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Collecting performances of N-dodecylethylene-diamine and its adsorption mechanism on mineral surface

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Abstract: The collecting performances of N-dodecylethylene-diamine (ND) to quartz and hematite were studied via single mineral flotation. Experimental results show that ND has stronger collecting ability to quartz than hematite. Different floatability of quartz and hematite was presented in the existence of depressant. Compared with lauryl amine, ND has stronger collecting performances to quartz. Satisfied separation result of artificially mixed sample was acquired with iron grade of concentrate of 59.92% and iron recovery of 88.85% when pulp pH value was 7.27 with 41.7 mg/L collector and 3.33 mg/L starch. Polar group properties calculation results indicated that ND has stronger collecting capability and better selectivity than lauryl amine. Measurement results of zeta-potentials and infrared spectrum showed that hydrogen bonding adsorption and electrostatic adsorption occur between the surface of ND and quartz.

Key words: N-dodecylethylene-diamine; collecting performances; quartz; hematite; adsorption mechanism

1 Introduction

Flotation is a cost-effective mineral processing method and is widely used in mineral separation to recover valuable minerals from gangue. It is the most commonly used concentration method in itabirite iron ores beneficiation[1−2]. In the past, direct flotation methods were proposed, but inverse flotation method is largely employed at present, in which the quartz gangue is floated while the iron oxides/hydroxides are depressed with the help of starches. Medium hydrocarbon chain amines with 10−12 carbon atoms are the cationic collectors used in iron ore reverse flotation[3−4].

The increasing world demand for mineral raw materials has evoked the exploitation of low-grade ores. This fact associated with more rigorous specification of concentrates, hard environmental legislation and a necessity to achieve lower operating costs led to numerous investigations aimed at more effective flotation reagents[5]. In recent years, studies on reverse flotation collectors of iron ores were conducted by many researchers. For example, the flotation performances of N-dodecyl-β-amino-propylamide[6], combined quaternary ammonium salt[1], dodecyl-ammonium ion[7] and medium-chain etheramine acetates were investigated extensively[8−9].

However, there are still some disadvantages in reverse flotation collectors. For example, anionic collectors have poor selectivity and cationic collectors have such flaws as low flotation efficiency, large viscosity and poor mobility of foam[10−11]. Therefore, further research on collectors used in reverse flotation of iron ores is launching to promote the utilization efficiency of iron ores.

N-dodecylethylene-diamine (ND) is a cationic collector containing a hydrocarbon chain of mixed aliphatic structure with an amino group and an imino group. However, its flotation performances to minerals have not been discussed.

The purpose of this work is to investigate the flotation behaviors of hematite and quartz with N-dodecylethylene-diamine acetates as collectors. The separation behavior of artificially mixed samples, which was a mixture of hematite and quartz, was investigated when corn starch was employed as a depressant. Interactions between diamine and mineral surface were studied by FT-IR analysis and zeta potentials measurement.

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2 Experimental

2.1 Preparation of minerals

Hand-picked hematite and quartz were gathered from Qidashan plant located in Liaoning Province of China. The samples were crushed and ground to smaller than 0.100 mm for further studies. They were of 96% purity based on mineralogical analysis, X-ray diffraction and chemical analysis. The chemical analysis results are listed in Table 1.

Table 1 Chemical compositions of hematite and quartz (mass fraction, %)

Sample	Fe_2O_3	SiO_2	P_2O_5	SO_3
Hematite	96.2	3.52	0.016 7	0.020 3
Quartz	0.077 5	96.2	0.007 0	0.014 8
Sample	CaO	Al_2O_3	MgO	K_2O
Hematite	0.021 9	0.196	−	−
Quartz	0.248	3.25	0.314	0.095 5

Artificially mixed samples were prepared by mixing hematite and quartz at a mass ratio of 2:3.

2.2 Reagents

Lauryl amine of chemically pure and ND were used as collectors. Lauryl amine was supported by Sinopharm Chemical Reagent Co. Ltd of China and ND was synthesized in laboratory. They were used as acetate solution with concentration of 1%. Corn starch of analytical quality was adopted as a depressant. Solutions of HCl and NaOH were used to adjust the pH values of the system.

2.3 Flotation experiments

Single mineral particles (5 g) or artificially mixed samples (5 g) were placed in a 30 mL XFG flotation cell, which was then filled with distilled water. The suspension was agitated for 3 min by a four-bladed plastic stirrer rotating at 1 260 r/min before the pH was adjusted to a desired value. Then starch and collector were added into the cell orderly with a 3 min interval of stirring before a flotation period of 5 min. The products and tailings were weighted and assayed separately after filtration and drying, and then the recovery was calculated.

2.4 FT-IR and zeta potentials measurement

The infrared spectra were recorded using a Nicolet 740FT-IR spectrophotometer. A pellet made of a mixture of 1 mg samples and 100 mg KBr was prepared for these studies. In order to verify the nature of species adsorbed in the quartz-aqueous solution interface, fine quartz particles were added into an aqueous solution of amine acetate collector with a concentration of 1.14×10^{-2} mol/L for 20 min. Then the particles were separated by filtration, thoroughly rinsed with distilled water and dried at room temperature for further investigation[12].

Zeta potentials of quartz were measured by means of JS94H Zeta Plus apparatus. Small amounts of finely ground quartz particles (<5 μm) were dispersed in 50 mL aqueous solution and agitated for 12 min to form the suspensions with mass concentration of 0.04%. When the pH value of suspension was regulated to a desired value by HCl and NaOH solution, the zeta potentials of quartz were measured and the average value of at least five individually measurements was accredited.

3 Results and discussion

3.1 Flotation of pure minerals

The influences of collector concentration on collecting efficiencies of ND and lauryl amine to quartz and hematite at the natural pH value (pH=6.65) were investigated and shown in Figs.1 and 2.

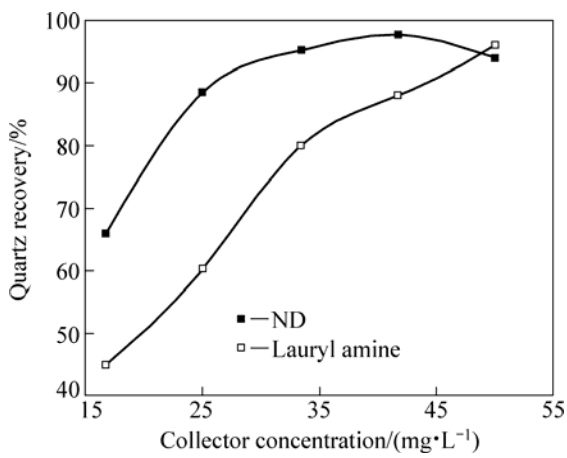

Fig.1 Influence of collector concentration on floatability of quartz

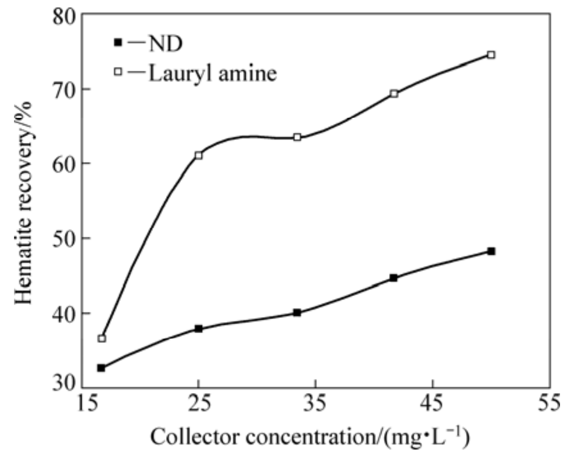

Fig.2 Influence of collector concentration on floatability of hematite

It can be seen that the recoveries of quartz and hematite rise with increasing the collector concentration.

The collecting capability of ND to quartz is stronger than that of lauryl amine. When the concentration of ND is 41.7 mg/L, the recovery of quartz gets its maximum which is 97.64%, while the recovery of quartz is only 87.98% when lauryl amine is used as collector.

The fact that lauryl amine has stronger collecting capability to hematite than ND can be seen from Fig.2. Under the experimental condition, the recovery of hematite is lower than 50% when ND is used as collector. The maximum recovery of 74.45% can be achieved when lauryl amine is used as collector.

When the collector concentration is 41.7 mg/L, the flotation recoveries of quartz at different pH values are shown in Fig.3.

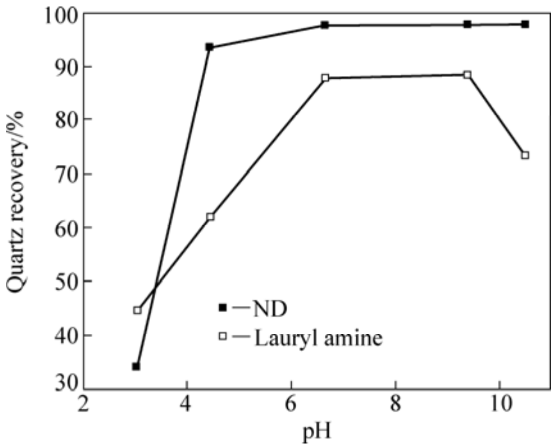

Fig.3 Influence of pH on floatability of quartz

It can be seen that ND has better collecting capability to quartz than lauryl amine. When ND is used as collector and the pH value of pulp is lower than 4.5, the flotation recovery of quartz increases sharply with the increase of pH value. After that, the flotation recovery of quartz keeps steady. When pH value is 6.6 and ND is used as collector, the flotation recovery of quartz gets its maximum of 98.10%. However, at this time, the flotation recovery of quartz is only 87.94% when lauryl amine is used as collector. Flotation recovery of quartz is higher than 90% in a wide range of pH values when ND is used as collector. This means ND has strong collecting capability to quartz and can be used in neutral and alkaline solutions to float quartz.

The influence of pH value on the flotation performances of hematite when the collector concentration is 41.7 mg/L is shown in Fig.4.

It can be seen that when lauryl amine is used as collector and pH value is lower than 9.6, along with the increasing pH value, the flotation recovery of hematite rises rapidly. After that, the flotation recovery of hematite decreases sharply. The maximum recovery is

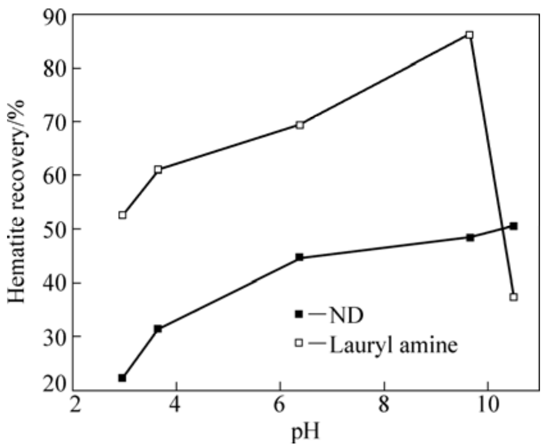

Fig.4 Influence of pH on floatability of hematite

obtained when pH value is 9.6. Compared with lauryl amine, the flotation recovery of hematite increases with the increase of pH value when ND is used as collector. Collecting efficiency of ND to hematite is weaker than that of lauryl amine, and the maximum recovery of hematite is no more than 55% under the whole experimental conditions.

From Figs.1−4, it can be seen that ND has stronger collecting performance to quartz than hematite. Therefore, different floatability of quartz and hematite may be presented in the existence of depressant. So starch is used to investigate the flotation performance of quartz and hematite. When ND concentration is 41.7 mg/L at natural pH, the influence of starch concentration on flotation performances of minerals is shown in Fig.5.

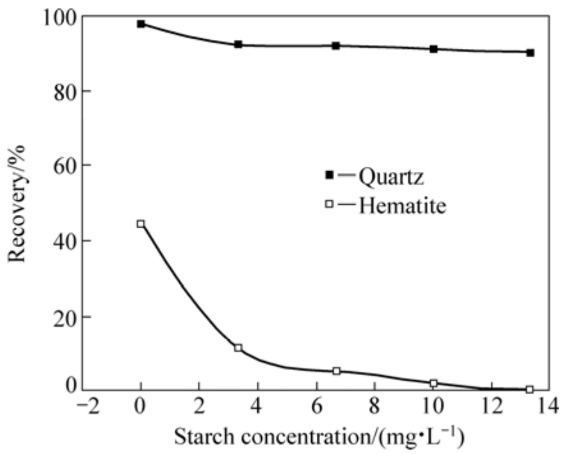

Fig.5 Influence of starch concentration on flotation performances of minerals

With increasing starch concentration, the recovery of quartz keeps stable which is more than 90% after a small decline, and the flotation recovery of hematite declines sharply. When the starch concentration is more than 6.67 mg/L, the flotation recovery of hematite is less than 10%. There is no floatability of hematite when the starch concentration is 13.33 mg/L.

3.2 Separation results of artificially mixed sample

Pure mineral flotation results show that with 6.67 mg/L corn starch, ND also has strong collecting performance to quartz. In order to demonstrate a good selectivity for quartz against hematite, reverse flotation separation of artificially mixed sample is adopted.

The separation efficiency of artificially mixed sample with 41.7 mg/L collector ND and 3.33 mg/L starch at different pH values is shown in Fig.6.

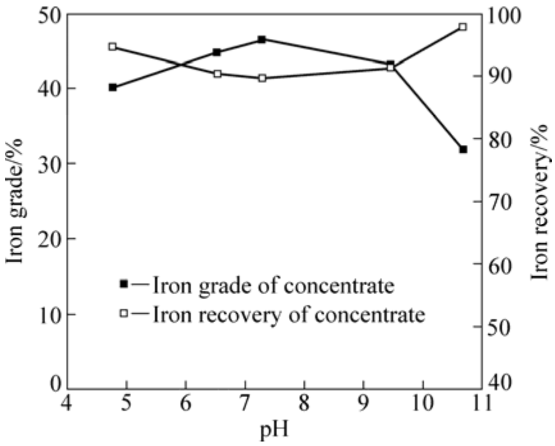

Fig.6 Influence of pH on separation results of artificially mixed sample

It can be seen that the iron grade of concentrate increases with increasing pH value when pH value is lower than 7.27. After that, the iron grade of concentrate decreases sharply. Better separation result of 59.92% iron grade and 88.85% iron recovery is obtained when the pulp pH value is 7.27 with 41.7 mg/L collector ND and 3.33 mg/L starch.

The separation efficiency of artificially mixed sample with the addition of starch is shown in Fig.7, when the pulp pH value is 7.27 and 41.7 mg/L collector is added.

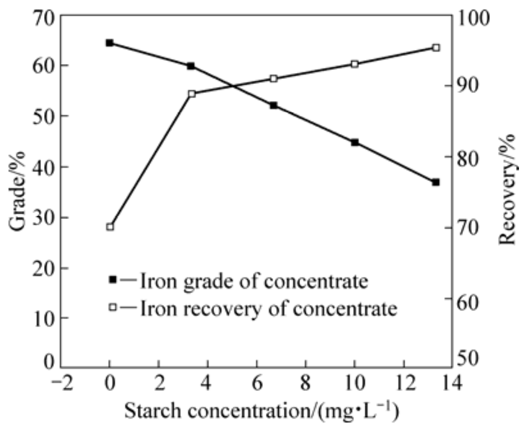

Fig.7 Influence of starch concentration on separation of artificially mixed sample

Figure 7 illustrates that with the increasing starch dosage, the iron recovery increases rapidly when the starch dosage is no more than 3.33 mg/L, and then increases smoothly when the starch dosage is more than 3.33 mg/L. However, the iron grade of concentrate decreases with the increase of starch dosage. The separation result of 59.92% iron grade and 88.85% iron recovery is acquired when the starch dosage is 3.33 mg/L.

The influence of collector concentration on the separation of artificially mixed sample is shown in Fig.8 when the pulp pH value is 7.27 and 3.33 mg/L starch is added.

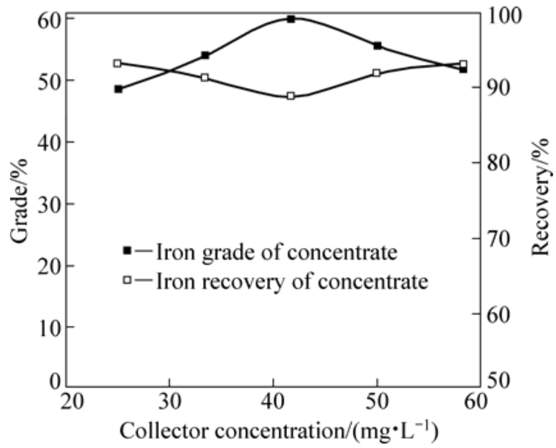

Fig.8 Influence of collector concentration on separation of artificially mixed sample

Figure 8 illustrates that when the collector concentration is less than 41.7 mg/L, the iron grade of concentrate increases with the increase of collector concentration; whereas, the iron recovery decreases gradually. When the collector concentration is over 41.7 mg/L, the iron grade of concentrate decreases with the increase of collector concentration, accompanying with increasing iron recoveries. Concentrate with 59.92% iron grade and 88.85% iron recovery is acquired when the pulp pH value is 7.27 with 41.7 mg/L collector and 3.33 mg/L starch.

4 Adsorption mechanisms

4.1 Properties of cationic group

Based on the structure theory of flotation reagents, the electronegativity of polar groups (χ_g) and radicle size of collector reflect the selectivity and mineral-adsorption intensity of collectors. Usually, high electronegativity implies strong mineral-adsorption intensity while large radicle size implies high selectivity of the collector[13−14].

The electronegativity of polar groups is not invariable for it is influenced by the contiguous atoms.

The electronegativity of polar groups of ND is calculated according to the calculating formulas mentioned by WANG[15], and the results are listed in Table 2.

Table 2 Electronegativity of ND's polar groups

Group	χ_g
—NH_2	3.7
—NH—	4.1

From the calculation, it can be seen that the electronegativity of ND in polar groups is (3.7+4.1)/2= 3.9, while that of lauryl amine is 3.7. So, ND can be used as collector for oxide minerals and its collecting performance is stronger than that of lauryl amine. This phenomenon can be testified by pure mineral flotation.

The radicle size of polar groups is also calculated according to the calculating formulas mentioned by WANG[15], and the results are listed in Table 3.

Table 3 Radicle size of ND

Polar group	Size/ nm
Primary amine group	d_{H-H}=0.36
Secondary amine group	d_{C-H}=0.5, d_{C-C}=0.68

From Table 3, it can be seen that the polar group radicle size of ND is much larger than that of lauryl amine. So ND is more selective than laurylamine on mineral separation, and ND can be used as collector in reverse flotation separation of iron ores.

4.2 Zeta-potentials studies

The zeta potentials of quartz before and after acting with ND are shown in Fig.9.

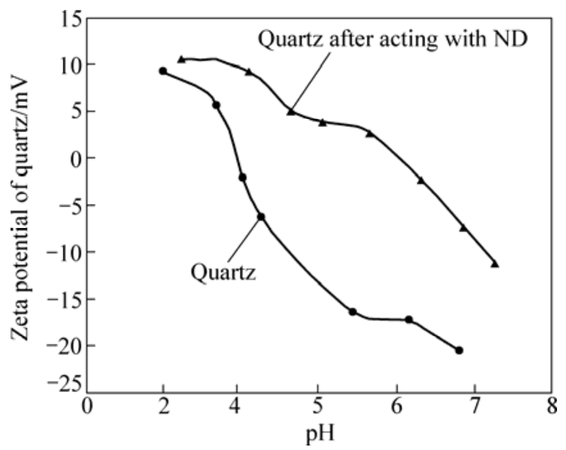

Fig.9 Zeta potential of quartz before and after acting with ND

The addition of ND leads to the zeta potential of quartz increasing. This indicates the cationic collector has adsorbed on mineral surface. When the pH value of solution is less than 3.7, the surface of quartz is electropositive. Under this condition, ND can be still adsorbed on minerals surface, which indicates the hydrogen bonding adsorption has taken place on the mineral surface. When the pH value of solution is higher than 3.7, the surface of quartz is electronegative, so electrostatic adsorption takes place between the surface of mineral and collector[16−17].

4.3 Infrared spectrum measurement

In order to investigate the adsorption mechanism of ND on quartz, infrared spectra of quartz before and after acting with ND are analyzed and shown in Fig.10.

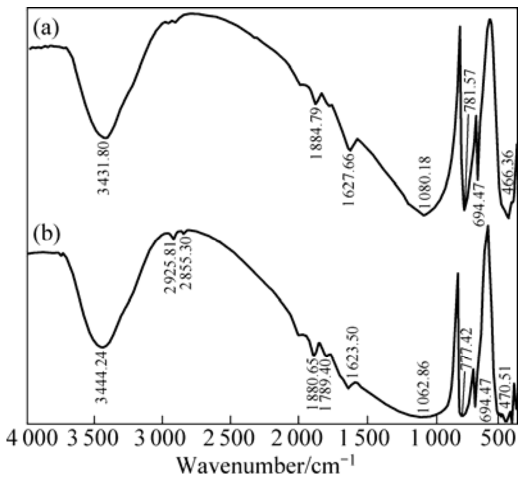

Fig.10 Infrared spectra of quartz before (a) and after (b) acting with ND

It can be seen from Fig.10(a) that the stretching vibration of Si—O is characterized at 1 080.18 cm^{-1}. The adsorption peak of hydroxyl group is visible in the figure, indicating the existence of crystal water in quartz.

After contacting with ND, there exist stretching liberations of CH_3— and —CH_2— at 2 925 cm^{-1} and 2 855 cm^{-1} although they are too weak, indicating the adsorption of ND on quartz surface. The diagnostic peaks of quartz are not changed clearly except red-shift, indicating there is no chemical adsorption on mineral surface[17]. After the adsorption of ND on quartz surface, the peak at 3 431.80 cm^{-1} shifts to 3 444.24 cm^{-1}, which indicates hydrogen binding adsorption on quartz surface[18].

5 Conclusions

1) The results of single minerals flotation test showed that ND has stronger collecting performances on quartz than hematite. Compared with lauryl amine, ND has stronger collecting performance to quartz.

2) Artificially mixed mineral separation results showed that ND can separate quartz from hematite in the existence of starch. Products with 59.92% iron grade and

88.85% iron recovery can be acquired with the addition of 41.7 mg/L collector and 3.33 mg/L starch when the pulp pH value is 7.27.

3) Polar group properties calculation verified that ND has stronger collectivity and better selectivity than lauryl amine.

4) Zeta-potentials measurements and infrared spectrum measurement showed that hydrogen bonding adsorption and electrostatic adsorption occur between the surface of quartz and ND.

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N-十二烷基乙二胺的捕收性能及其在矿物表面的吸附特性

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摘要：通过单矿物实验考察 N-十二烷基乙二胺（ND）对石英和赤铁矿的捕收能力。结果表明，ND 对石英具有很强的捕收能力，而对赤铁矿的捕收能力较弱。在抑制剂存在的情况下，石英和赤铁矿体现出不同的浮游特性。与十二胺相比，ND 对石英具有更强的捕收能力。人工混合矿分选实验结果表明，在矿浆 pH 值为 7.27、捕收剂用量为 41.7 mg/L、抑制剂用量为 3.33 mg/L 时取得较好的分选效果，此时精矿中的铁品位为 59.92%、铁回收率为 88.85%。极性基团性能计算结果表明，与十二胺相比，ND 具有更强的捕收能力和更好的选择性。Zeta 电位测试和红外光谱分析结果表明，ND 与石英表面发生静电和氢键吸附。

关键词：N-十二烷基乙二胺；捕收性能；石英；赤铁矿；吸附机理

(Edited by FANG Jing-hua)