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Flotation separation of quartz from magnesite using carboxymethyl cellulose as depressant

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Abstract: Carboxymethyl cellulose (CMC) was introduced as a depressant in reverse flotation separation of quartz from magnesite. The flotation behavior and surface properties of magnesite and quartz exposed to CMC were studied by zeta potential tests, atomic force microscopy imaging and contact angle measurements. The addition of CMC as the depressant in reverse flotation using dodecylamine (DDA) as the collector exhibited a selectively depressive performance towards magnesite and achieved an improved recovery of magnesite. The study of surface properties demonstrated that CMC and DDA exhibited different adsorption strengths on the surface of magnesite and quartz. It was found that the adsorption of CMC on magnesite surface was stronger than that of DDA, which hindered the subsequent adsorption of DDA on magnesite surface. On the contrary, the quartz surface was strongly adsorbed by DDA instead of CMC, which proved that the addition of CMC did not influence the flotation of quartz.

Key words: flotation separation; carboxymethyl cellulose; dodecylamine; magnesite; quartz

1 Introduction

Magnesite is one of the most important basic raw materials for the production of refractories due to its high fire resistance and good cohesiveness. In recent years, magnesium-containing products have been widely applied in metallurgy, construction, chemical industries and many other areas [1,2]. In ore deposits, magnesite is usually associated with quartz, dolomite and feldspar [3]. Among these minerals, quartz is one of the most widely existed gangue minerals in the magnesite ores and could exhibit negative influence on the strength of refractories [4]. The reverse flotation is a common method to separate the magnesite and the coexisting quartz by floating the quartz to the froth and retaining the magnesite concentrate in the flotation cell [5–7]. Amine collectors are widely used in the reverse flotation separation of magnesite from

quartz [8–10]. However, the loss of magnesite during reverse flotation is unavoidable as amine collectors have a certain ability to float magnesite [11-13].

Organic and inorganic depressants, such as sodium silicates, organic sulfate [14], sodium hexametaphosphate, citric acid and oxalic acid [15], are commonly used for minimizing the loss of magnesite during the reverse flotation separation of magnesite from quartz by selectively adsorbed on the surface of magnesite [11]. However, those reagents were found to exhibit depression effect on the quartz flotation [12-16], which results in growing demand for introducing а a new environmentally friendly reagent to achieve efficient flotation separation of quartz and magnesite [17].

Carboxymethyl celloluse (CMC) is a naturally existing non-toxic chemical reagent. It can be easily obtained from many cellulose-containing plants by

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simple alkali treatment [18]. It is usually used as a modifier in flotation because of the carboxyl substituent groups along the cellulose chain [19] and is expected to be able to exhibit high chemical activity towards many metal ions at mineral/water interfaces [20]. It was reported that talc could be depressed by CMC and Mg ions could be adsorbed on the talc surface. The adsorption of Mg ions on the talc surface was considered to be able to "bridge" the mineral surface with CMC and enhance the adsorption of CMC on the talc surface [21]. Considering that the magnesite might have been exposed to active metal sites on the particle surface, CMC also has the potential to act as a selective depressant in the magnesite-quartz separation [22]. However, little research was conducted on using CMC as the depressant in the reverse flotation of quartz from magnesite and investigating the mechanism of effects of CMC on the mineral surface properties.

Therefore, in this work, CMC was introduced in reverse flotation separation of quartz from magnesite using DDA as the collector. The selective depression effect of CMC towards magnesite was studied through surface characterization methods including contact angle measurement, zeta potential test and AFM imaging analysis, on the basis of which the adsorption behaviors of CMC and DDA on the surface of quartz and magnesite were modeled and discussed.

2 Experimental

2.1 Minerals and reagents

The pure magnesite and quartz used in this study were obtained from Haicheng Mine, Liaoning province, China. The pure magnesite and quartz minerals were crushed to the size fraction of 1-3 mm by a roll crusher. The crushed minerals were further ground to <20 µm by a ceramic ball mill [23]. The well-prepared pure minerals were then stored in vacuum for subsequent flotation tests and zeta potential measurements. The D_{50} values of mineral samples were 11.77 µm for magnesite and 11.19 µm for quartz, which were measured with a Malvern Mastersizer 2000 by light scattering. According to the X-ray diffraction results in Fig. 1 and the chemical analysis results in Table 1, the purities of the magnesite and quartz samples were 99.498% and 99.650%, respectively.



Fig. 1 XRD patterns of pure magnesite (a) and quartz (b) samples

 Table 1 Chemical compositions of pure magnesite and quartz samples (wt.%)

Sample	Fe	CaO	SiO ₂	MgO	LOI
Magnesite	0.22	0.15	0.08	47.38	52.17
Quartz	0.088	0.101	99.650	0.078	0.083

The magnesite-bearing ore used for bench flotation tests was obtained from Liaoyang Mine, Liaoning Province, China. The chemical analysis indicates that the ore contained 45.05% MgO, 3.74% SiO₂, 0.79% CaO and 0.26% Fe₂O₃ (mass fraction). The XRD patterns show that the magnesite-bearing ore was composed of 93.22% magnesite, 3.61% quartz and 2.55% dolomite (mass fraction).

The dodecylamine (DDA, $CH_3(CH_2)_{11}NH_2$) used in this study was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. It was used as dual-function flotation reagent, i.e., the collector and frother of quartz. The CMC ([C₆H₇O₂(OH)₂OCH₂COONa]_n) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China. The CMC was used as the magnesite depressant in the reverse flotation separation of quartz from magnesite. Five types of CMC with different relative molecular masses and degrees of substitution as listed in Table 2 were used in this study. The molecular structures of DDA and CMC were shown in Fig. 2. HCl and NaOH were used as pH regulators. All micro-flotation reagents used in this study were analytical ones. Deionized water (Resistivity=18.2 M Ω ·cm) was used for single and mixed binary mineral flotation tests, zeta potential measurement, AFM imaging and contact angle measurement. Beijing tap water was used for all the bench flotation tests.

Table 2 Properties of five types of CMC

<u>1</u>	V 1		
CMC type	Relative molecular mass	Degree of substitution	
Ι	90000	0.9	
II	250000	0.7	
III	250000	0.9	
IV	250000	1.2	
V	700000	0.9	

2.2 Flotation tests

Micro-flotation tests were conducted using an XFG flotation machine (Jilin Prospecting Machinery Factory, China), equipped with a plexiglass flotation cell (40 mL) at an agitation rate of 1800 r/min [24].

For single mineral flotation experiments, the flotation pulp was prepared by adding 2.0 g of single mineral particles into the flotation cell and dispersed with 40 mL deionized water at 1800 r/min. After 1 min conditioning, the pH regulator (if needed, with agitation time of 3 min), depressant (if needed, with agitation time of 3 min) and collector (with agitation time of 3 min) were added into the

flotation cell in sequence. The flotation time was 3 min. After flotation, the froth and tailing were collected, filtered, dried and weighed. The flotation recovery was calculated based on the mass distribution between the two flotation products. In this study, all single mineral flotation tests were repeated at least 3 times and the mean value was reported. The standard deviation of each flotation test was also calculated and presented as the error bars in the figures.

For the mixed binary mineral flotation test, a 2.0 g of mineral mixture composed of 95% magnesite and 5% quartz was used to study the efficiencies of flotation separation of quartz and magnesite. The flotation procedure was the same as the single mineral flotation. After flotation, the froth products (termed as the flotation tailings) and the solids remained in the cell (termed as the flotation concentrate) were separately collected, weighed and chemically analyzed for Si and Mg. The grades of products were calculated based on chemical analysis results. The magnesite flotation recovery was calculated based on the content distributions of MgO in the concentrate and tailing products.

The bench flotation tests were conducted with the magnesite-bearing ore using an XFG flotation machine (Jilin Prospecting Machinery Factory, China), equipped with a 1.5 L plexiglass flotation cell at an agitation rate of 1800 r/min [25,26]. After flotation, the concentrate and tailing products were collected, dried, and weighed. The contents of MgO and SiO₂ in products were analyzed and used for the calculation of the recoveries of minerals.

2.3 Zeta potential measurement

Zeta potential of the mineral was applied in this study to reveal the interaction between the reagent and mineral surface [27,28]. The zeta potentials of the magnesite and quartz treated with DDA, CMC, and both reagents were measured



Fig. 2 3D ball-stick models of DDA (a) and CMC (b) used in this research

under different pulp pH values. The zeta potential measurement was conducted with a Delsa 440sx zeta potential analyzer (Malvern Instruments Ltd., Co., United Kingdom) using KCl solution (0.01 mol/L) as the background electrolyte solutions [29].

For each measurement, the mineral sample was firstly ground to $\leq 2 \mu m$ with an agate mortar. Then, the mineral suspension with a pulp density of 0.01% was prepared by agitating in a beaker at room temperature (25 °C). The pulp pH was adjusted using the pH regulator solutions. The flotation reagents were added separately during the flotation tests. The conditioning time for each reagent was maintained at 10 min. After conditioning, the supernatant solution with mineral particles was collected for zeta potential measurement on the analyzer. In this study, each zeta potential measurement was repeated three times. The mean value of the three results was reported and the standard deviation was presented as the error bars in the final figures.

2.4 AFM imaging

The atomic force microscopy (AFM) imaging was conducted to investigate the adsorption performance of the reagent on the mineral surface. In this study, the AFM imaging was performed on the mineral with reagent treatment using tapping mode with a MultiMode SPM AFM (Dimension icon, BRUKER). The single mineral crystals of magnesite and quartz were carefully selected, embedded in resin and were carefully cut into cubic pieces. The crystal pieces were polished using a diamond grinding disk for a flat surface. After the polishing, the mineral surface was further polished with alumina powder $(0.05 \,\mu\text{m})$ with a silk polishing cloth. For the AFM measurement of mineral pieces treated with certain flotation reagents, the prepared sample surface was firstly immersed in reagent solutions at a desired concentration with very gentle agitation for 20 min. After the conditioning, the mineral pieces were gently washed with deionized water and vacuum dried at 35 °C. The AFM imaging was operated at 25 °C.

Every AFM imaging measurement for a mineral was duplicated using the same sample. In order to compare the results, the reagent adsorption sites were located in the microscope view by the

same dent on the mineral surface. As the mineral surface morphology varied largely across different samples, only images with the same adsorption sites and dent distributions were presented in the AFM results.

2.5 Contact angle measurement

Contact angle is usually used to evaluate the hydrophobicity of the particle surface [30]. In this study, the advancing contact angles of the magnesite and quartz with different reagent scheme treatments were measured by the sessile drop technique using a JC2000D1 contact angle meter [31]. The reagent treatment of the minerals in contact angle measurement was the same as that in AFM imaging section.

In the contact angle measurement, a $3 \mu L$ water was slowly dropped on the mineral surface. The profile of the water drop on the solid surface was automatically taken and the readings of contact angles were presented. After the measurement, the sample surface was carefully cleaned with acetone and deionized water, and was polished again to get a new fresh surface for the next measurement [32]. In this study, each reagent condition on the mineral surface was repeated at least 10 times. The average value was reported as the final results for the surface characterization.

3 Results and discussion

3.1 Micro-flotation results

The flotation performance of magnesite and quartz as a function of collector DDA, depressant CMC and pulp pH was systematically investigated in this study. Figure 3 shows the effect of collector dosage and pulp pH on the flotation of magnesite and quartz in the presence of only DDA. As shown in Fig. 3(a), the flotation recoveries of magnesite and quartz increased in varying degrees with the increase of the DDA concentration. When DDA concentration was 1×10^{-4} mol/L, the recovery of quartz was 78.02%, while that of magnesite was 30%. With the increase of DDA concentration to 2×10^{-4} mol/L, the flotation recoveries of two minerals exhibited similar increasing trends: the recovery of quartz increased to 85.15% and that of magnesite increased to 61.30%. The results indicated that DDA could display similar collecting ability towards both quartz and magnesite. The

effect of the pulp pH on the collecting ability of DDA was shown in Fig. 3(b). During the whole monitored pH range of 4–11, the recovery of quartz was kept at a high level which was over 70%, indicating that the collecting ability of DDA towards quartz was independent of the pulp pH [33]. However, it was shown that the collecting ability of DDA towards magnesite was remarkably dependent on the pulp pH [34]. When the pulp pH was decreased from natural magnesite pulp pH of 8.4 to 6.5, the magnesite was still floatable with a recovery over 30%.



Fig. 3 Flotation recoveries of magnesite and quartz at different DDA concentrations and natural magnesite pulp pH of 8.4 (a), and different pulp pH with 2×10^{-4} mol/L DDA (b)

The floatability difference between quartz and magnesite determines the feasibility of reverse flotation separation of quartz from magnesite. However, in practice, large amount of magnesite present in flotation feed minerals would keep the pulp pH in the range of 8–9 [35]. This would make it infeasible to separate the quartz from magnesite in the presence of only DDA through adjusting the

pulp pH to 6. Therefore, the depressant is essential to decrease the floatability of magnesite in the DDA system in order to achieve the floatation separation of quartz from magnesite.

CMC was applied as the depressant and the effect of CMC types (with different relative molecule masses (MW) and degrees of substitution (DS)) on the separation process at pulp pH of 8.4 was discussed in this study. Figure 4 shows the flotation behavior of quartz and magnesite in the presence of CMC with different MW and DS as a function of CMC dosage. As the CMC dosage increased, the quartz flotation was hardly affected while the magnesite flotation was significantly inhibited. With the concentration of CMC increasing from 0 to 30 mg/L, the quartz recovery remained at a high level which was up to 90%, but the magnesite recovery decreased from 55.10% to different degrees depending on the types of CMC (to 15.95% for CMC with MW of 90000; to 18.35% for CMC with MW of 250000; to 36.05% for CMC



Fig. 4 Flotation recoveries of magnesite and quartz under different kinds of CMC, pH 8.4 and 2×10^{-4} mol/L DDA: (a) Different MWs with DS of 0.9; (b) Different DSs with MW of 250000

with MW of 700000) as shown in Fig. 4(a). The decreased flotation recovery of magnesite induced by the CMC indicates that CMC can enlarge the floatability difference between quartz and magnesite while using DDA as collector. It should also be noted that the MW has an effect on the selective depression of CMC towards magnesite. The smaller the MW of CMC is, the more the magnesite is inhibited, as shown in Fig. 4(a). Figure 4(b) shows the depressant effect of CMC with different DSs (MW of 250000) at different CMC dosages. The flotation results were found to be in a similar trend with the recovery curves presented in Fig. 4(a), that is, the magnesite flotation could be well depressed by 30 mg/L CMC. Besides, it was found that the CMC with smaller DS value might exhibit better depression on magnesite flotation. When the CMC concentration was 30 mg/L, the magnesite flotation recovery was 16.73% (CMC-DS-0.7), 22.35% (CMC-DS-0.9) and 36.05% (CMC-DS-1.2), respectively. The results indicate that CMC with smaller MW and DS is suitable to be selected for effectively depressing magnesite in quartz flotation using DDA as collector. Therefore, the optimum reagent scheme for the reverse flotation separation of quartz from magnesite is deemed to be 30 mg/L CMC (MW of 90000 and DS of 0.7) and 2×10^{-4} mol/L DDA at pH 8.4.

The single mineral flotation results proved the possibility to selectively float quartz from magnesite by depressing the magnesite using CMC as the depressant and DDA as the collector at pH 8.4. Micro-flotation tests on the mixed binary minerals (95% magnesite + 5% quartz) were performed at pH 8.4 and various concentrations of CMC (MW=90000 and DS=0.7). The results are shown in Fig. 5.

It could be seen from Fig. 5 that when the DDA was used without addition of CMC, the magnesite recovery in the concentrate was 72.48%, indicating that quite an amount of the magnesite was floated and concentrated in the froth product. The quartz grade in the concentrate was 2.10% (5% in the flotation feed). This could be proved that it is difficult to achieve the flotation separation of quartz from magnesite without adding depressant. As the CMC concentration increased from 0 to 30 mg/L, the magnesite recovery in the concentrate was enhanced from 72.48% to 84.88%, showing that a

certain amount of magnesite was depressed and remained in the flotation cell. Meanwhile, the quartz grade in concentrate slightly decreased from 2.10% to 1.23% over the whole range of CMC dosage, suggesting that the quartz flotation induced by the DDA was barely affected by the presence of CMC.



Fig. 5 Flotation behavior of mixed binary ore as function of CMC (MW of 90000 and DS of 0.7) concentration at pH 8.4 and DDA concentration of 2×10^{-4} mol/L in magnesite concentrate

3.2 Bench flotation results

To further verify the selective depressant effect of CMC in magnesite-bearing ore flotation, the reverse flotation desilication of magnesite in the presence and absence of CMC (MW of 90000 and DS of 0.7) was conducted with the flotation process as shown in Fig. 6. The flotation results are shown in Table 3. It could be seen that the addition of 200 g/t CMC could raise the magnesite recovery from 64.86% to 72.95% while the grade of magnesite in concentrate was maintained at nearly the same level. Meanwhile, the quartz grade in the concentrate decreased from 0.21% to 0.18%, indicating that the separation of quartz from magnesite was well achieved by the presence of CMC. Therefore, it was deduced that CMC could selectively depress magnesite and promote the enrichment of magnesite in concentrate product during reverse flotation.

The flotation results of the artificially mixed binary minerals and magnesite-bearing ore described above further confirmed the selective depressant effect of the CMC towards magnesite in the reverse flotation for desilication. In order to reveal the selective depression mechanism of CMC



Fig. 6 Flotation flowsheet for magnesite ore

 Table 3 Flotation results of magnesite ore sample

towards magnesite in the presence of DDA, the characterization of surface properties including surface charge, surface microscopy imaging and surface wettability was conducted.

3.3 Zeta potential results

In this study, the zeta potential was used to represent the surface charge of mineral particles treated with different reagent schemes, which was further adopted to evaluate the strength of the interactions between reagent and mineral surface.

Figure 7 shows zeta potentials of magnesite and quartz under different reagent schemes and concentrations. It was clear that bare quartz was negatively charged at pH 8.4 (zeta potential of -30.5 mV), and bare magnesite was nearly neutrally charged (zeta potential of -0.28 mV). The zeta potentials of quartz and magnesite decreased with increasing CMC concentration. As shown in Fig. 7(a), the zeta potential of quartz decreased to

Dosage of CMC/ (g·t ⁻¹)	Product	Yield/%	Grade/%		Recovery/%	
			Magnesite	Quartz	Magnesite	Quartz
0	Concentrate	62.48	46.72	0.21	64.86	3.47
	Middling	20.81	45.14	3.85	20.87	21.16
	Tailings	16.71	38.43	17.05	14.27	75.36
	Feed	100	45.01	3.78	100.00	100.00
200	Concentrate	70.22	46.75	0.18	72.95	3.35
	Middling	17.13	44.74	4.35	17.03	19.73
	Tailings	12.65	35.65	22.95	10.02	76.92
	Feed	100.00	45.00	3.77	100.00	100.00



Fig. 7 Zeta potentials of magnesite and quartz as function of CMC concentration (a) and DDA concentration at 30 mg/L CMC (b) under pH 8.4

-47.83 mV and that of magnesite decreased to -34.16 mV while CMC concentration increased to 30 mg/L, indicating that the CMC could interact with both minerals.

Figure 7(b) displays the zeta potentials of quartz and magnesite as a function of the concentration of collector DDA in the absence and presence of pre-treatment with 30 mg/L CMC. With the DDA concentration increasing from 0 to 2×10^{-4} mol/L without pre-treatment of CMC, the zeta potentials of magnesite and quartz increased from -0.28 to 34.77 mV and from -30.5 to -14.23 mV, respectively. The significant increase in the surface charge on both minerals implies that the collector DDA has influence on the particle surface properties. After pre-treatment by 30 mg/L CMC, the zeta potentials of magnesite and quartz displayed different trends with the increasing DDA concentration. The zeta potential of quartz pre-treated by CMC increased with increasing concentration of DDA. When DDA concentration increased from 0 to 2×10^{-4} mol/L, the zeta potential of quartz increased from -51.23 to -26.1 mV, showing that the DDA could still interact with quartz in the presence of CMC and it was of high possibility that the interaction between DDA and quartz was stronger than that between CMC and quartz. However, the zeta potential of magnesite pre-treated by CMC was almost unaffected by the increasing concentration of DDA. When the DDA concentration increased from 0 to 2×10^{-4} mol/L, the zeta potential of magnesite slightly increased from -34.16 to -31.11 mV, demonstrating that the CMC pre-treatment dominated the surface properties and could inhibit the influence of DDA on the magnesite surface. In addition, it is very likely that the interaction between CMC and magnesite is stronger than that between DDA and magnesite, which forms the basis of the selective depression of CMC towards magnesite.

To systemically compare the interactions between those two reagents and two minerals, the zeta potentials of quartz and magnesite treated with different reagent schemes were measured as a function of pulp pH. The results are shown in Fig. 8.

As shown in Fig. 8(a), the zeta potential of magnesite decreased gradually as pulp pH increased and changed from positive to negative at the pH value of 6.3. The treatment with 30 mg/L



Fig. 8 Zeta potentials of magnesite (a) and quartz (b) under different reagent schemes as function of pulp pH (ρ (CMC)=30 mg/L, *c*(DDA)=2×10⁻⁴ mol/L)

CMC significantly reduced the zeta potential of magnesite, which indicated that the CMC could effectively make the magnesite negatively charged across the whole monitored pH range. On the contrary, the enhanced zeta potential of magnesite treated with 2×10^{-4} mol/L DDA over the monitored pH range revealed that the cationic reagent DDA could increase the surface charge of magnesite. For treatment with both CMC and DDA, the zeta potential of magnesite basically remained at the similar level as that of treatment with only CMC, indicating that the CMC dominated the surface properties of magnesite under this flotation reagent scheme over the whole investigated pH range. As shown in Fig. 8(b), the zeta potential trend of quartz with treatment under corresponding reagent schemes over the monitored pH range was slightly influenced by reagent type, which also demonstrated that the DDA rather than the CMC could dominate the quartz surface.

Considering the interaction intensity between the flotation reagents and mineral surfaces, it is clear that CMC adsorption is stronger than DDA adsorption on magnesite surface while DDA adsorption is stronger than CMC adsorption on quartz surface. The results facilitated the explanation of the selective depressant effect of the CMC towards magnesite and the elucidation of the mechanism of the action of CMC on the flotation separation of quartz from magnesite.

3.4 AFM imaging results

To further understand the reagent adsorption on two mineral surfaces and the subsequent separation, atomic force microscopy (AFM) imaging of bare minerals and minerals treated with the flotation reagent scheme was performed, and the results are shown in Figs. 9-11.



Fig. 9 2D (a_1-d_1) and 3D (a_2-d_2) AFM images of DDA adsorption $(2 \times 10^{-4} \text{ mol/L})$ on mineral surface: (a_1, a_2) Bare magnesite; (b_1, b_2) Magnesite + DDA; (c_1, c_2) Bare quartz; (d_1, d_2) Quartz + DDA



Fig. 10 2D (a_1-c_1) and 3D (a_2-c_2) AFM images of magnesite surface under different reagent schemes: (a_1 , a_2) Bare magnesite; (b_1 , b_2) Magnesite + 30 mg/L CMC; (c_1 , c_2) Magnesite + 30 mg/L CMC + 2×10⁻⁴ mol/L DDA

Figure 9 provides a series of AFM images of bare minerals and minerals pre-treated by 2×10^{-4} mol/L DDA. The surface of bare magnesite was quite smooth as shown in Figs. 9(a₁, a₂). With DDA adsorption, it was observed that a large number of densely packed peaks were lined in order on the magnesite surface (Figs. 9(b₁, b₂)). The 2D and 3D images of the magnesite surface with DDA coverage showed a significant increase in the surface roughness, indicating that the DDA molecules were well adsorbed and distributed on the magnesite surface. It could be seen in the 2D and 3D images in Figs. 9(c₁, c₂) that the surface of bare quartz was much rougher than that of magnesite. A large number of densely packed peaks also appeared on the surface of quartz with DDA treatment (Figs. $9(d_1, d_2)$), showing that DDA could physically be adsorbed on the quartz surface. The AFM imaging results intuitively displayed the adsorption of the DDA on both minerals.

Figure 10 presents the AFM images of magnesite surface treated under different flotation reagent schemes. It was found that the CMC (30 mg/L) treatment induced a certain increase in the surface roughness on the magnesite by comparing the Figs. $10(a_1, a_2)$ with Figs. $10(b_1, b_2)$. It could be seen that the CMC adsorption made a net-work structure form and cover on the magnesite surface. The adsorbing morphology of CMC seemed to be quite different with the DDA by



Fig. 11 2D (a_1-c_1) and 3D (a_2-c_2) AFM images of quartz surface under different reagent schemes: (a_1, a_2) Bare quartz; (b_1, b_2) Quartz + 30 mg/L CMC; (c_1, c_2) Quartz + 30 mg/L CMC + 2×10⁻⁴ mol/L DDA

comparing Figs. $9(b_1, b_2)$ with Figs. $10(b_1, b_2)$. For treatment with both CMC and DDA, a typical adsorption of CMC rather than DDA on surface of magnesite was shown in Figs. $10(c_1, c_2)$. The adsorption actions of the reagents consolidate the depressant effect of CMC towards magnesite in the DDA collector system.

Figure 11 shows the AFM images of the quartz surface under different flotation reagent schemes. It was shown that CMC coverage also appeared on the quartz surface, as can be judged by comparing Figs. $11(a_1, a_2)$ with Figs. $11(b_1, b_2)$. It should be noted that the adsorption density of the CMC towards quartz surface was smaller than that on the magnesite surface by comparison between Figs. $11(b_1, b_2)$ and Figs. $10(b_1, b_2)$. The DDA adsorption significantly increased after treatment with both CMC and DDA. The adsorption of DDA was mostly on the adsorption sites or in the interspace of the CMC molecules. It was obvious that the surface of quartz was mostly occupied by DDA with only a small amount adsorption of CMC. The AFM imaging results illustrated the selective depressant effect of CMC towards magnesite in the reverse flotation of quartz.

3.5 Contact angle measurement results

Since the CMC induced different floatabilities between magnesite and quartz, the surface wettability of the mineral surfaces was studied by measuring the contact angles under corresponding flotation reagent schemes. The results are shown in Figs. 12 and 13.



Fig. 12 Contact angles of magnesite with different reagent scheme treatments ($c(DDA)=2\times10^{-4}$ mol/L; $\rho(CMC)=30$ mg/L)



Fig. 13 Contact angles of quartz with different reagent scheme treatments ($c(DDA)=2\times10^{-4} \text{ mol/L}$; $\rho(CMC)=30 \text{ mg/L}$)

Figure 12 presents contact angles of magnesite under different reagent schemes. It was noted that the 2×10^{-4} mol/L DDA treatment significantly increased the contact angle of bare magnesite surface from 18.1° to 38.3°, indicating that the DDA could increase the surface hydrophobicity of magnesite and consequently improve the efficiency of selective flotation separation of quartz from magnesite. It was observed that the addition of 30 mg/L CMC slightly decreased the contact angle of bare magnesite from 18.1° to 15.2°, showing that the CMC could increase the surface hydrophilicity of magnesite. With the treatment of 30 mg/L CMC and 2×10^{-4} mol/L DDA, the contact angle of magnesite was 19.5°, showing that the CMC could determine the magnesite surface wettability in the presence of DDA [36]. The contact angle results agree well with the micro-flotation results that the CMC could selectively depress the magnesite flotation in the DDA flotation system.

Figure 13 shows the contact angle of quartz under different flotation reagent schemes. The contact angle of bare quartz was 15.5° . The contact angle increased significantly from 15.5° to 49.5° after treatment with 2×10^{-4} mol/L DDA, suggesting that the DDA could effectively increase the surface hydrophobicity of quartz. With 30 mg/L CMC treatment, no significant change on the contact angle of the quartz surface was observed, implying that the CMC may not exhibit any influence on the quartz flotation. The contact angle of the quartz surface with treatment by both CMC and DDA was very similar to that with only DDA treatment.

The contact angle results of quartz under different reagent schemes also agree well with the corresponding flotation results, implying that the flotation reagents, i.e., CMC and DDA, probably work by impacting the mineral surface properties. Those two reagents may competitively be adsorbed on the particle surface or selectively interact with one mineral in flotation pulp, which finally results in the selective separation.

3.6 Action model of selective depression of magnesite

Based on the flotation results, zeta potential measurements, contact angle measurements and AFM imaging, the possible action model (Fig. 14) was established to reveal the reagent adsorption and different flotation behaviors of quartz and magnesite in the presence of CMC and DDA.

As DDA could be adsorbed on surface of both magnesite and quartz and increase their floatability, it is difficult to separate magnesite and quartz under the condition of which only DDA was used in flotation. The addition of CMC could induce remarkable difference on the floatability of those two minerals. Only seldom CMC molecules could be adsorbed on the surface of quartz due to the strong electrostatic repulsion actions. There are enough sites for the adsorption of subsequent DDA (cationic collector) on the surface of quartz particle after the pre-treatment of CMC. In terms of magnesite, the CMC molecule could be easily adsorbed on Mg sites and cover the particle surface. This could effectively hinder the subsequent DDA coverage. As a result, the separation of quartz and magnesite was achieved under the CMC and DDA scheme.

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Fig. 14 Action model of reagent adsorption on particle surface and subsequent flotation separation of quartz from magnesite in the presence of CMC and DDA

4 Conclusions

(1) The CMC was found to be able to induce efficient separation of quartz from magnesite. A reagent scheme, i.e., 30 mg/L CMC and 2×10^{-4} mol/L of DDA, was figured out to achieve the separation of the quartz from magnesite under natural pulp pH condition.

(2) CMC and DDA displayed different adsorption strengths on the magnesite and quartz surfaces. The adsorption of CMC on surface of magnesite was stronger than that of DDA, which led to the domination of CMC on the magnesite surface and the depression of magnesite. However, the adsorption of CMC on the surface of quartz was quite weak and could not hinder the subsequent adsorption of DDA, making the flotation separation of the magnesite particles from fine quartz particles possible.

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以羧甲基纤维素为抑制剂浮选分离石英和菱镁矿

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摘 要:研究羧甲基纤维素(CMC)作为抑制剂在菱镁矿反浮选脱硅过程中的作用,通过动电位测试、原子力显微 镜检测和接触角测试考察在 CMC 作用下菱镁矿与石英的浮选行为与表面性质变化。当以十二胺(DDA)为捕收剂 时,以 CMC 为抑制剂进行菱镁矿脱硅反浮选,CMC 的添加对菱镁矿表现出良好的选择性抑制作用,并提高菱镁 矿回收率。表面性质研究表明,在菱镁矿和石英表面 CMC 和 DDA 的吸附强度存在明显差异,CMC 在菱镁矿表 面的吸附强于 DDA,从而阻碍后续 DDA 的吸附;而在石英表面则相反,DDA 的吸附强于 CMC,因此 CMC 基 本不影响石英的可浮性。

关键词: 浮选分离; 羧甲基纤维素; 十二胺; 菱镁矿; 石英

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