

Received April 24, 2018; reviewed; accepted June 10, 2018

## Oil-assisted flotation of fine hematite using sodium oleate or hydroxamic acids as a collector

Hao Li<sup>1</sup>, Mingxia Liu<sup>2</sup>, Qi Liu<sup>1</sup>

<sup>1</sup> Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 1H9

<sup>2</sup> School of Minerals Processing and Bioengineering, Central South University, Changsha, Hunan, P.R. China 410083

Corresponding author: [qi.liu@ualberta.ca](mailto:qi.liu@ualberta.ca) (Qi Liu)

**Abstract:** Micro-flotation and batch flotation tests were carried out on fine (-20 μm) hematite to investigate the influences of non-polar oil when sodium oleate, octyl hydroxamic acid, or oleoyl hydroxamic acid was used as a collector. Both micro-flotation and batch flotation tests were performed using single hematite mineral and/or artificial mixed minerals (hematite:quartz = 1:1), and kerosene was utilized as the neutral oil. The experimental results showed that the addition of a kerosene emulsion benefited hematite recovery in the micro-flotation tests where a froth layer did not exist. In the batch flotation where a froth layer existed, kerosene behaved differently when used in conjunction with the three collectors. Kerosene helped improve the batch flotation when sodium oleate or oleoyl hydroxamic acid was used as a collector. However, it reduced concentrate weight yield, grade and recovery to a noticeable extent when octyl hydroxamic acid was used as a collector, especially at low dosages. In addition, single hematite batch flotation kinetics tests coupled with water recovery measurement were carried out to study the roles of kerosene at different collector dosages. It was observed that water drainage and the resulting froth destabilization by kerosene was dominant at low collector dosages, especially in the flotation using octyl hydroxamic acid. At higher collector dosages, the water drainage and froth destabilization effect by kerosene was possibly counter-balanced by the higher hematite surface hydrophobicity and bubble surface tension gradient, which led to more stable froth layer.

**Keywords:** Micro-flotation, Batch Flotation, Hematite, Kerosene, Sodium oleate, Octyl hydroxamic acid, Oleoyl hydroxamic acid

### 1. Introduction

The minerals industry is facing a steady decline in ore grade, compounded by increasing complexity of mineral dissemination. As a result, the ore has to be ground sufficiently fine to have a suitable degree of mineral liberation, which produces large percentages of fine and ultrafine particles outside of optimal size range for ore dressing. Due to the unique characteristics of fine particles, i.e., small mass, high specific surface area, and the resulting problems such as increased solubility of complex minerals (Finkelstein, 1997; Fornasiero and Ralston, 2005), high reagent consumption, fast surface oxidation in the case of sulfides (Klassen and Mokrousov, 1963; Collins and Read, 1971), severe particle entrainment (Neethling and Cilliers, 2002; Zheng et al., 2006; Neethling and Cilliers, 2009), low flotation rates (Ye and Miller, 1988; Santana et al., 2008), slime coating (Parsonage, 1984; Mitchell et al., 2005), etc., flotation performance of these finely ground ores is typically poor in terms of low concentrate grade and value mineral recovery.

Extensive research efforts have been made in the past several decades to deal with these problems, and some novel flotation methods have been proposed (Rao, 2004), including electro-flotation (Miettinen et al., 2010), dissolved air flotation (Solari, 1980; Rubio et al., 2003), column flotation (Yoon et al., 1989; Li et al., 2003; Sobhy and Tao, 2013). In these flotation processes, fine bubbles are generated to increase their collision and adhesion efficiencies with fine and ultrafine mineral particles. Another

school of thought has focused on particle size enlargement (Mathur et al., 2000; Laskowski, 2001; Song et al., 2001), which was accomplished by aggregation of fine mineral particles into floatable flocs by adding collectors, polymeric electrolytes and non-polar oils. The intensifying effects of non-polar oil in the flocculation process was proved successful in several reports (Laskowski, 1992). Hydrophobicity enhancement and oil bridging are the two major roles played by non-polar oils in hydrophobic flocculation (Dai and Lu, 1991; Song et al., 2002). To be specific, the intrinsic hydrophobic properties of non-polar oils in an aqueous minerals suspension allow it to preferentially attach and spread on the surface of naturally or collector-induced hydrophobic particles, leading to a coating of oil layer and higher hydrophobicity. In addition, this "hydrophobic force" was stronger than van der Waals force within a very short range of particle separation (Israelachvili and Pashley, 1984; Pashley et al., 1985). As a result, the energy barrier of the interaction forces between two particles was significantly lowered, benefiting particles bridging into larger and stronger aggregates.

Unless the oil droplets and mineral surfaces carry opposite charges, whether oil droplets attach to mineral particles or not is determined by the hydrophobicity of particle surfaces. Naturally hydrophobic minerals, such as native gold, coal, and molybdenite, can be recovered by froth flotation simply with non-polar oils as collectors in the absence of surfactant collectors (O'Connor and Dunne, 1994; Zanin et al., 2009; Song et al., 2012; Barraza et al., 2013). For oxide minerals with hydrophilic surfaces, collectors are necessary prior to particle-oil droplet interactions. The choice of collectors to alter mineral surface wettability is therefore important in the oil-assisted separation process. Sodium oleate (NaOl), salt of long hydrocarbon chain fatty acid, is the most extensively used anionic collector in oxide mineral flotation due to its strong collecting capability. When used in conjunction with non-polar oils, enhanced performances were observed in a number of studies involving hematite (Song and Lu, 1994; Song et al., 1999), rhodochrosite (Lu et al., 1988), calcite (Sadowski, 1994), talc (Ozkan et al., 2016) and apatite (Sis and Chander, 2003). In addition to sodium oleate, long-chain petroleum sulfonates, amines, and tall oil are also widely used, alone or in combination with non-polar oils, to float fine oxide minerals (Liu et al., 2014; Wang, 2016).

However, it is worth noting that in many reported studies regarding oil-assisted flocculation-flotation processes, many efforts have been devoted to characterizing flocculation performance to emphasize non-polar oil's interactions with minerals, rather than the froth flotation. In addition, the most widely used collectors in oil-assisted flocculation-flotation of oxidized minerals were sodium oleate and long-chain amines with more than 12 carbon atoms. Ni (2013) attempted to enhance the flotation performance of pyrochlore from a niobium ore with octyl hydroxamic acid (OHA) by adding kerosene, but observed a sharp decrease in pyrochlore recovery and grade upon the addition of kerosene. The authors are unaware of any publications in the open literature that report effective flocculation-flotation with non-polar oil when collectors have less than 10 carbons to deal with oxidized minerals.

The aim of this work is to use micro-flotation and conventional batch flotation method to investigate the role of non-polar oil in fine hematite flotation using sodium oleate and octyl hydroxamic acid. To decouple the effects of chain length and functional polar (ionizable) groups, oleoyl hydroxamic acid (OLHA), which has the same hydrocarbon tail as sodium oleate but has hydroxamic acid as the polar group, was synthesized and used in this study. The flotation efficiency and kinetics are measured to assess the differences of the three collectors in oil-assisted flotation of the fine hematite.

## 2. Materials and methods

### 2.1. Materials

High purity hematite mineral sample used in this study was obtained from a spiral concentrate stream of an iron ore mine from eastern Canada. The hematite sample was wet ground in a laboratory 20 cm diameter ball mill, and wet screened to collect the -20  $\mu\text{m}$  fraction for testing. Distilled water was used during grinding and sieving. The sieved -20  $\mu\text{m}$  fraction was decanted, filtered, dried and homogenized. A high purity -15  $\mu\text{m}$  quartz sample was purchased from US Silica and used in flotation without any treatment. Table 1 shows the chemical composition of the hematite sample determined by whole rock analysis.

Table 1. Chemical composition of hematite and quartz

Components	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO
Hematite	4.44	0.11	90.94	<0.01	0.01	<0.01	0.03	0.02	<0.01	3.65
Quartz	99.52	0.19	0.07	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01

Odorless kerosene, purchased from Fisher Scientific, was used as the non-polar oil in this study. Kerosene emulsion was prepared by injecting 1 cm<sup>3</sup> kerosene into 200 cm<sup>3</sup> distilled water followed by agitation in a high-speed blender for 3 min.

Sodium oleate (NaOl) (≥82 % oleic acid basis) was purchased from Sigma-Aldrich and was used as a collector without any further purification. The NaOl dosage was expressed on the basis of the active ingredient (i.e., 82%). High purity octyl hydroxamic acid (OHA) and oleoyl hydroxamic acid (OLHA) were synthesized in our lab by hydroxylamine hydrochloride/sodium hydroxide method and prepared as hydroxamate solution with sodium hydroxide in this study (Liu et al., 2015). Fig. 1 shows the structures of octyl hydroxamic acid, oleoyl hydroxamic acid and sodium oleate.

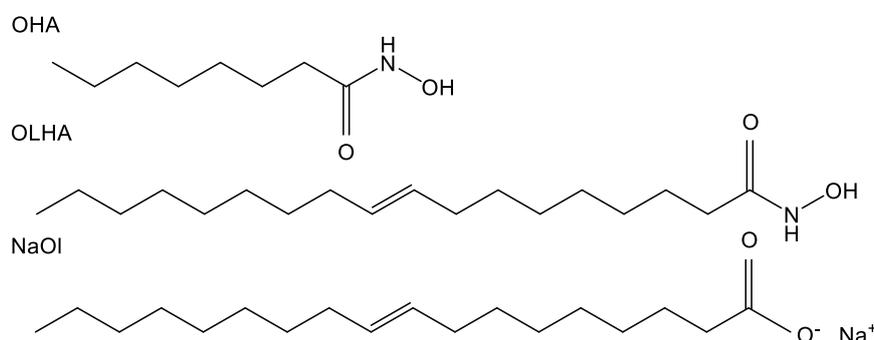


Fig. 1. Structures of octyl hydroxamic acid, oleoyl hydroxamic acid and sodium oleate

## 2.2 Sample characterization

X-ray diffraction (XRD) was used for qualitative identification of mineralogical compositions for both the hematite and quartz samples. Coupling XRD diffractometer (Bruker D8 XRD) was operated at 40 kV, 44 mA and 4 degree/min scan rate. Scanning electron microscopy and energy dispersive X-ray spectrometry (SEM/EDS) was used to image the mineral grains as well as to identify mineral species and elemental composition. Fine hematite sample was mounted on an aluminum pin stub using a carbon adhesive tab, and examined in a Zeiss EVO LS 15 SEM using a beam voltage of 15 kV. The flotation products were assayed by a commercial assay lab in Vancouver, Canada. The particle size of hematite, quartz and kerosene emulsion droplets were measured using a Malvern Mastersizer 3000. The operation parameters for the Mastersizer 3000 were as follows: Hematite: refractive index 2.42, absorptive index 0.003 (Cornell and Schwertmann, 2003); Quartz: refractive index 1.54, absorptive index 0.008 (Mitchell, 2004); Kerosene droplets: refractive index 1.43, adsorptive index 0.001 (Tummons, 2016).

## 2.3 Micro-flotation test

Micro-flotation tests were performed in a glass tube at ambient temperature (22°C). The tube has a sintered glass disc at the bottom to allow the passage of gas while a magnetic stir bar can be placed on the sintered glass disc to agitate the mineral sample. The top of the micro-flotation tube was modeled after Siwek et al. (1981). A 1.5 g hematite sample was conditioned in 170 cm<sup>3</sup> distilled water in a beaker under moderate magnetic agitation. A desired dosage of a collector was added and conditioned for 3 min. When used, kerosene emulsion was also added into the mineral suspension and conditioned for another 3 min. The pH of the pulp was adjusted by NaOH or HCl solutions using a plastic pipette. After conditioning, the hematite suspension was transferred into the micro-flotation tube and agitated with a magnetic stirrer at 400 rpm. A 3-min flotation time was employed at 14 cm<sup>3</sup>/min nitrogen gas flow rate. No frother was used. The concentrate and tailings were weighed separately after filtration and drying.

Hematite recovery was calculated as the weight percentage of the concentrate against the original sample weight. The results were reproducible within  $\pm 5\%$ . The stirring in both the beaker and the micro-flotation tube was intended to maintain the mineral particles in suspension rather than to cause intensive shear.

## 2.4 Batch flotation test

Batch flotation tests of artificial mixed minerals (hematite:quartz = 1:1) were conducted in a Metso D-12 laboratory flotation machine under natural pH of 6.5~7.5. Two hundred grams of the hematite/quartz mixture and 1 dm<sup>3</sup> tap water are added into a 1.5 dm<sup>3</sup> stainless steel cell and stirred at 900 rpm for 2 min. A desired dosage of a collector was added and conditioned for another 2 min. When used, 1 kg/Mg emulsified kerosene was added subsequently and conditioned for 2 min. No frother was used. Following conditioning, air was turned on at an aeration rate of 2.5 dm<sup>3</sup>/min (equivalent to a superficial air velocity of 0.36 cm/s) and the flotation froth was scraped every 1 s until 5 min 30 seconds when froth is barren. The temperature of batch flotation tests was ambient to room temperature, which was maintained at 22°C. Finally, the concentrate and tailings products were filtered, dried, weighed and sub-samples were assayed by a commercial assay lab in Vancouver. To evaluate the selectivity and efficiency of the batch flotation, the separation efficiency  $E$  was calculated using the modified Hancock Equation (1), where  $\alpha$ ,  $\beta$  are the Fe<sub>2</sub>O<sub>3</sub> grade of the feed and the concentrate product, and  $\gamma$  is the yield of the concentrate (Hancock, 1918):

$$E = \frac{100(\beta - \alpha)\gamma}{(100 - \alpha)\alpha} \times 100\% \quad (1)$$

For batch flotation of single hematite minerals, the procedures were the same as above except that two hundred grams of the hematite minerals were used in each test, and that the rougher concentrates were collected every 30 seconds to study the kinetics of the flotation. The weights of both water and the mineral were recorded. In addition to mineral recovery, water recovery was also calculated, which was the ratio of recovered water against the total amount of water added to the flotation process.

In addition, agglomeration flotation tests were conducted to compare with conventional batch flotation tests of single hematite minerals. For each agglomeration test, 200 g hematite sample was mixed with tap water in a baffled container (inner diameter: 10.3 cm; baffle width: 1.5 cm) after adding predetermined concentration of collector or/and kerosene emulsion. The suspension was then sealed and additional tap water was injected to the sealed container to remove air voids to minimize air vortex during agitation. The mineral suspension (25 wt.%) was then agitated at 1200 rpm for 20 min, followed by transferring to the Denver flotation cell to 16.7 wt.% solids. After another 2 min conditioning, the froth flotation test was carried out as previously described.

## 3. Results and discussion

### 3.1 Sample characterization

As seen in Fig. 2, the XRD patterns of hematite sample match closely with that of standard hematite, confirming that the sample was mainly hematite. Quartz and pyrolusite were the main impurities, which were indicated by minor peaks shown in Fig. 2a. In Fig. 2b, all the peaks belong to quartz patterns with no impurity peaks.

A SEM image of the -20  $\mu\text{m}$  hematite sample is presented in Fig. 3, showing the morphology of the hematite sample. As can be seen, many particles were much smaller than 20  $\mu\text{m}$  and were indeed of an ultrafine size. EDS spectrum of a selected area scan, shown in a yellow rectangular box and labeled as hematite\_1, indicated an overall composition of 54.36% Fe, 3.67% Si and 2.47% Mn (Table 2). The EDS spectra of the two points, hematite\_2 and hematite\_3, showed that these are possibly magnetite and a mixture of hematite and pyrolusite, respectively.

The particle/droplet size distribution of hematite, quartz and kerosene emulsions were measured by a Malvern Mastersizer 3000 particle size analyzer, and are shown in Fig. 4. As can be seen, both the hematite and the quartz were very fine, with a mode of about 7-8  $\mu\text{m}$ . The kerosene emulsion had similar size distribution as the two mineral samples, with a mode around 3  $\mu\text{m}$ .

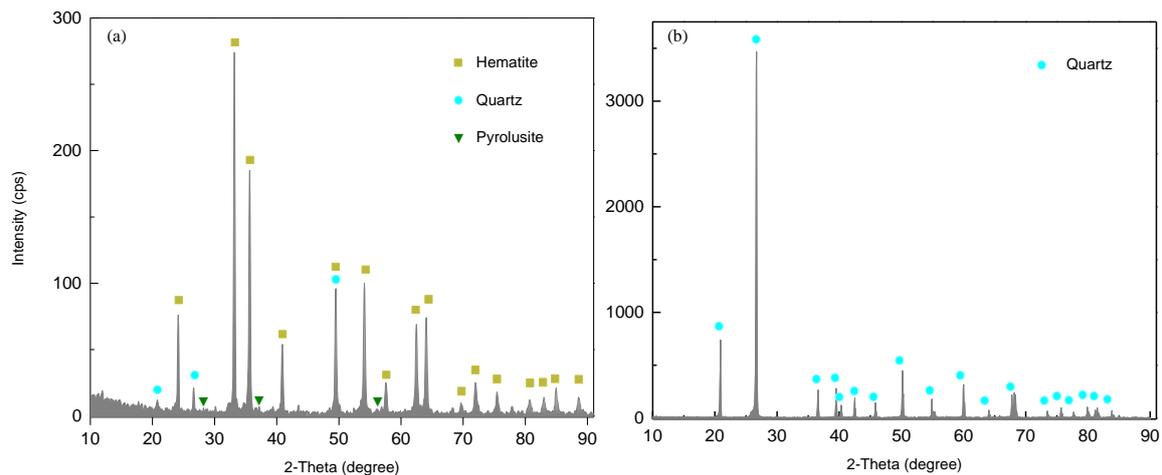


Fig. 2. XRD patterns of hematite (a) and quartz (b) samples

Table 2. EDS analysis with elemental composition of hematite sample

Element, wt %	Fe	O	Si	Mn
Hematite_1	54.36	21.40	3.67	2.47
Hematite_2	60.41	18.97	0.80	0.11
Hematite_3	38.67	24.00	16.63	1.49

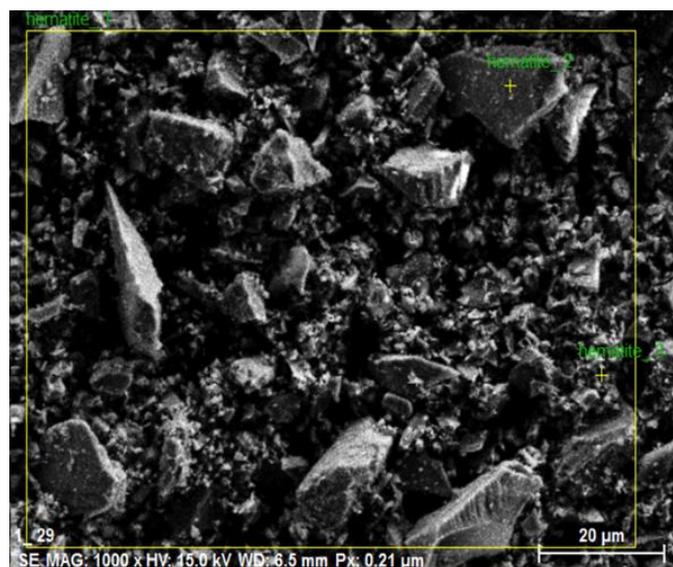


Fig. 3. SEM secondary electron micrograph of the -20 µm hematite

### 3.2 Effect of kerosene on micro-flotation of hematite minerals

The micro-flotation tests were performed to exam the flotation responses of hematite with or without kerosene when different collectors were used at room temperature. The effect of pH, collector concentration and kerosene concentration were investigated and the results are shown in Figs. 5 to 7.

To investigate the effect of pH, experiment were carried out with 40 mg/dm<sup>3</sup> NaOl, OHA or OLHA as a collector in the presence or absence of 100 mg/dm<sup>3</sup> kerosene emulsion at pH 6 to 10. As seen in Fig. 5, the floatability of hematite varies significantly within the tested pH range. The optimum flotation without kerosene occurs in the vicinity of 6.5 to 8.5 for NaOl, 6 to 8 for OHA, and 6 to 7 for OLHA, respectively. With the addition of kerosene, the flotation recoveries of hematite were positively influenced regardless of the type of collectors, and the maximum flotation recoveries were also observed at the optimum flotation pH range.

When hydroxamic acid was used, the hematite recovery dropped with increasing pH. This was likely caused by the poor solubility of the hydroxamic acid at the high pH, which is especially true for the OLHA.

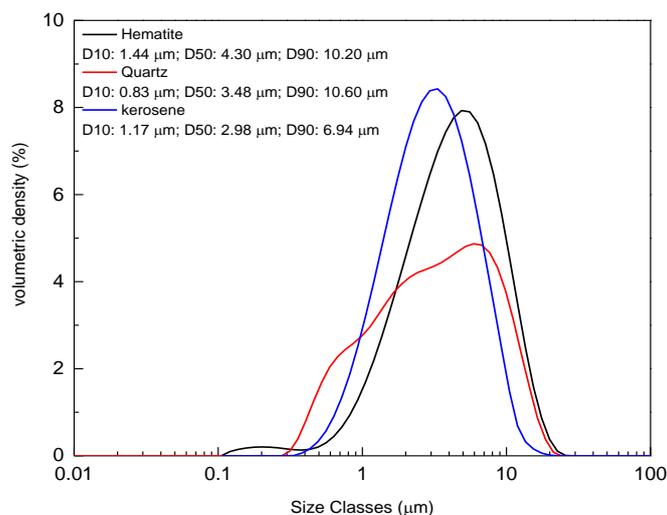


Fig. 4. Particle size distribution of hematite, quartz and kerosene droplets

The effect of collector concentration on hematite flotation responses with or without 100 mg/dm<sup>3</sup> kerosene at pH 7 was shown in Fig. 6. In the absence of kerosene, NaOl, OHA and OLHA were effective collectors for fine hematite. The flotation recovery increased steadily with higher collector dosages. It was found that the NaOl displayed the strongest collecting ability over the other two hydroxamic acids. Of the hydroxamic acids, OHA showed a much better flotation performance than OLHA. This is in good agreement with previous reports (Hughes, 2006; Pattanaik et al., 2000; Pavez et al., 1996). The flotation performance of hematite using OLHA as a collector was inferior to NaOl or OHA. Again this is likely because OLHA has limited solubility in water (Vaysse et al., 1997), leading to a low concentration of dissociated collector anions at pH 7.

The addition of 100 mg/dm<sup>3</sup> kerosene generally increased the flotation recovery of the -20 μm fine hematite, especially at high collector concentrations, but the responses are different between oleate and hydroxamic acids. As indicated in Fig. 6, at NaOl concentrations below 30 mg/dm<sup>3</sup>, the addition of kerosene did not seem to have any effect on hematite flotation. At NaOl concentrations higher than 30 mg/dm<sup>3</sup>, the addition of the 100 mg/dm<sup>3</sup> kerosene led to a 5 percentage point increase in hematite recovery. On the other hand, the addition of 100 mg/dm<sup>3</sup> kerosene caused an increase in hematite recovery for both hydroxamic acids OHA and OLHA at all collector concentrations tested, and the increase was more pronounced at collector concentrations higher than 30 mg/dm<sup>3</sup>. In fact, the addition of 100 mg/dm<sup>3</sup> kerosene together with 40~50 mg/dm<sup>3</sup> OLHA caused about 25 percentage point increase in hematite recovery from about 70% to about 95%, on par with the other two collectors NaOl and OHA. It seems that the addition of kerosene counter-balanced the negative effects of the low solubility of OLHA, making it behave similarly to soluble collectors.

The influence of kerosene concentration on hematite flotation at pH 7 was shown in Fig. 7, at a fixed collector concentration of 40 mg/dm<sup>3</sup>. It can be seen that the recovery of hematite increases gradually with kerosene concentration at a fixed collector concentration of 40 mg/dm<sup>3</sup>. When the concentration of kerosene increased from 0 to 300 mg/dm<sup>3</sup>, hematite recovery increased from 79.5% to 91% for NaOl, 80% to 96% for OHA, and 70% to 96.5% for OLHA, respectively. The addition of kerosene improved the flotation of hematite more when the hydroxamic acids were used.

Clearly, the micro-flotation results listed in Figs. 5 to 7 showed the positive effects of kerosene in promoting mineral flotation, consistent with literature reports in which kerosene was used as a promoting reagent in the flotation where minerals are hydrophobised by long-chain collectors (Liu et al., 2014; Pascoe and Doherty, 1997; Rubio et al., 2007; Song and Valdivieso, 1998).

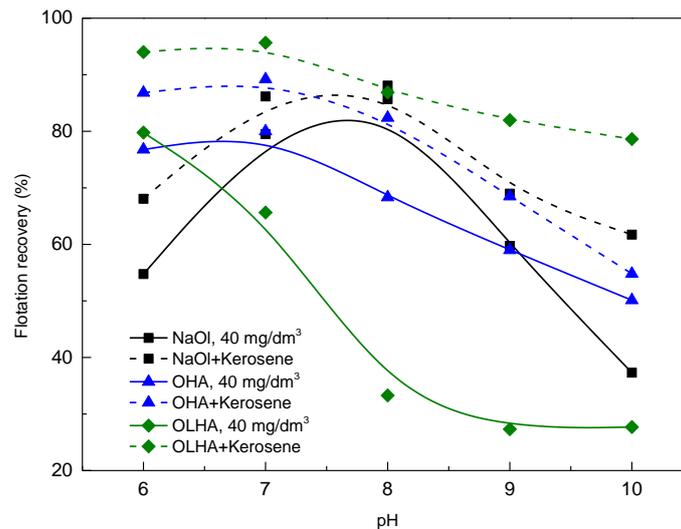


Fig. 5. Micro-flotation recovery of -20  $\mu\text{m}$  hematite as a function of pH with or without 100  $\text{mg}/\text{dm}^3$  kerosene

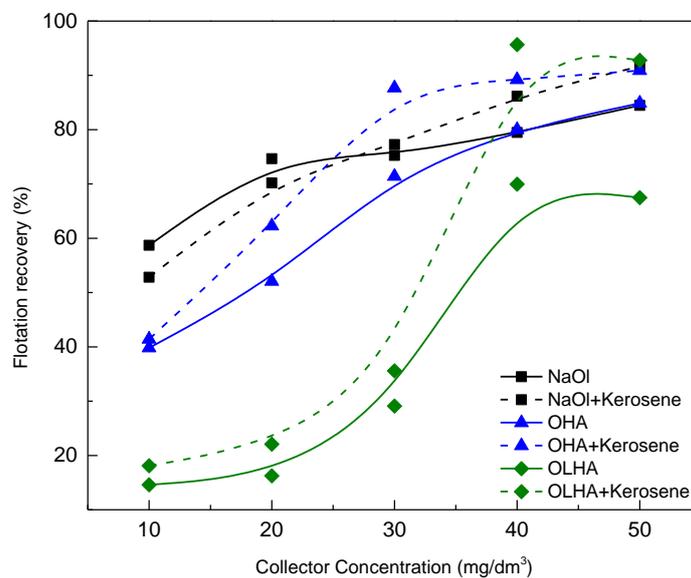


Fig. 6. Micro-flotation recovery of -20  $\mu\text{m}$  hematite as a function of collector dosage at pH 7 with or without 100  $\text{mg}/\text{dm}^3$  kerosene

### 3.3 Effect of kerosene on batch flotation of hematite minerals

#### 3.3.1 Reproducibility of the conventional batch flotation tests

Four replication tests were performed on single hematite mineral under the same test conditions to determine the reproducibility of the flotation tests. The results are shown in Table 3. As can be seen, the standard error was 0.567 and the flotation recovery was reproducible within  $\pm 1\%$ .

Table 3. Reproducibility of batch flotation of hematite single mineral

Test No.	OHA, g/Mg	Recovery, %	Deviation from mean, %
1	750	80.10	-0.59
2	750	80.96	+0.27
3	750	80.34	-0.35
4	750	81.34	+0.65
Average		80.69	

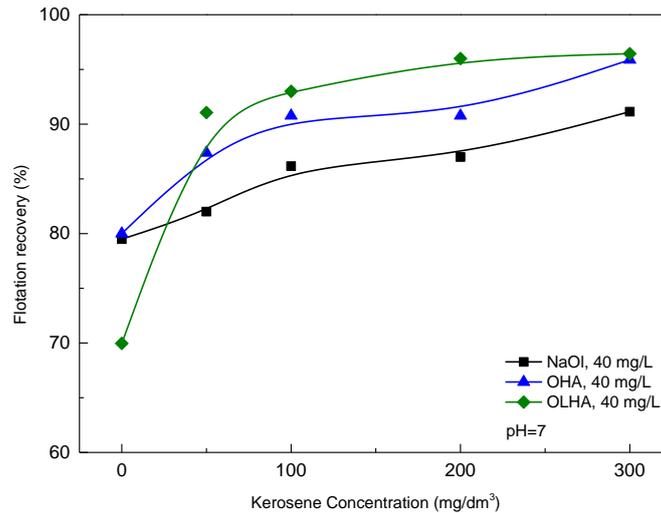


Fig. 7. Micro-flotation recovery of -20 μm hematite as a function of kerosene concentration at pH 7

### 3.3.2 Comparison between conventional flotation and agglomeration flotation

Agglomeration flotation is often employed to improve the recovery of fine particles by hydrophobic aggregation or oil-assisted agglomeration (Coleman et al., 1995; Jiangang et al., 2012). In both cases, sufficient mechanical energy input, desired amount of bridging oil and selective wetting of particles are the major controlling parameters that determines the size and the strength of flocs/agglomerates, which influence the follow-up flotation efficiency (Mehrotra et al., 1983). Therefore, the conventional batch flotation and agglomeration flotation tests were carried out to observe their differences with or without oil addition. The batch flotation results of hematite single mineral are shown in Figs. 8 and 9, for conventional flotation and agglomeration flotation, respectively. Flotation was carried out with different collectors at desired dosages with or without 1 kg/Mg kerosene emulsion. The agglomeration process is operated at 1200 rpm for 20 min prior to flotation.

The results of conventional flotation and agglomeration flotation using NaOl, OHA or OLHA were very different from each other. The difference between “conventional flotation” (CF) and “agglomeration flotation” (AF) was the intensive agitation, which was used in AF but was not in CF. When NaOl was used as a collector, the flotation results of the fine hematite were very similar whether the 1 kg/Mg kerosene was used or not, and whether the intensive agitation step was used or not. The addition of 1 kg/Mg kerosene only showed a minor adverse effect on hematite recovery at low dosages of NaOl (<500 g/Mg), but the effect was gradually eliminated at the higher NaOl dosages. The advantages of neutral oil was not observed when NaOl was used as a collector.

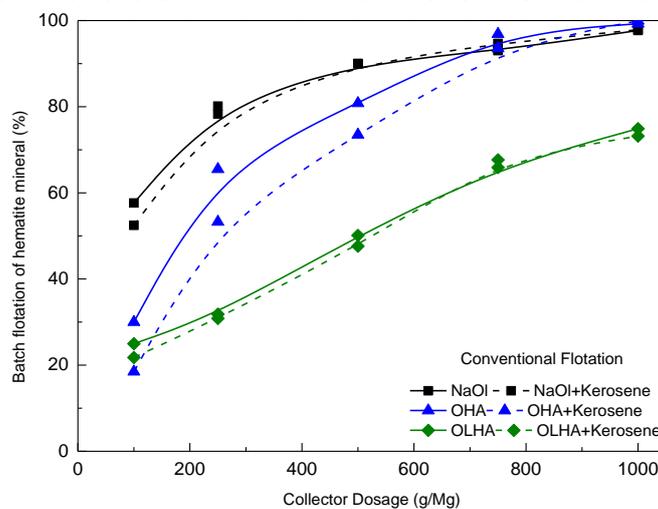


Fig. 8. Conventional flotation (CF) recovery of fine hematite using NaOl, OHA, or OLHA as a collector with or without 1 kg/Mg kerosene

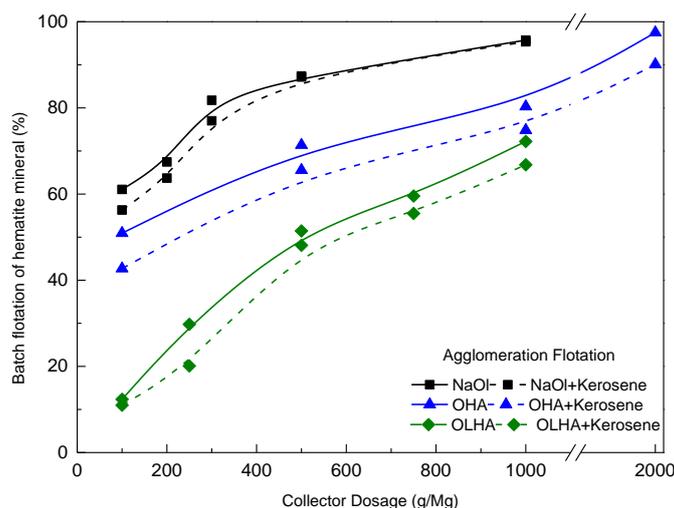


Fig. 9. Agglomeration flotation (AF) recovery of fine hematite using NaOl, OHA, or OLHA as a collector with or without 1 kg/Mg kerosene

When OLHA was used as a collector, and when no intensive agitation was used, hematite flotation results were similar to when NaOl was used. Interestingly, by employing an intensive agitation prior to conventional batch flotation, hematite flotation recovery was consistently slightly lower than that of conventional flotation (without the intensive agitation step), and the addition of kerosene even further lowered the hematite flotation recovery in the AF flotation.

When OHA was used as a collector, the intensive agitation seemed to adversely affect the flotation of hematite (except for 100 g/Mg OHA which may be an outlier). The addition of kerosene caused a lowering of hematite recovery in both the conventional flotation and the agglomeration flotation procedures. This decrease in hematite recovery was gradually compensated by higher dosages of OHA in the conventional flotation procedure. However, in the agglomeration flotation procedure, hematite recovery was still lowered after adding the 1 kg/Mg kerosene even when the OHA dosage was increased to 2 kg/Mg. Therefore, in the following tests, the intensive agitation step was not used.

### 3.3.3 Effect of kerosene on batch flotation kinetics of hematite single minerals

Figs. 10-12 show the effect of kerosene on fine hematite flotation kinetics using NaOl, OHA and OLHA as collectors, respectively. As can be seen in Fig. 10, at 100 g/Mg NaOl, the addition of 1 kg/Mg kerosene caused no more than 3 percentage points cumulative hematite recovery loss. Therefore, kerosene had limited detrimental effect when NaOl was used as a collector. This limited detrimental effect was compensated and counter-balanced at higher NaOl dosages. Above 500 g/Mg NaOl, the addition of kerosene started to show positive impact and accelerated flotation rates of the hematite. Similar trend of the effect of kerosene was also noticed with OLHA in Fig. 12. Despite its poor collecting power and reduced frothing ability due to the low solubility of OLHA, the adverse effect of kerosene when OLHA was used as a collector was small and was offset at higher OLHA dosages.

However, when OHA was used as the collector, the detrimental effect of kerosene was obvious, especially at low OHA dosages (Fig. 11). In fact, in the range of OHA dosages tested from 100 to 750 g/Mg, the addition of 1 kg/Mg kerosene caused a significant reduction in hematite recovery. The magnitude of the reduction was higher at lower OHA dosages. It was observed during the flotation tests that at 100 g/Mg OHA, the mineralization of the froth decreased drastically after adding 1 kg/Mg kerosene. Bubbles were turning fragile and easily ruptured during aeration and froth scraping. This was also observed at 250 g/Mg OHA. A similar phenomenon was noticed by Ni (2013) when he attempted to use 1 kg/Mg or higher dosages of emulsified kerosene to improve the OHA flotation of a niobium oxide ore, even when using Dowfroth 250 as a frother. Such a detrimental effect on the froth behavior, however, was not visually observed when NaOl or OLHA was used as a collector.

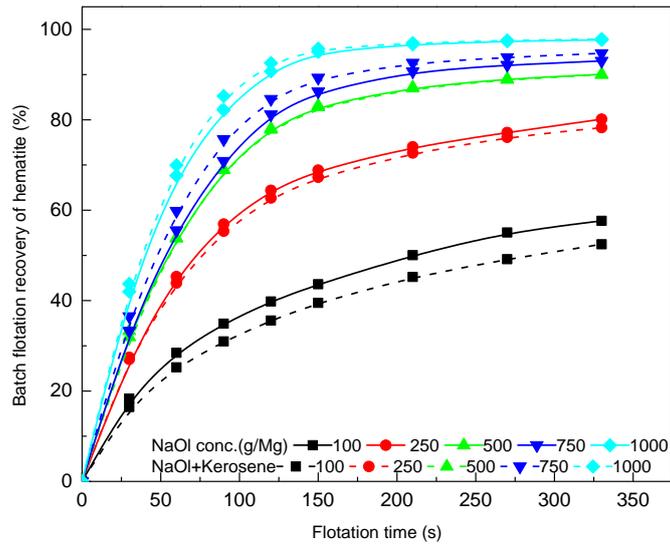


Fig. 10. Flotation of hematite using NaOl as a collector with or without kerosene

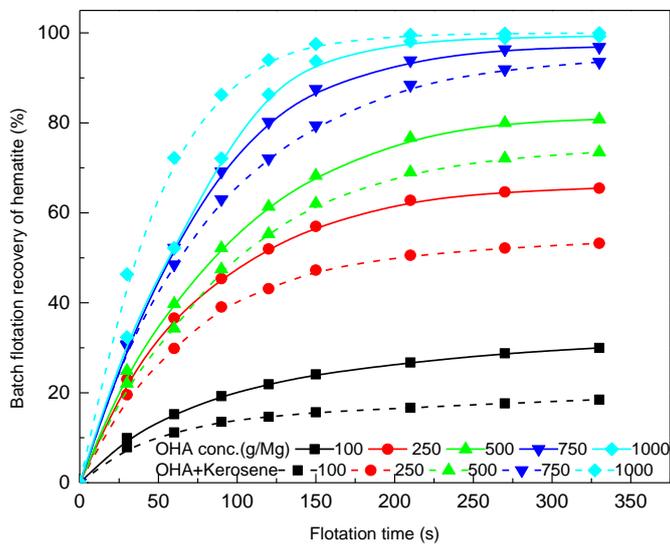


Fig. 11. Flotation of hematite using OHA as a collector with or without kerosene

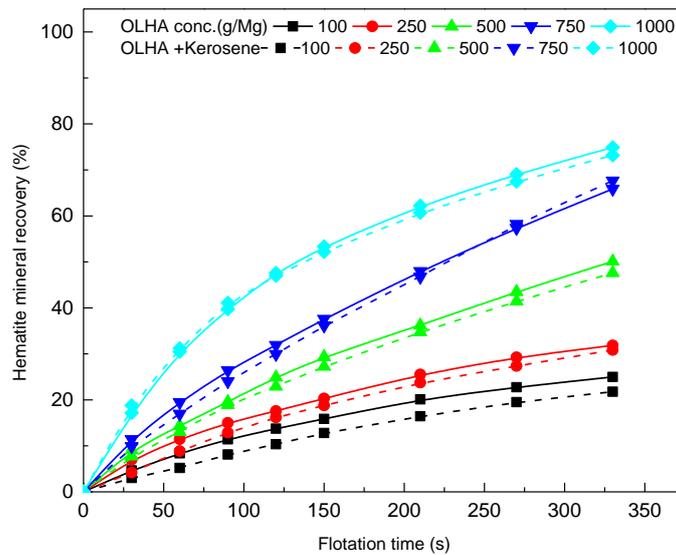


Fig. 12. Flotation of hematite using OLHA as a collector with or without kerosene

### 3.3.4 Effect of collector dosages on batch flotation of hematite and quartz mixtures

Comparative batch flotation tests of hematite and quartz mixtures were performed at natural pH (pH 6.5~7.5), and the results are shown in Table 4 to 6. The objective of the tests was to investigate the effects of collector chain lengths and functional polar groups of NaOl, OHA and OLHA in the flotation in the presence of a non-polar oil such as kerosene. Fine quartz was chosen as gangue mineral since it does not react with the collectors. Its recovery to the concentrate would indicate the degree of mechanical

Table 4. Batch flotation of hematite/quartz mixtures with NaOl and kerosene

NaOl, g/Mg	Kerosene	Conc. weight, %	Assay		Distribution		Efficiency, %
			Fe <sub>2</sub> O <sub>3</sub> , %	SiO <sub>2</sub> , %	Fe <sub>2</sub> O <sub>3</sub> , %	SiO <sub>2</sub> , %	
50	0	17.1	55.69	41.48	21.3	13.5	7.8
	1 kg/Mg	15.3	56.94	40.22	19.6	11.6	8.0
125	0	33.1	61.20	35.77	45.4	22.6	22.8
	1 kg/Mg	33.2	61.92	35.35	45.4	22.5	22.9
250	0	46.2	61.52	35.60	62.6	31.6	31.0
	1 kg/Mg	46.4	62.75	34.48	63.9	30.9	33.0
375	0	57.7	61.62	35.44	77.6	39.7	37.9
	1 kg/Mg	55.3	62.50	34.61	75.6	37.0	38.6
500	0	62.4	61.59	36.67	83.4	43.9	38.9
	1 kg/Mg	64.4	67.61	30.50	92.5	38.3	53.1

Table 5. Batch flotation of hematite/quartz mixtures with OHA and kerosene

OHA, g/Mg	Kerosene	Conc. weight, %	Assay		Distribution		Efficiency, %
			Fe <sub>2</sub> O <sub>3</sub> , %	SiO <sub>2</sub> , %	Fe <sub>2</sub> O <sub>3</sub> , %	SiO <sub>2</sub> , %	
50	0	10.9	47.12	49.94	11.5	10.4	1.1
	1 kg/Mg	7.4	44.90	52.12	7.4	7.3	0.1
125	0	36.8	54.57	42.67	44.4	30.0	14.4
	1 kg/Mg	29.3	52.06	45.32	33.9	25.2	8.7
250	0	60.6	61.47	35.72	81.6	41.8	39.8
	1 kg/Mg	54.7	62.20	35.11	74.5	37.1	37.4
375	0	66.0	62.93	34.15	91.1	43.4	47.7
	1 kg/Mg	65.8	62.88	34.23	90.6	43.5	47.1
500	0	72.0	61.57	36.66	94.1	51.5	41.9
	1 kg/Mg	71.1	63.42	34.78	94.8	48.7	45.2

Table 6. Batch flotation of hematite/quartz mixtures with OLHA and kerosene

OLHA, g/Mg	Kerosene	Conc. weight, %	Assay		Distribution		Efficiency, %
			Fe <sub>2</sub> O <sub>3</sub> , %	SiO <sub>2</sub> , %	Fe <sub>2</sub> O <sub>3</sub> , %	SiO <sub>2</sub> , %	
50	0	8.2	52.76	43.96	9.5	7.0	2.5
	1 kg/Mg	5.3	56.75	39.64	6.7	4.0	2.7
125	0	21.2	53.85	42.92	24.8	17.7	7.1
	1 kg/Mg	20.3	55.48	41.14	24.5	16.3	8.2
250	0	28.0	64.15	32.48	39.5	17.4	22.1
	1 kg/Mg	25.5	67.09	29.48	37.2	14.7	22.5
375	0	35.1	69.60	26.72	52.2	18.6	33.6
	1 kg/Mg	31.4	71.35	25.13	49.1	15.2	33.9
500	0	42.3	80.77	17.48	72.7	14.4	57.3
	1 kg/Mg	44.7	87.08	11.34	83.2	9.8	72.4

entrainment, and was directly related to the amount of water reporting to the froth concentrate (Boylu and Laskowski, 2007). The collector dosages were lowered to half of those used in single mineral flotation tests to account for the decreased amount of hematite.

As can be seen from Tables 4 to 6, in the absence of kerosene, all the added surfactants, NaOl, OHA and OLHA acted as hematite collectors. Both the  $\text{Fe}_2\text{O}_3$  grade and recovery increased with increasing collector dosages. The  $\text{SiO}_2$  recovery was also increased despite its lower grade in the floated concentrate at the higher collector dosages, a result caused by the higher concentrate weight yield due to the higher froth stability at the high collector dosages. Different from NaOl and OHA, the flotation response using OLHA was not satisfactory despite its long hydrocarbon chain. It was observed that OLHA was sparingly soluble in the slurry and was thus less effective. Interestingly, the short chain hydroxamic acid OHA was not only better than OLHA but also better than NaOl.

The addition of 1 kg/Mg kerosene, however, resulted in different responses using the three collectors. Table 4 and Table 6 showed the beneficial effects of kerosene in promoting the flotation performance of the fine hematite when NaOl or OLHA was used as a collector. Below 500 g/Mg collector dosage, the assayed  $\text{Fe}_2\text{O}_3$  grades of the concentrates were consistently higher than those without kerosene. This could be due to the higher surface hydrophobicity of the hematite induced by the kerosene, and/or by the lower entrainment of quartz due to the defrothing effect of kerosene. Once the defrothing effect of kerosene was minimized by a stabilized froth layer produced by higher dosage of collectors (500 g/Mg in current study), kerosene's addition improved the flotation response. As shown in Tables 4 and 6, both assayed  $\text{Fe}_2\text{O}_3$  grades in the concentrate and the Fe recoveries improved significantly after adding the 1 kg/Mg kerosene at the highest collector dosage tested.

On the other hand, when the short chain hydroxamic acid OHA was used as a collector, the addition of kerosene had a detrimental effect (Table 5). Hematite recovery was not improved but rather, was reduced when 1 kg/Mg kerosene was added at low OHA dosages (50-250 g/Mg). Above 375 g/Mg OHA, the detrimental effect of kerosene seemed to have been eliminated and the hematite recovery was maintained at similar or slightly higher values as that when no kerosene was used. At low OHA dosages, the addition of 1 kg/Mg kerosene caused a reduction on concentrate weight yield,  $\text{Fe}_2\text{O}_3$  grades and  $\text{Fe}_2\text{O}_3$  recovery. While the reduction in concentrate weight yield was likely the result of the defrothing effect of kerosene, the slight reduction of concentrate  $\text{Fe}_2\text{O}_3$  grade was puzzling. It seemed that the surface hydrophobicity of the hematite was not improved following kerosene addition when it is made hydrophobic by low dosages of OHA.

Table 7. Batch flotation of hematite/quartz mixtures with NaOl and kerosene.

NaOl	Kerosene, kg/Mg	Conc. weight, %	Assay		Distribution		Efficiency, %
			$\text{Fe}_2\text{O}_3$ , %	$\text{SiO}_2$ , %	$\text{Fe}_2\text{O}_3$ , %	$\text{SiO}_2$ , %	
500 g/Mg	0	62.4	61.59	36.67	83.4	43.9	38.9
	0.5	64.2	65.42	32.97	88.3	41.6	45.9
	1	64.4	67.61	30.50	92.5	38.3	53.1
	2	62.2	68.85	29.35	90.8	35.7	54.1
	3	59.2	70.98	27.09	89.0	31.4	56.5
	10	53.0	58.76	37.81	66.8	39.8	25.8

Table 8. Batch flotation of hematite/quartz mixtures with OHA and kerosene.

OHA	Kerosene, kg/Mg	Conc. weight, %	Assay		Distribution		Efficiency, %
			$\text{Fe}_2\text{O}_3$ , %	$\text{SiO}_2$ , %	$\text{Fe}_2\text{O}_3$ , %	$\text{SiO}_2$ , %	
500 g/Mg	0	72.0	61.57	36.66	94.1	51.5	41.9
	0.5	73.5	61.90	35.36	95.9	51.7	42.7
	1	71.1	63.42	34.78	94.8	48.7	45.2
	2	71.4	64.46	33.72	97.1	47.4	48.8
	3	70.1	62.32	35.81	95.1	47.8	46.3
	10	66.5	63.20	33.57	92.4	43.0	47.6

### 3.3.5 Effect of kerosene dosages on batch flotation of hematite and quartz mixtures

The effect of kerosene dosage on batch flotation of fine hematite and quartz was studied with a high dosage of collectors (500 g/Mg). The results are shown in Tables 7 to 9. Due to the stable and rich frothing layers at high collector dosage, the flotation responses in terms of concentrate Fe<sub>2</sub>O<sub>3</sub> grade and recovery improved dramatically with increasing addition of kerosene. This positive effect was very strong, leading to a much higher separation efficiency, which may be attributed to a higher surface hydrophobicity and the formation of larger hydrophobic flocs when kerosene was added. At low kerosene dosages, the defrothing effect of kerosene was not obvious judging by the stable mineralized froth. Once oil addition reached a "critical dosage" (3 kg/Mg with NaOl, 2 kg/Mg with OHA, and 0.5 kg/Mg with OLHA), further increase in kerosene dosage resulted in a decrease in separation efficiency – most likely as the kerosene droplets were starting to play a role in lowering froth stability. For instance, when 10 kg/Mg kerosene was added in the flotation pulp where 500 g/Mg NaOl was used as a collector, the concentrate weight yield, grade and recovery as well as entrained quartz decreased significantly, implying unstable froths due to excessive oil in the flotation pulp.

Table 9. Batch flotation of hematite/quartz mixtures with OLHA and kerosene.

OLHA	Kerosene, kg/Mg	Conc. weight, %	Assay		Distribution		Efficiency, %
			Fe <sub>2</sub> O <sub>3</sub> , %	SiO <sub>2</sub> , %	Fe <sub>2</sub> O <sub>3</sub> , %	SiO <sub>2</sub> , %	
500 g/Mg	0	42.3	80.77	17.48	72.7	14.4	57.3
	0.5	48.6	84.94	13.20	87.9	12.5	74.1
	1	44.7	87.08	11.34	83.2	9.8	72.4
	2	43.6	82.55	15.55	76.6	13.2	62.2
	3	42.5	82.55	15.68	74.4	13.0	60.3
	10	40.0	81.07	17.01	68.9	13.3	54.6

### 3.4 Defrothing effect of kerosene

Hydrocarbon oils such as kerosene are known to flatten the froth in the flotation cell (Pugh, 1996). In froth flotation, mineral flotation recovery not only depends on mineral surface hydrophobicity but also on froth stability. The latter can be reflected by water recovery into the flotation concentrate. Therefore, water recovery was calculated in order to investigate the defrothing effect of kerosene at different collector dosages.

Fig. 13 shows water recovery before and after adding 1 kg/Mg kerosene in the batch flotation of -20 µm hematite. Water recovery decreased significantly from 33.4% to 17.7% after adding kerosene at 100 g/Mg OHA, which coincided with a reduction in hematite recovery (Fig. 11). This large difference in water recovery was gradually reduced with increasing OHA dosage. However, when NaOl or OLHA was used as a collector, the water recovery was not significantly affected after adding the 1 kg/Mg kerosene at all dosages of the collectors tested from 100 to 1000 g/Mg.

Froth flotation is a complex process in which the additives have various functions, some of which can be contradictory to achieve desired flotation results. It is obvious that the stability of the bubbles and froth is an important requirement for a satisfactory flotation performance. Froth stabilization was controlled by the adsorbed surfactants at the gas/water interface which modulate the mechanical and dynamic properties of bubble surface layer (Leja, 1982; Pugh, 1996). For successful froth flotation, a stable froth layer needs to be formed, thus a high surface tension gradient is required (Pugh, 1996). In this study, as no frother was used, the froth was generated by the added collectors. When collector dosage was low, the bubbles were unstable and sensitive to the surfactant concentration, yielding low degree of surface tension gradient. Due to molecular structure differences between OHA, OLHA and NaOl, the non-polar group of NaOl and OLHA were twice the length of OHA. Beneventi et al. (2001) pointed out that longer hydrocarbon chains slowed water drainage and strengthened froth stability. Therefore, NaOl and OLHA, with long hydrocarbon chain, were expected to lower water drainage rate. In OHA flotation, water migration kinetics in the froth films was comparatively slow. Once oil entered and spread on the bubble surface, it will gradually eliminate the surface tension gradient and elasticity, leading to faster water drainage and bubble ruptures. At high collector concentration regardless of

collector type, the froth layer was stable because the Marangoni effect plays a critical role and provides a strong restoring force to film thinning caused by kerosene. Therefore, the effect of water drainage by kerosene droplets was counter-balanced by surface tension gradient. In addition, hematite fines help froth stabilization during flotation (Johansson and Pugh, 1992). The hematite surface is expected to be more hydrophobic at higher collector dosages. Once the surface of hematite particle achieved a critical degree of hydrophobicity, the stabilizing effect would be maximized and the water drainage effect caused by kerosene would be minimized.

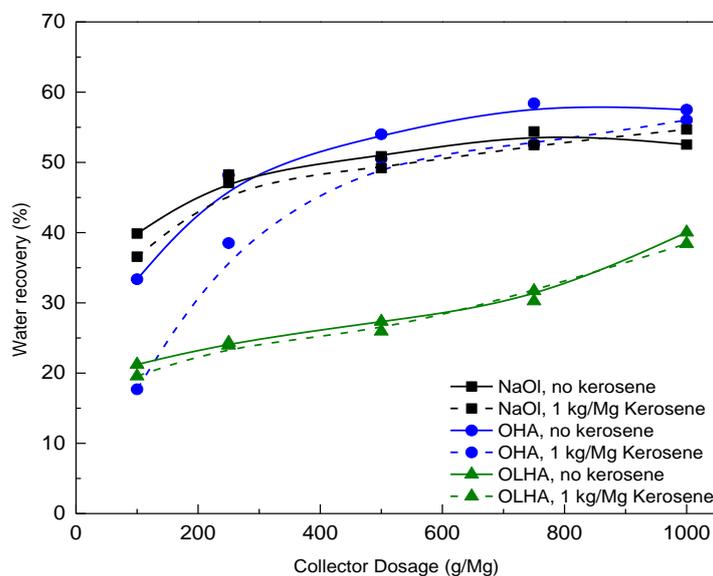


Fig. 13. The effect of 1 kg/Mg kerosene on water recovery in the batch flotation of -20  $\mu\text{m}$  hematite using different dosages of NaOl, OHA and OLHA

#### 4. Conclusions

The micro-flotation and batch flotation of fine hematite/quartz mixtures and single hematite mineral using sodium oleate (NaOl), octyl hydroxamic acid (OHA), or oleoyl hydroxamic acid (OLHA) as a collector and with or without kerosene were investigated.

It was observed that in micro-flotation tests where a froth layer did not exist, emulsified kerosene exhibited beneficial role on hematite flotation regardless of the types of collectors. However, in batch flotation tests where a stable froth layer was required, kerosene showed positive impact on hematite flotation when NaOl or OLHA was used as a collector. However, when OHA was used as a collector, the concentrate weight yield, hematite grade, mineral recovery as well as water recovery were reduced at low OHA dosages when kerosene was added.

The different effects observed of kerosene on the batch flotation were due to its simultaneous detrimental role (defrothing) and beneficial role (surface hydrophobicity enhancement, and oil-assisted aggregation). This preliminary batch flotation study seemed to reveal a delicate balance between the two conflicting roles when different collectors, with different polar groups and hydrocarbon chain lengths, were used in fine particle flotation. With a fixed oil dosage (1 kg/Mg), the defrothing effect of kerosene was found to be significant with a shorter chain collector such as OHA, especially at low OHA dosages, than longer chain collectors such as NaOl and OLHA. However, this detrimental defrothing effect was gradually counter-balanced by higher collector dosages, which probably caused higher surface tension gradient on bubble surfaces, and higher degrees of hydrophobicity of the fine hematite surfaces, both of which helped stabilize the froth layer. At high collector dosage (500g/Mg in the flotation of hematite/quartz mixtures), the defrothing effect of kerosene was suppressed by stabilized bubbles and the beneficial role of kerosene was dominating. Once kerosene addition reached its critical point, oil droplets will in turn exhibit its defrothing effect and adversely affect froth flotation performance.

## Acknowledgments

The authors are grateful to financial support to this research through a Collaborative Research and Development project sponsored by COREM and the Natural Sciences and Engineering Research Council (NSERC) of Canada.

## References

- BARRAZA, J., GUERRERO, J., PIÑERES, J. (2013). Flotation of a refuse tailing fine coal slurry. *Fuel processing technology*, 106, 498-500.
- COLLINS, D., READ, A. (1971). The treatment of slimes. *Mineral Science and Engineering*, 3, 19-31.
- DAI, Z., LU, S. (1991). Hydrophobic interaction in flocculation and flotation 2. Interaction between non-polar oil drop and hydrophobic mineral particle. *Colloids and Surfaces*, 57(1), 61-72.
- FINKELSTEIN, N. (1997). The activation of sulphide minerals for flotation: a review. *International Journal of Mineral Processing*, 52(2), 81-120.
- FORNASIERO, D., RALSTON, J. (2005). Cu (II) and Ni (II) activation in the flotation of quartz, lizardite and chlorite. *International Journal of Mineral Processing*, 76(1), 75-81.
- HANCOCK, R. (1918). The rating of concentration tests. *Mining Magazine*, 19, 144-145.
- ISRAELACHVILI, J., PASHLEY, R. (1984). Measurement of the hydrophobic interaction between two hydrophobic surfaces in aqueous electrolyte solutions. *Journal of colloid and interface science*, 98(2), 500-514.
- KLASSEN, V. I., MOKROUSOV, V. A. (1963). *An introduction to the theory of flotation*: Butterworths.
- LASKOWSKI, J. (1992). Oil assisted fine particle processing *Colloid Chemistry in Mineral Processing* (pp. 361-394): Elsevier Amsterdam.
- LASKOWSKI, J. (2001). Coal flotation and fine coal utilisation. *Chapter 9 Particle Size Enlargement* (1st ed.). New York: Amsterdam: Elsevier.
- LI, B., TAO, D., OU, Z., LIU, J. (2003). Cyclo-microbubble column flotation of fine coal. *Separation Science and Technology*, 38(5), 1125-1140.
- LIU, A., FAN, M., FAN, P. (2014). Interaction mechanism of miscible DDA-Kerosene and fine quartz and its effect on the reverse flotation of magnetic separation concentrate. *Minerals Engineering*, 65, 41-50.
- LU, S., SONG, S., DAI, Z. (1988). *The hydrophobic and magnetic combined aggregation of paramagnetic minerals, a new way of fine particles separation*. Paper presented at the Proceedings of XVI International Mineral Processing Congress.
- MATHUR, S., SINGH, P., MOUDGIL, B. (2000). Advances in selective flocculation technology for solid-solid separations. *International Journal of Mineral Processing*, 58(1), 201-222.
- MIETTINEN, T., RALSTON, J., FORNASIERO, D. (2010). The limits of fine particle flotation. *Minerals Engineering*, 23(5), 420-437.
- MITCHELL, T. K., NGUYEN, A. V., EVANS, G. M. (2005). Heterocoagulation of chalcopyrite and pyrite minerals in flotation separation. *Advances in Colloid and Interface Science*, 114, 227-237.
- NEETHLING, S., CILLIERS, J. (2002). The entrainment of gangue into a flotation froth. *International Journal of Mineral Processing*, 64(2-3), 123-134.
- NEETHLING, S., CILLIERS, J. (2009). The entrainment factor in froth flotation: Model for particle size and other operating parameter effects. *International Journal of Mineral Processing*, 93(2), 141-148.
- NI, X. (2013). *Direct Flotation of Niobium Oxide Minerals from Carbonatite Niobium Ores*: University of Alberta.
- O'CONNOR, C., DUNNE, R. (1994). The flotation of gold bearing ores—a review. *Minerals Engineering*, 7(7), 839-849.
- OZKAN, A., DUDNIK, V., ESMELI, K. (2016). Hydrophobic flocculation of talc with kerosene and effects of anionic surfactants. *Particulate Science and Technology*, 34(2), 235-240.
- PARSONAGE, P. (1984). Effects of slime and colloidal particles on the flotation of galena. *Flotation of sulphide minerals*, 111-139.
- PASHLEY, R. M., MCGUIGGAN, P. M., NINHAM, B. W., EVANS, D. F. (1985). Attractive forces between uncharged hydrophobic surfaces: direct measurements in aqueous solution. *Science*, 229, 1088-1090.
- RAO, S. R. (2004). *Surface Chemistry of Froth Flotation Reagents and Mechanisms* (2nd ed. Vol. 2). New York: Kluwer Academic/Plenum Publishers.

- RUBIO, J., CAPPONI, F., MATIOLO, E., NUNES, D., GUERRERO, C., BERKOWITZ, G. (2003). *Advances in flotation of mineral fines*. Paper presented at the Proceedings of the XXII International Mineral Processing Congress, Cape-Town, Africa do Sul.
- SADOWSKI, Z. (1994). A study on hydrophobic aggregation of calcite aqueous suspensions. *Powder Technology*, 80(2), 93-98.
- SANTANA, R. C., FARNESE, A. C., FORTES, M. C., ATAÍDE, C. H., BARROZO, M. A. (2008). Influence of particle size and reagent dosage on the performance of apatite flotation. *Separation and Purification Technology*, 64(1), 8-15.
- SIS, H., CHANDER, S. (2003). Reagents used in the flotation of phosphate ores: a critical review. *Minerals Engineering*, 16(7), 577-585.
- SIWEK, ZEMBALA, M., POMIANOWSKI, A. (1981). A method for determination of fine-particle flotability. *International Journal of Mineral Processing*, 8(1), 85-88.
- SOBHY, A., TAO, D. (2013). Nanobubble column flotation of fine coal particles and associated fundamentals. *International Journal of Mineral Processing*, 124, 109-116.
- SOLARI, J. (1980). Selective dissolved air flotation of fine minerals particles. *Doctor thesis, University of London-Imperial College*, 292p.
- SONG, LOPEZ-VALDIVIESO, A., DING, Y. (1999). Effects of nonpolar oil on hydrophobic flocculation of hematite and rhodochrosite fines. *Powder Technology*, 101(1), 73-80.
- SONG, S., LOPEZ-VALDIVIESO, A., ALEJANDRO, J. (2002). Parametric aspect of hydrophobic flocculation technology. *Mineral Processing and Extractive Metallurgy Review*, 23(2), 101-127.
- SONG, S., LOPEZ-VALDIVIESO, A., REYES-BAHENA, J., LARA-VALENZUELA, C. (2001). Floc flotation of galena and sphalerite fines. *Minerals Engineering*, 14(1), 87-98.
- SONG, S., LU, S. (1994). Hydrophobic flocculation of fine hematite, siderite, and rhodochrosite particles in aqueous solution. *Journal of colloid and interface science*, 166(1), 35-42.
- SONG, S., ZHANG, X., YANG, B., LOPEZ-MENDOZA, A. (2012). Flotation of molybdenite fines as hydrophobic agglomerates. *Separation and Purification Technology*, 98, 451-455.
- WANG, D. (2016). Collectors for Nonsulfide Minerals *Flotation Reagents: Applied Surface Chemistry on Minerals Flotation and Energy Resources Beneficiation* (pp. 69-113): Springer.
- YE, Y., MILLER, J. (1988). Bubble/particle contact time in the analysis of coal flotation. *Coal Preparation*, 5(3-4), 147-166.
- YOON, R., LUTTRELL, G., ADEL, G., MANKOSA, M. (1989). Recent advances in fine coal flotation. *Advances in Coal and Mineral Processing Using Flotation*, 211-218.
- ZANIN, M., AMETOV, I., GRANO, S., ZHOU, L., SKINNER, W. (2009). A study of mechanisms affecting molybdenite recovery in a bulk copper/molybdenum flotation circuit. *International Journal of Mineral Processing*, 93(3), 256-266.
- ZHENG, X., JOHNSON, N., FRANZIDIS, J.-P. (2006). Modelling of entrainment in industrial flotation cells: water recovery and degree of entrainment. *Minerals Engineering*, 19(11), 1191-1203.