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The effect of non-polar oil on fine hematite flocculation and flotation using sodium oleate or hydroxamic acids as a collector

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ABSTRACT

The effects of non-polar oil on hydrophobic flocculation and micro-flotation of fine hematite (−20 μm) were studied when sodium oleate, octyl hydroxamic acid, or oleoyl hydroxamic acid was used as a collector. The micro-flotation test was carried out under neutral pH, and kerosene was used as the non-polar oil. Focused Beam Reflectance Measurement (FBRM) particle size analysis coupled with optical microscopy was performed to monitor the real-time evolution of hematite particles during flocculation. In addition, contact angles and zeta potentials of hematite were determined and used as parameters in the extended-DLVO theory interaction force estimation. The micro-flotation tests showed a beneficial effect of kerosene at high collector dosages regardless of the type of collectors used. The FBRM and optical image analysis indicated that the sizes of hematite aggregates induced by sodium oleate or oleoyl hydroxamic acid was much larger than by octyl hydroxamic acid; and the addition of kerosene further enhanced the aggregate size differences. The extended-DLVO theory calculation was carried out to explain the differences in the aggregation behaviors. The results indicated that the hydrophobic interaction energies between hydrophobic hematite particles induced by sodium oleate or oleoyl hydroxamic acid were stronger than by octyl hydroxamic acid. When kerosene was added, the aggregates grew to a much larger size due to the strong hydrophobic interaction between hematite particles and kerosene droplets.

1. Introduction

Non-polar oil, also known as neutral oil, is a naturally occurring water-immiscible hydrocarbon mixture produced from crude oil. The major components of non-polar oil are n-paraffins, iso-paraffins, aromatics, and naphthalene (Hobson & Pohl, 1973). In the field of mineral processing, the addition of non-polar oils often results in larger floc size (Song et al., 1999; Song et al., 2002), faster flotation rate (Soto & Iwasaki, 1986; Rubio et al., 2007), less slime entrainment (Ying et al., 2015), lower collector consumption (Liu et al., 2014), and higher concentrate grades and value recoveries (Song et al., 2001). Therefore, non-polar oil is often used as an auxiliary collector or promotor in flotation processes. Medium-density non-polar oils, such as kerosene, diesel and other petroleum distillates, characterized by hydrocarbon chain lengths from C9 to C20 (Speight, 2014), are frequently added from a very low dosage up to a few kg/ton in froth flotation. Depending on the dosage of the non-polar oils, the oil-assisted flotation processes can be classified as extender flotation, emulsion flotation, and agglomeration flotation or floc-flotation, in addition to oil agglomeration and liquid/liquid extraction that use sizing and phase separation as the separation methods, respectively (Subrahmanyam & Forssberg, 1990; Laskowski, 1992; Warren, 1992). The action mechanisms of the oil droplets to the mineral particles were generally quoted in terms of hydrophobicity enhancement and oil bridging effect due to hydrophobic interactions (Dai & Lu, 1991; Laskowski, 1992; Song et al., 1998). To be specific, the intrinsic hydrophobic properties of non-polar oils in an aqueous mineral suspension allow them to preferentially attach and spread on the surface of hydrophobic particles, leading to a coverage of oil layer and higher hydrophobicity. In addition, the hydrophobic particles and small flocs were bridged by the oil droplets into larger and stronger flocs that can resist shear forces that could otherwise break the flocs.

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 & Dunne, 1994; Harris et al., 1995;

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Zanin et al., 2009). 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 & Lu, 1994; Song et al., 1999), rhodochrosite (Lu et al., 1988), calcite (Sadowski, 1994), talc (Ozkan et al., 2016) and apatite (Sis & 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, 2016a).

However, the application of alkyl hydroxamic acids and related salts in conjunction with non-polar oil were rarely discussed in the open literature. Due to their strong complexation capability with transition and rare earth metal ions, hydroxamic acids exhibited better performance than conventional fatty acids when it was used to float fine minerals (Natarajan, 2013; Wang, 2016b). However, Ni (2013) showed that the addition of kerosene in the batch flotation of a niobium oxide ore using octyl hydroxamic acid (OHA) significantly deteriorated the flotation performance.

As indicated by Pascoe and Doherty (1997), an increase in collector hydrocarbon chain length could produce larger and stronger mineral flocs. In the presence of non-polar oil, the enhancement of hydrophobic flocculation would be much more significant by collectors with longer hydrocarbon chain lengths (Ozkan et al., 2016). Considering this effect, collectors with short chain hydrocarbons were not suggested when non-polar oil was used in the processes (Zollars & Ali, 1986). On the other hand, many researchers reported the beneficial effect of non-polar oil even with short-chain collectors (e.g. isopropyl or amyl xanthate in the flotation of partially hydrophobic sulfide minerals), provided that mineral surfaces were rendered sufficiently hydrophobic to induce a strong hydrophobic interaction (Song et al., 2000; Song et al., 2001; Rubio et al., 2007).

Therefore, this paper attempts to understand and contrast the effect of non-polar oil in the flocculation and flotation using different collectors. To facilitate the comparison, collectors with the same polar (ionizable) groups but with different hydrocarbon chain lengths, and collectors with the same hydrocarbon chains but with different polar (ionizable) groups were studied. This rationale resulted in the selection of sodium oleate, oleoyl hydroxamic acid, and octyl hydroxamic acid as collectors for the flocculation and flotation of fine hematite (−20 µm) with and without using kerosene. Zeta potential, contact angles and focused beam reflectance measurement (FBRM) particle/aggregate size measurement, as well as extended-DLVO theory calculations were used to understand the observed differences in the flocculation and flotation performances.

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. Its XRD patterns (Fig. 1) show that the sample was pure hematite with minor impurity peaks of quartz and pyrolusite. The hematite sample was wet ground in a laboratory 8″ diameter ball mill, and wet screened to collect the −20 µm fraction for testing. Distilled water was used during grinding and sieving. The sieved −20 µm fraction was decanted, filtered, dried and homogenized. Table 1 shows the chemical composition of the hematite sample determined by whole rock analysis.

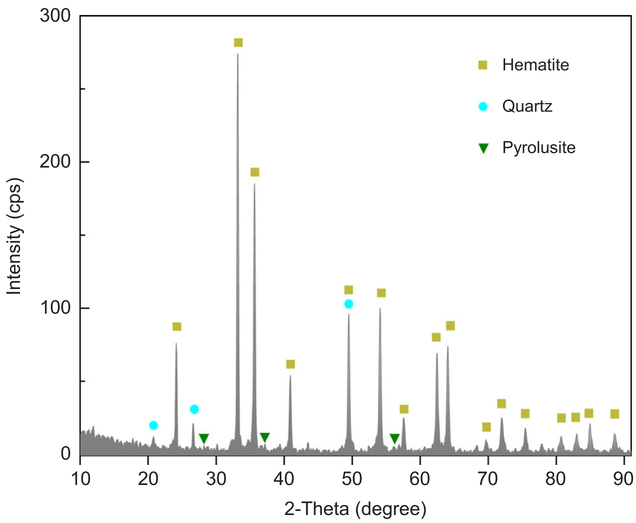

Fig. 1. XRD pattern of hematite sample.

The particle size distribution of the −20 µm hematite sample was determined by a Malvern Mastersizer 3000 particle size analyzer, and the results are shown in Fig. 2. As can be seen, the particle size of the −20 µm hematite sample ranged from 0.1 to 20 µm, with a mode of about 3–5 µm, and approximately 90% of the particles are between 1 and 12 µm.

Odorless kerosene, purchased from Fisher Scientific, was used as the non-polar oil in this study. Kerosene emulsion was prepared by injecting 1 mL kerosene into 200 mL distilled water followed by agitation in a high-speed blender for 3 min. After standing approximately 5 min, the kerosene emulsion had a small D_{50} of 2.98 µm, and the D_{90} was 6.94 µm, as determined by the Malvern Mastersizer 3000.

Sodium oleate (NaOl) (≥82% oleic acid basis) was purchased from Sigma-Aldrich and was used as a collector without 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 labs by hydroxylamine hydrochloride/potassium hydroxide method and prepared as hydroxamate solution with sodium hydroxide in this study (Liu et al., 2015). Fig. 3 shows the 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 the mineralogical composition of the hematite sample. The coupling XRD diffractometer (Bruker D8 XRD) was operated at 40 kV, 44 mA and 4°/min scan rate. The particle size of hematite 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 & Schwertmann, 2003); Kerosene droplets: refractive index 1.43, absorptive index 0.001 (Tummons, 2016).

2.3. Micro-flotation test

Micro-flotation tests were performed in a glass tube at ambient temperature (22 °C). A schematic diagram of the microflotation tube is shown in Fig. 4. The tube has a sintered glass disc at the bottom to allow the passage of gas while a magnetic stir bar can be placed at the sintered glass disc to agitate the mineral sample. The top of the micro-flotation tube was modeled after Siwek et al. (1981). 1.5 g hematite sample was conditioned in 170 mL 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 controlled at 7 by NaOH or HCl solution. After