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Reverse flotation of ultrafine magnetic concentrate by using mixed anionic/cationic collectors

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Abstract: Compared to reverse cationic flotation, the advantages of reverse anionic flotation include relatively lower sensitivity to slimes and lower reagent cost. Besides, anionic collectors were found to have excellent capability of selectively separating an ultrafine magnetite ore. Addition of a small amount of cationic collector into the anionic collector as the collector mixture can improve the metallurgical results of removing silicates in reverse flotation. In this paper, NaOL and DDA were used for reverse flotation of the ultrafine magnetic concentrate. The separation performance of the collector mixture was investigated at different ratios of NaOL and DDA. The results showed that a better separation performance was obtained for the collector mixture than for NaOL alone. There was an optimal molar ratio between NaOL and DDA equal to 10:1. In the flotation system with the presence of the collector mixture, the good selectivity was found when starch was used as a depressor for magnetite and CaO was used as an activator for quartz. The influences of starch and CaO dosages on the separation performance of magnetite, quartz and chlorite had been investigated through micro-flotation tests. The infrared spectral analysis showed stretching vibration peaks of chemical adsorption of the collector mixture on the magnetite surface. The peaks were not present when starch was used as the depressor for magnetite. The closed flotation tests on the magnetic concentrate with the particle size of -25 μm were performed in the laboratory. The Fe concentrate assaying 64.52 % was obtained with Fe recovery of 80.66%, for the Fe content of feed equal to 52.98%.

Keywords: *ultrafine magnetite; collector mixture; reverse flotation; closed flotation*

Introduction

Reverse anionic flotation of magnetite is conducted at a higher pH value (pH 11–12) than reverse cationic flotation (pH 10–10.5). Since the point of zero charge (PZC) of pure magnetite is around pH 6.5, the surface charge of magnetite in reverse cationic flotation (pH 10–10.5) would be less negatively charged than that at pH 11–12 (Li et al., 2009; Filippov et al., 2014). Before adding starch to the pulp, the repulsive electrostatic forces between quartz and magnetite particles with negative charge in reverse anionic flotation are supposed to be stronger than that in reverse cationic flotation

(Bhagyaraxmi et al., 2013). Consequently, heterocoagulation of magnetite and quartz particles can be expected to be less significant in reverse anionic flotation. Therefore, it could increase selectivity of starch adsorption, which contributes to higher selectivity of reverse anionic flotation in the presence of ultrafine particles.

After adding lime into the pulp, the surface charge of quartz is reversed from negative to positive, and it accommodates adsorption of fatty acids. Meanwhile, lime causes coagulation of quartz particles. However, in reverse anionic flotation, since starch molecules are chemically adsorbed on magnetite surfaces, coagulation caused by lime cannot interfere with selective adsorption of starch (Neymayer et al., 2013). For ultrafine particles ($<10\ \mu\text{m}$), the metal loss in reverse cationic flotation is over 92% due to entrainment of hematite ultrafine particles. However, in reverse anionic flotation, metal loss is as low as 42% in the particle size range of 5 to 10 μm , meanwhile, most of the quartz ultrafine particles are rejected (Ma et al., 2011). In recent years, reverse anionic flotation has been successfully applied in the China major iron ore area, Anshan (Shen and Huang, 2005; Zhang et al., 2006). In addition, reverse anionic flotation was conducted without desliming shortening the time of flotation process (Houot, 1983).

The mixtures containing cationic and anionic collectors were suggested to improve the metallurgical results for reverse flotation of silicates, including iron-bearing and aluminum-bearing silicates (Hanumantha and Forssberg, 1993; 1997). These mixtures can provide the increased selectivity of flotation compared to each separate reagent, as well as a significant reduction in collector consumption (Hanumantha et al., 1990; Lu et al., 2016). The collector mixture demonstrated three synergetic effects, namely enhanced mineral recovery, improved adsorption behavior of the main collector on the target mineral surface, and enhanced adsorption selectivity (Holland and Rubingh, 1992; Rao and Forssberg, 1997). The important method of increasing collector effectiveness is addition of a small amount of cationic collector into the anionic collector as the collector mixture. In addition, the molar ratio of anionic and cationic collector has an important effect on the separation efficiency of flotation. When the molar ratio of anionic and cationic collectors is more than 5:1, iron-bearing and aluminum-bearing silicates will be more efficiently removed than that by using the collector alone (Filippov et al., 2010).

Magnetic separation is an important method of recovering magnetite from magnetite ores. However, most of ferrous quartzite and disseminated fine-grained magnetite cannot be rejected as tailings in a magnetic separation process, and it will reduce the content of concentrate from magnetic separation. Since a silica content in the iron concentrate is the limit factor for a steelmaking process in the metallized pellets and electric-arc smelting, hence, removing silicates and increasing the Fe content are important issues. However, it is difficult to reject most of the different silicates, such as quartz and other Fe-bearing minerals at the same time, which is due to their different floatability. In this paper, Fe-bearing minerals and fine quartz were concentrated in the magnetic product, and they resulted in the decrease of the Fe content in the concentrate. For upgrading the magnetic concentrate with the particle size of $-25\ \mu\text{m}$, the mixed

anionic/cationic collectors were used for improving the selectivity of the separation performance as well as rejecting quartz and Fe-bearing mineral (chlorite) simultaneously by micro-flotation and batch flotation tests. The mechanisms underlying the mineral-reagent interaction were further investigated by an infrared spectral analysis. The results provide a reference for effective recovery of ultrafine magnetite.

Materials and methods

Pure minerals and reagents

Pure magnetite, chlorite and quartz were sourced from Anshan, Huaheng, and Haicheng city in China, respectively. Magnetite, chlorite, and quartz were 98, 99, and 94% pure based on the results of chemical analysis, respectively. According to the results of chemical analysis, the content of Fe was 71.27 % in pure magnetite. X-ray diffraction of magnetite, chlorite, and quartz are shown in Fig. 1. The -25 μm fraction was used in the flotation tests.

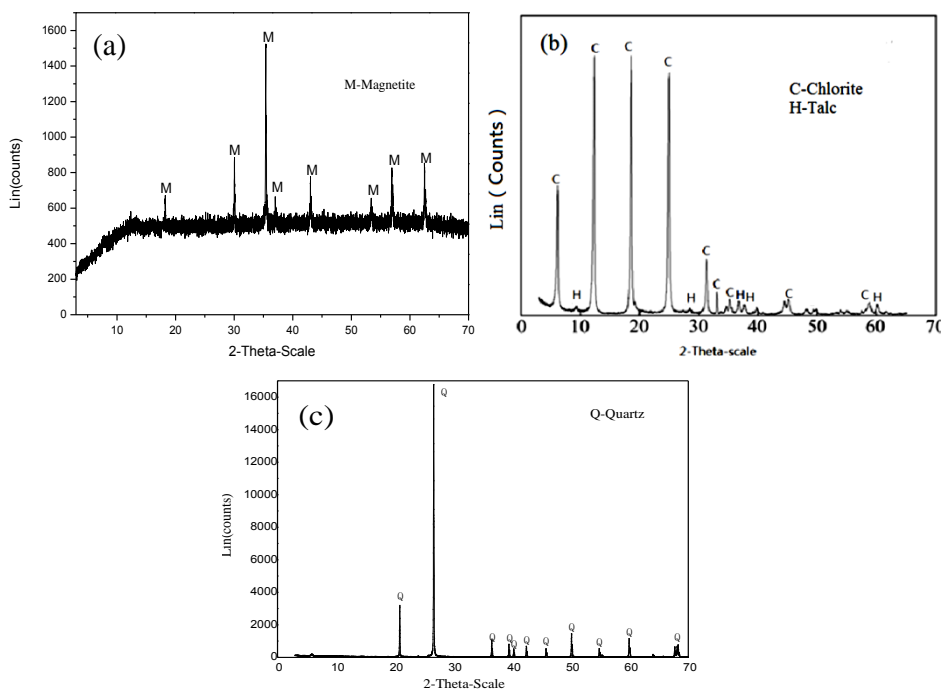


Fig. 1. X-ray diffraction of magnetite, chlorite, and quartz

The cationic surfactant dodecylamine and anionic surfactant NaOL with 99% purity were obtained from Sinopharm Chemical Reagent Co., Ltd. The dodecylamine-hydrochloride (DDA) solution was prepared by mixing equimolar mixtures of

dodecylamine and hydrochloric acid (HCl). NaOL and DDA collectors were freshly prepared for 1% solution to avoid precipitation. HCl and NaOH were used for pH adjustment. Non-modified corn starch from Guangdong province was used as the depressor. The amylopectin and amylose contents in corn starch were 75 and 25%, respectively. For each series of experiments, a fresh 1% solution of alkaline starch was prepared, with NaOH content at 25%. CaO with 99% purity from Tianjing city was used as the activator. Deionized water with a resistivity of more than 18 M Ω ·cm was used for all experiments.

Flotation experiment

Micro-flotation tests were carried out in an XFG flotation machine with a 40 cm³ plexiglass cell, at an impeller speed of 1800 rpm. The mineral suspension was prepared by adding 3.0 g of minerals into the distilled water with the volume of 40 cm³. pH of the mineral suspension was firstly adjusted after adding either NaOH or HCl. Once the desired reagent was added, the suspension was agitated for 3 min, and the pH was measured before flotation. Prior the collector addition, the starch was firstly added as the depressor for magnetite, and CaO was added as the activator for quartz. Flotation lasted for 4 min before the products were collected. Then, the flotation products were dried and weighed. The recovery was calculated based on the weight of the dry product obtained.

Infrared spectral analysis

For IR spectral studies, the diffuse reflectance infrared Fourier transform technique was selected for a solid sample. Prior to the test, an exact portion (3.0 g) of pure minerals with particle size of $\sim 2 \mu\text{m}$ was put into beaker with 40 cm³ pH regulator solution, stirred for 5 min with magnetic stirrer, and added reagents to stir for 60 min in turn. The concentration of starch, CaO and YOA used in the FTIR study were 40, 20 and 100 mg/dm³, respectively. The fully interacted sample was filtered and washed three times with the corresponding pH solution. The solid obtained was dried in a vacuum desiccator. The mineral samples were not mixed with KBr because independent measurements reported by Chernyshova et al. (2000) revealed that KBr dissolution lowered the sensitivity of the DRIFT spectra with respect to the adsorbed layers. Fourier transform infrared spectra were recorded with a Nicolet TM 740 FTIR spectrometer (Thermo Scientific, Waltham, MA, USA) at 25 °C in the range of 4000-500 cm⁻¹. The spectra of the untreated mineral samples (blank) were obtained by using the same procedure, and they were used for the mineral sample interacting with reagents.

The transmission technique was used for obtaining the spectra of starch samples after its gelatinisation with NaOH and YOA (molar ratio of NaOL and DDA =10:1). The starch solution with 1% concentration and YOA solution with 1% concentration were dried at 60 °C for 12 h. The typical spectrum was an average of 64 scans measured at a 2 cm⁻¹ resolution.

Results and discussion

Microflotation

The molar ratio of the collector mixture (anionic/cationic collector) was found to be an important factor in mineral flotation (Mingione, 1984; Critchley and Riaz, 1991; Valdiviezo and Oliveira, 1993; Bradshaw, 1997; Deng et al., 2010). The flotation behavior of magnetic, chlorite and quartz using the collector mixture of NaOL and DDA at different molar ratio was investigated. As shown in Fig. 2, the recovery of magnetic and quartz decreased gradually with the increase of molar ratio of NaOL and DDA. However, the recovery of chlorite had a less decrease than that of magnetic and quartz. There was a marked selectivity of flotation between magnetite and chlorite with the mixed collectors NaOL/DDA. The chlorite recovery was up to 60.1% at a molar ratio of 10:1 at pH 12, while the magnetite recovery was only 40.8%. Compared with the results from using NaOL alone as the collector (Fig. 2). The marked differences in the recovery of magnetite and chlorite implied that the optimal separation performance was achieved when molar ratio of NaOL and DDA was 10:1 in the anionic/cationic mixed collectors.

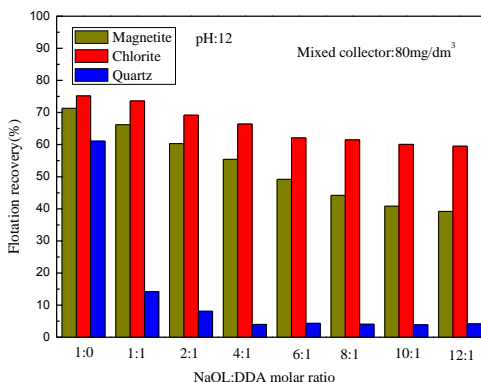


Fig. 2. Effect of molar ratio of NaOL/DDA on flotation behavior of magnetic, chlorite and quartz

Firstly, using YOA (molar ratio of NaOL and DDA =10:1) as the collector at pH of 12 without any depressor and activator, the effect of YOA dosage on the flotation performance of magnetite, chlorite and quartz was evaluated by the micro-flotation test. As shown in Fig. 3, the recovery of magnetite, chlorite and quartz was low with the lack of the collector, and increased with increasing the YOA dosage in the high-alkali system. At the YOA dosage of 100 mg/dm³, the recovery of chlorite, magnetite and quartz increased to 71.30, 42.10 and 7.65%, respectively. For further addition of mixed collector the recovery of three minerals would decrease slightly. Obviously, the YOA had a better collecting capacity on chlorite than that on quartz. Separating chlorite from magnetite is difficult due to their same active Fe sites which both can interact with

anionic collectors. The results indicate that it is necessary to depress magnetite and activate quartz for achieving good separation in this reverse flotation system.

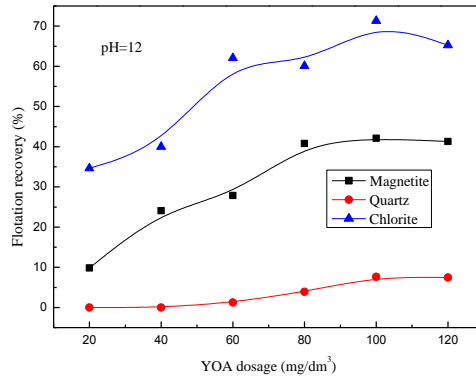


Fig. 3. Effect of YOA dosage on flotation behavior of magnetite, chlorite and quartz

When the dosage of YOA was 100 mg/dm^3 at pH of 12, the effects of starch dosage on flotation behavior of magnetite, chlorite and quartz was evaluated. As shown in Fig. 4, the recovery of magnetite was high in the absence of starch. The recovery of magnetite decreased with the increase of starch dosage. Increasing the starch dosage from 0 to 20 mg/dm^3 caused that the recovery of magnetite decreased from 42.10 to 7.56 %, and the recovery of chlorite and quartz changed only slightly. For further addition of starch, the recovery of quartz will increase slightly. Therefore, under condition of using starch as the depressor, chlorite can be separated from magnetite by using YOA as the collector. In YOA flotation system, although the same active Fe sites exist on the surface of magnetite and chlorite, there has good selectivity, and chlorite flotation will not be depressed when starch is used as the depressor for magnetite. The results imply that it is necessary to activate quartz for achieving the good magnetite product.

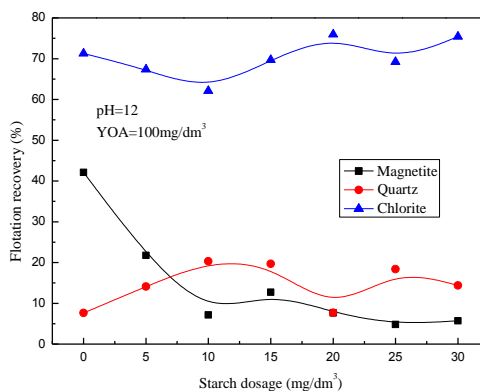


Fig. 4. Effect of starch dosage on flotation behavior of magnetite, chlorite and quartz using YOA as the collector

When the dosage of YOA was 100 mg/dm^3 at pH of 12, the effect of CaO dosage on flotation behavior of magnetite, chlorite and quartz was evaluated without starch. As shown in Fig. 5, the recovery of quartz was low in the absence of CaO. Floatability of chlorite was better than that of magnetite and quartz without addition of CaO. The recovery of quartz and magnetite increased with the increase of CaO dosage. With increasing the CaO dosage from 0 to 20 mg/dm^3 , the recovery of quartz increased from 7.65 to 84.25% (11-fold), and that of magnetite increased from 42.10 to 89.90% (2-fold). However, the recovery of chlorite changed slightly with the increase of CaO dosage. Obviously, the CaO dosage had a stronger effect on magnetite and quartz than chlorite flotation. The results imply that it is necessary to activate quartz and depress magnetite for achieving a good separation efficiency.

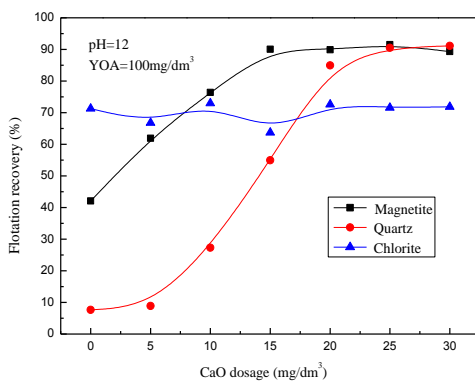


Fig. 5. Effect of CaO dosage on flotation behavior of magnetite, chlorite and quartz using YOA as the collector

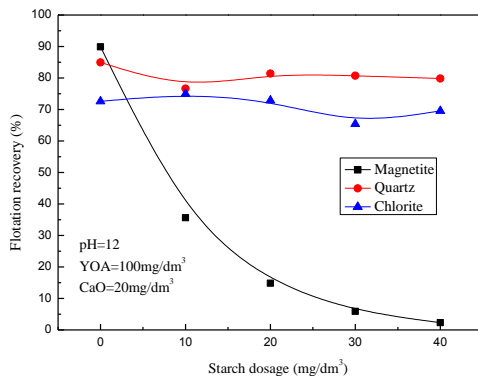


Fig. 6. Effect of starch dosage on flotation behavior of magnetite, chlorite and quartz using YOA as the collector, and CaO as the activator

When the dosage of YOA was 100 mg/dm^3 and CaO was 20 mg/dm^3 at pH of 12, the effect of starch dosage on the flotation behavior of magnetite, chlorite and quartz was

evaluated. As shown in Fig. 6, the recovery of activated quartz by CaO slightly changed after using starch as the depressor, while, the recovery of activated magnetite decreased greatly with increase of starch dosage. At the starch dosage of 40 mg/dm³, the recovery of magnetite decreased to 2.30 %, and the recovery of quartz and chlorite changed slightly and was equal to 79.85 and 69.55%, respectively. Magnetite can be separated efficiently from quartz and chlorite in this reverse flotation system.

Infrared spectral analysis

As shown in Fig. 7, 726.0 cm⁻¹ is rocking vibration absorption peak of -CH₂, 2926.5 cm⁻¹ and 2853.3cm⁻¹ are symmetric and asymmetric stretching vibration absorption peaks of C-H in -CH₂. 3008.7 cm⁻¹ is symmetric stretching vibration absorption peak of -CH, 1462.2 cm⁻¹ is asymmetric bending vibration absorption peak of -CH₃, and 1709.7 cm⁻¹ is stretching vibration absorption peak of -C=O (Sun et al., 2014; Sun et al., 2015). Asymmetric and symmetric stretching vibration peaks of -CH₂ in 2792.4 cm⁻¹ and 2892.3 cm⁻¹ were found in the IR spectrum of magnetite after adsorption of YOA. Analysis results of IR spectrum showed that YOA may absorb on the magnetite surface in the form of chemical adsorption. Compared spectrums of YOA, stretching vibration peaks had shifted in the IR spectrum of magnetite. It indicates on the effect of hydrogen bonding.

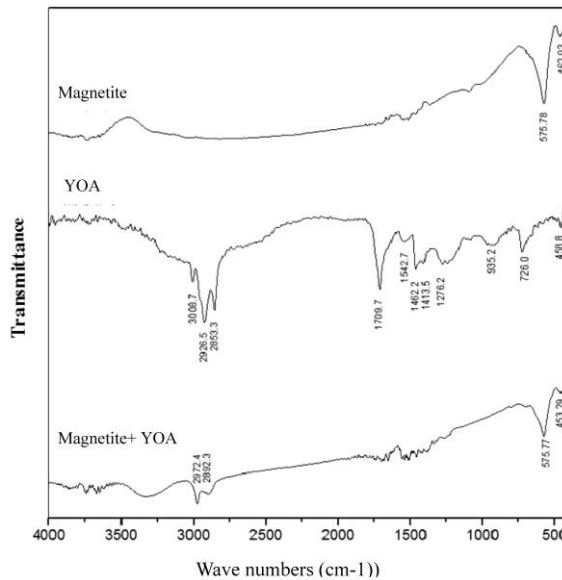


Fig. 7. IR spectra in the absence and presence of YOA (pH = 12)

The collector YOA was added after magnetite interaction with starch and the infrared spectral patterns of magnetite are showed in Fig. 8. The IR spectrum of magnetite shown in Fig. 8 was consistent with the standard spectrum of magnetite. The

characteristic peaks of $-\text{CH}_2$ at 2972.4 cm^{-1} and 2892.3 cm^{-1} disappeared. This phenomenon suggested that the interaction between YOA and magnetite was significantly affected by starch in the high-alkali environment. Adsorption of starch prevented chemical adsorption of YOA on magnetite. The results of the infrared spectral analysis were consistent with the data of the flotation tests (Filippov et al., 2010).

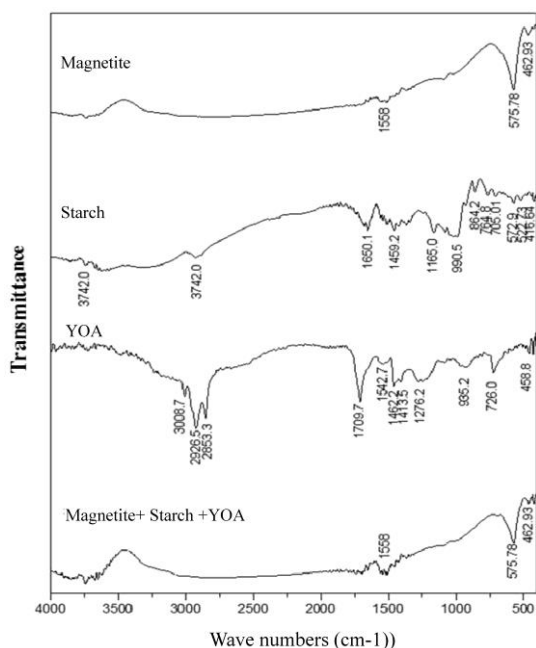


Fig. 8. IR spectra in the absence and presence of starch and YOA (pH = 12)

Flotation flowsheet of magnetite concentrate

The materials containing magnetite in flotation were produced by magnetic separation, and they were obtained from Xinjiang, China. X-ray diffraction of this materials is shown in Fig. 9. The main minerals are magnetite, quartz, chlorite and stilpnomelane in this magnetic concentrate. Ultrafine particles with the size smaller than $25\text{ }\mu\text{m}$ constitute about 95 % in this materials.

Based on the optimized flotation conditions and open circuit tests, the bench-scale locked cycle tests were carried out on this materials containing 52.98 % Fe. The detailed flotation flowsheet and corresponding flotation conditions are listed in Fig. 10. Results of the locked cycle tests are shown in Table 1. The results indicated that the mixed collectors YOA (NaOL/DDA at molar ratio of 10:1) had good selectivity for removing the gangues from the magnetic concentrate with the particle size of 95% passing $25\text{ }\mu\text{m}$ size. The Fe concentrate assaying 64.52 % was produced with Fe recovery of 80.66%.

The collector YOA had an excellent selectivity to reverse flotation of fine magnetite, and showed a great potential for industrial application.

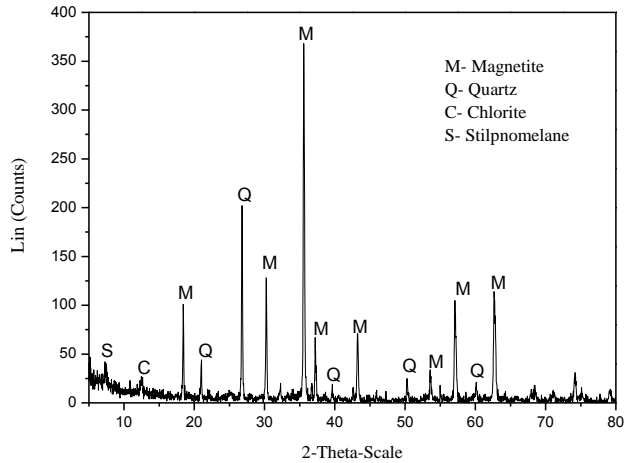


Fig. 9. X-ray diffraction of magnetite concentrate

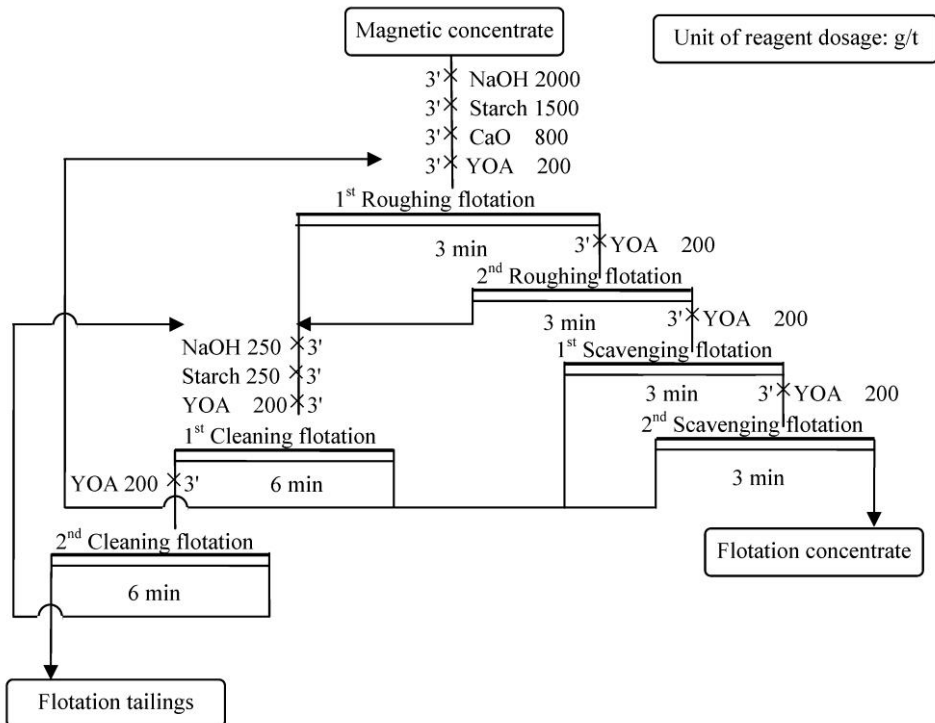


Fig. 10. Closed circuit flotation flowsheet of magnetic concentrate

Table 1. Results of the closed flotation tests performed on magnetic concentrate

Products	Yield/wt%	Fe	
		Grade (%)	Recovery(%)
Concentrate	66.23	64.52	80.66
Tailings	33.77	30.34	19.34
Magnetic concentrate	100.00	52.98	100.00

X-ray diffractions of flotation concentrate and tailings are shown in Fig. 11. It was obvious that most of quartz and Fe-bearing mineral (chlorite) were rejected from the magnetic concentrate simultaneously. The results of X-ray diffraction on the final products were consistent with the results from the flotation tests. Micrographs of flotation concentrate and tailings are shown in Fig. 12. As shown in Fig. 12(a), Fe grade of magnetic concentrate increased due to the decrease of the gangues, such as quartz and chlorite. Loss of Fe in tailings was present as the ultrafine particles smaller than 3 μm and particles associated with quartz.

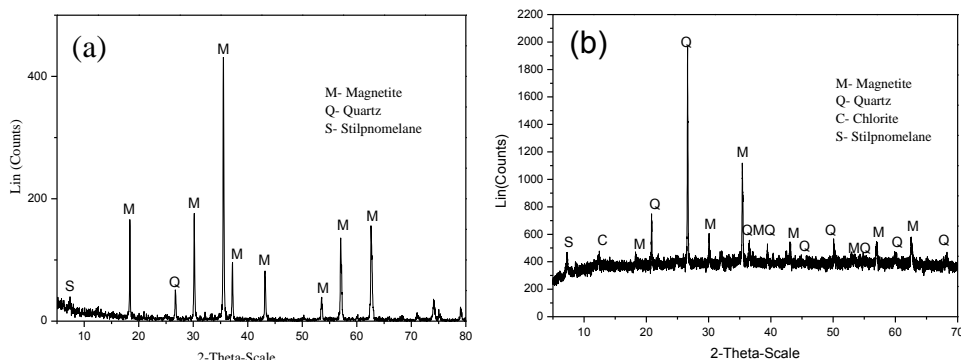
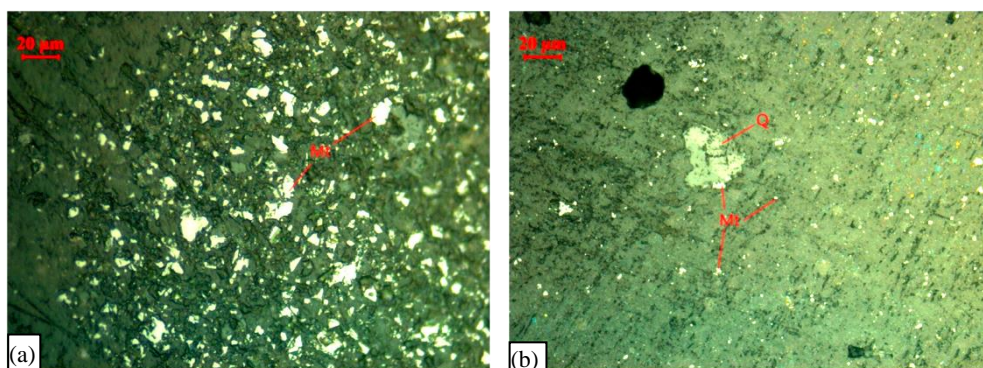


Fig.11. X-ray diffraction of flotation concentrate (a) and tailing (b)



Mt – Magnetite; Q – Quartz

Fig.12. Micrographs of flotation concentrate (a) and tailing (b)

Conclusions

In this study, reverse flotation of the ultrafine magnetic concentrate was studied with a collector mixture of NaOL and DDA. It can be noted that, when anionic and cationic collectors were mixed for reverse flotation, most of quartz and Fe-bearing mineral (chlorite) were rejected from the magnetic concentrate simultaneously, meanwhile, ultrafine magnetite was depressed by starch. Although particles size was less than 25 μm , a good separation efficiency was obtained. In addition, there was an optimal molar ratio between anionic and cationic collectors.

The infrared spectral analysis suggested that mixed collector can absorb on the surface of magnetite, however, the stretching vibration peaks disappeared after interaction with starch. It indicates that the gangues can be removed from magnetite by using the collector mixture in reverse flotation.

The closed flotation tests on the magnetic concentrate with particle size of $-25 \mu\text{m}$ were performed in the laboratory scale. The Fe concentrate assaying 64.52 % was produced with the Fe recovery of 80.66% from a feed containing 52.98 % Fe. Loss of Fe in tailings was present as the ultrafine particles smaller than 3 μm and the particles associated with quartz. The collector mixture YOA exhibited great potential for industrial application in ultrafine magnetite flotation.

Acknowledgements

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