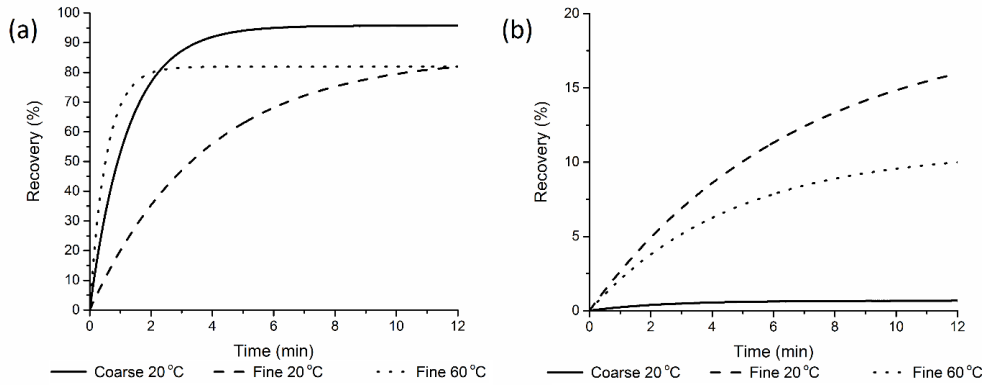


Figure 9 (a) Malachite and (b) quartz recovery for coarse (-150 +38  $\mu\text{m}$ ) and fine (-38  $\mu\text{m}$ ) particle flotation, using BHA at 20 and 60 °C. Recovery vs. time curves were generated from the first-order flotation rate model

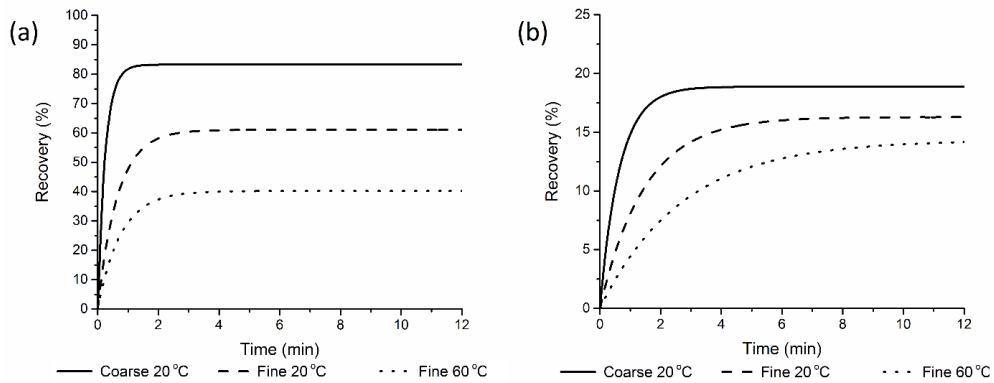


Figure 10 (a) Malachite and (b) quartz recovery for coarse (-150 +38  $\mu\text{m}$ ) and fine (-38  $\mu\text{m}$ ) particle flotation, using OHA at 20 and 60 °C. Recovery vs. time curves were generated from the first-order flotation rate model

Table 6 Output of non-linear regression fitting to first-order rate equation for coarse and fine particle flotation experiments at 20 °C and 60 °C

Collector	Particle Size (µm)	Temperature (°C)	Malachite					Quartz					SI (Malachite /Quartz)
			k (min <sup>-1</sup> )	R <sub>max</sub> (%)	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	K <sub>M</sub>	k (min <sup>-1</sup> )	R <sub>max</sub> (%)	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	K <sub>M</sub>	
BHA	-150 +38	20	0.81	95.7	0.99	0.99	77.1	0.42	0.68	0.87	0.86	0.28	272
	-38	20	0.27	85.4	0.98	0.98	22.7	0.15	19.2	0.99	0.99	2.84	8
	-38	60	1.82	81.9	0.99	0.99	149.5	0.22	10.8	0.97	0.97	2.33	64
OHA	-150 +38	20	3.98	83.3	0.99	0.99	331.8	1.53	18.8	0.96	0.95	29	12
	-38	20	1.52	61.0	0.99	0.99	92.6	0.68	16.3	0.98	0.98	11.1	8
	-38	60	1.31	40.2	0.99	0.99	52.8	0.37	14.3	0.97	0.97	5.28	10

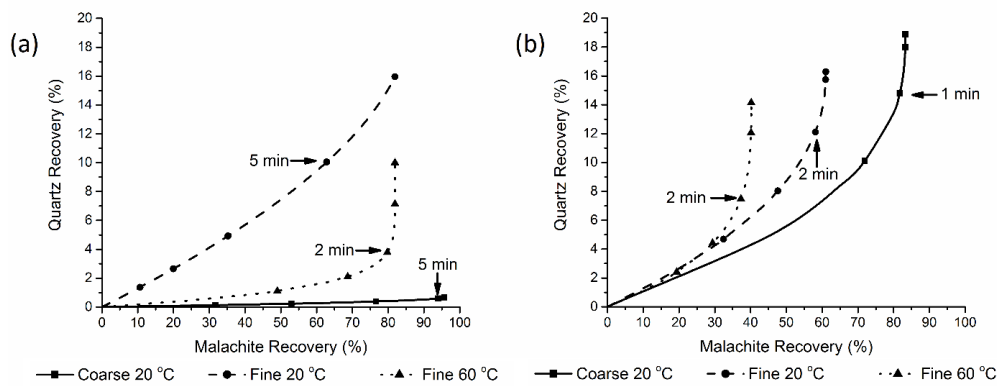


Figure 11 Plot of cumulative malachite recoveries as a function of cumulative quartz recoveries for coarse (-150 +38 µm) and fine (-38 µm) particle flotation, using (a) BHA and (b) OHA as collectors. Data points indicate times where flotation concentrates were taken (0.5, 1, 2, 5 and 12 min)

Table 8 Cumulative grade and recovery of malachite at optimal flotation times and 12 minutes

Collector	Particle Size (µm)	Temperature (°C)	Optimal Flotation Time			12 Minutes	
			Time (min)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)
BHA	-150 +38	20	5	95	94	94	96
	-38	20	5	41	63	36	82
	-38	60	2	70	80	48	82
OHA	-150 +38	20	1	38	82	33	83
	-38	20	2	34	58	29	61
	-38	60	2	35	37	24	40

## 4. Conclusions

This work investigated the separation of malachite from quartz using seven different hydroxamate collectors. The investigation included zeta-potential measurements to understand reagent interactions with malachite and quartz; and bench scale flotation experiments on a synthetic malachite ore to evaluate the differences in malachite recovery and selectivity obtained with each collector. The hydroxamate collectors showing the best results were further evaluated for fine particle flotation at both 20 and 60 °C to determine the effects of particle size and temperature on flotation. The conclusions are as follows:

1. Zeta potential measurements suggest that all seven hydroxamate collectors investigated selectively adsorb onto the surface of malachite
2. BHA and the two C<sub>8</sub> alkyl hydroxamates result in the best flotation response; with all other collectors resulting in low malachite recoveries.
3. The greatest malachite selectivity can be achieved using BHA, however, similar malachite recoveries and significantly higher flotation kinetics were observed with much lower concentrations of the two C<sub>8</sub> alkyl hydroxamates
4. OHA and POH result in a similar flotation performance; suggesting that the use of hydroxamic acids vs hydroxamate salts does not affect flotation results
5. Significant reductions in flotation performance using both BHA and OHA were observed when floating fine particles; with elevated temperatures offering significant improvements in flotation when using BHA but not OHA
6. Flotation kinetics are generally fast when using hydroxamate collectors; and the selective separation of malachite from quartz can be optimized by exploiting differences in flotation kinetics

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