

Article

Selective Depression of Biotite by Carboxymethyl Chitosan in Apatite-Biotite Flotation: Effects of Particle Size

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Abstract

Biotite in mica-bearing phosphate ores is prone to sliming and forms fine intergrowths with apatite, impairing flotation selectivity. Taurine, sodium lignosulfonate, chitosan, hydroxypropyl distarch phosphate, and carboxymethyl chitosan (CMCS) were screened by single-mineral and artificial-mixture flotation tests. Contact angle, adsorption, zeta potential, FTIR, and XPS analyses focused on the -0.023 mm fraction. At pH 9 and a collector dosage of 268 mg/L, CMCS retained selectivity in favor of apatite. In single-mineral tests, CMCS dosages of 30, 60, and 150 mg/L produced apatite–biotite recovery differences of 47.57, 40.51, and 20.59 percentage points for the $+0.074$, $-0.074 + 0.023$, and -0.023 mm fractions, respectively. In artificial-mixture tests, selected dosages of 20, 120, and 180 mg/L yielded P_2O_5 recoveries of 95.50%, 95.58%, and 74.37% and grades of 28.02%, 26.47%, and 21.10%, respectively. As particle size decreased, the required CMCS dosage increased and separation deteriorated. Contact-angle measurements showed that CMCS pretreatment preserved the strong collector-induced hydrophobicity of apatite while slightly weakening that of biotite, thereby increasing the wettability contrast between the two minerals. Biotite showed a larger negative zeta-potential shift and greater CMCS adsorption than apatite; at 180 mg/L, the adsorption amounts were 1.17 and 0.76 mg/g, respectively. Together with the adsorption results, FTIR and XPS suggested stronger CMCS–biotite interfacial interactions involving carboxyl and hydroxyl-containing groups, with possible participation of Mg-related surface sites. These findings demonstrate the particle-size dependence of CMCS-assisted apatite-biotite flotation and reveal preferential CMCS interaction with biotite under fine-particle conditions.

Keywords: apatite; biotite; carboxymethyl chitosan; selective depression; particle-size effect; adsorption



Academic Editors: Ruxia Chen and Zeyu Feng

Received: 28 August 2026

Revised: 23 September 2026

Accepted: 28 September 2026

Published: 30 September 2026

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1. Introduction

Phosphate ores are commonly associated with carbonate and silicate gangue minerals. Flotation is the principal method used to improve the grade and recovery of phosphate

concentrates, and common phosphate flotation flowsheets include direct, reverse, and combined flotation. Direct flotation generally employs fatty acid collectors to hydrophobize apatite and promote its flotation, whereas reverse flotation commonly uses amine collectors to remove silicate gangue minerals such as quartz, feldspar, and mica [1–3]. With increasingly fine mineral dissemination, fine particles are more susceptible to aggregation, slime coating, and mechanical entrainment, leading to higher reagent consumption and reduced flotation selectivity [4,5]. Fine hydrophilic gangue particles may also adhere to valuable mineral surfaces or be carried into the concentrate with entrained froth water, further decreasing the concentrate grade.

Biotite is a representative phyllosilicate gangue mineral in mica-bearing phosphate ores. Owing to its perfect cleavage and tendency to delaminate along the interlayer planes, biotite readily forms fine platy particles during grinding. Previous studies have shown that the flotation separation of apatite and mica minerals is governed by differences in mineral surface composition, exposed active sites, and reagent adsorption [6]. The basal and edge surfaces of phyllosilicates exhibit pronounced anisotropy in surface charge, wettability, broken-bond density, and reagent adsorption behavior [7]. Interlayer cations exposed on mica cleavage surfaces may undergo hydration, migration, and ion exchange in aqueous solutions, further complicating the surface states of minerals in flotation pulps [8,9]. Consequently, variations in particle size may affect not only the specific surface area of biotite but also the relative exposure of different crystallographic surfaces and the accessibility of active sites, thereby altering the adsorption and selective depression performance of polymeric reagents.

Polymeric depressants can increase the floatability contrast between minerals through selective adsorption, interactions with surface metal sites, the formation of hydrophilic surface layers, and interference with collector adsorption [10]. In recent years, bio-based and modified polymers, including carboxymethyl chitosan, N-carboxybutyl chitosan, sodium dextran sulfate, and lignosulfonates, have been investigated for the flotation separation of apatite from carbonate gangue minerals. Their selectivity is primarily attributed to differences in polymer adsorption between mineral surfaces [11–14]. Previous studies have shown that CMCS adsorbs considerably more strongly on calcite than on apatite and selectively depresses calcite through interactions between its carboxyl groups and surface metal sites. CMCS has also been investigated as a depressant for layered silicates such as talc [15,16]. However, biotite possesses a layered crystal structure comprising Mg, Fe, and Al, and its surface chemistry differs substantially from that of calcite, dolomite, and talc. The particle-size effects of CMCS in the apatite-biotite flotation system and its differential adsorption under fine-particle conditions have not yet been systematically elucidated.

To compare depressants with different molecular architectures and functional groups, five reagents were selected for preliminary screening. Taurine represents a low-molecular-weight molecule containing amino and sulfonic acid groups; sodium lignosulfonate is an aromatic sulfonated polymer; chitosan is an amino-containing polysaccharide; hydroxypropyl distarch phosphate is a phosphorylated starch derivative; and CMCS is a carboxylated chitosan derivative containing abundant carboxyl and hydroxyl groups. Their comparison was intended to evaluate the response of the apatite-biotite system to depressants with different chemical functionalities.

Although CMCS has been investigated mainly in apatite–carbonate flotation systems and as a depressant for several layered silicate minerals, its interaction with biotite remains insufficiently understood. More importantly, the influence of particle size on the dosage requirement and separation performance of CMCS in the apatite–biotite system has rarely been systematically compared, particularly under fine-particle conditions. Therefore, the present study combines depressant screening with particle-size-resolved single-mineral

and artificial-mixture flotation tests. In this study, taurine (Tau), sodium lignosulfonate (LS-Na), chitosan (CS), hydroxypropyl distarch phosphate (HPDSP), and carboxymethyl chitosan (CMCS) were evaluated as candidate depressants. Their flotation separation performance was compared through single-mineral tests using the $-0.074 + 0.023$ and -0.023 mm fractions, and CMCS, which exhibited comparatively robust selectivity across the tested particle-size fractions, was selected for further investigation. CMCS dosage tests and artificial-mixture flotation tests were subsequently conducted on the $+0.074$, $-0.074 + 0.023$, and -0.023 mm fractions to examine the effects of reagent dosage and particle size on the separation of apatite and biotite. Because biotite readily forms fine platy particles during grinding and the greatest loss of flotation selectivity occurred in the -0.023 mm fraction, this difficult-to-treat fraction was selected for contact angle, adsorption, zeta potential, FTIR, and XPS analyses to characterize the differential adsorption of CMCS on the two mineral surfaces. This study aims to elucidate the particle-size dependence of CMCS-assisted apatite-biotite flotation separation and to provide experimental evidence for the selective depression of biotite through interfacial characterization of the fine fraction. The findings also provide a scientific basis for optimizing reagent regimes in mica-bearing phosphate flotation and for subsequent validation using actual ores.

2. Materials and Methods

2.1. Mineral Samples and Reagents

Commercial apatite and biotite specimens originating from the Lianyungang mining area in Jiangsu Province, China, were used. Well-crystallized mineral specimens were crushed, manually sorted to remove visible impurities, and ground to below 0.15 mm. The ground samples were subsequently wet-sieved using standard sieves to obtain three particle-size fractions: $-0.150 + 0.074$ mm (hereafter denoted as the $+0.074$ mm fraction), $-0.074 + 0.023$ mm, and -0.023 mm. These fractions were used in the subsequent flotation tests. Artificial mineral mixtures were prepared by mixing pure apatite and biotite at a mass ratio of 1:1.

The mineralogical compositions of the apatite and biotite samples were characterized by X-ray diffraction (XRD) using a Malvern Panalytical X'Pert PRO MPD diffractometer (Malvern Panalytical, Almelo, The Netherlands) equipped with a Cu K α radiation source ($\lambda = 1.5406$ Å). The X-ray tube was operated at 45 kV and 40 mA. Diffraction patterns were collected over a 2θ range of 10 – 80° with a step size of 0.02° and a counting time of 0.5 s per step. The chemical compositions of the mineral samples were determined using a PANalytical Axios wavelength-dispersive X-ray fluorescence (WDXRF) spectrometer (Malvern Panalytical, Almelo, The Netherlands) equipped with an Rh-anode end-window X-ray tube with a maximum power of 4.0 kW (maximum ratings of 60 kV and 125 mA). Prior to XRF analysis, the samples were dried and prepared as pressed-powder pellets. Quantitative elemental analysis was performed using the PANalytical Omnian analysis procedure, and the results were normalized and reported as oxide concentrations.

The chemical compositions of the samples were determined by X-ray fluorescence spectroscopy (XRF), while their mineral phases were identified by X-ray diffraction (XRD). The results are presented in Tables 1 and 2 and Figure 1. The apatite sample was identified as fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), with a P_2O_5 content of 38.58%. According to the supplier specifications, the nominal purities of the apatite and biotite samples were approximately 96% and 98%, respectively. The XRD patterns displayed the characteristic diffraction peaks of apatite and biotite, with only minor impurity peaks, indicating that both samples were sufficiently pure for single-mineral flotation tests.

Table 1. Chemical composition of the pure apatite sample (%).

Component	CaO	P ₂ O ₅	F	SiO ₂	SO ₃	Fe ₂ O ₃	SrO	MgO	MnO
Content	56.51	38.58	1.53	1.10	0.85	0.09	0.07	0.04	0.04

Table 2. Chemical composition of the pure biotite sample (%).

Component	IL	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂
Content	2.06	17.10	40.72	13.95	0.18	15.88	8.82	0.10	0.89

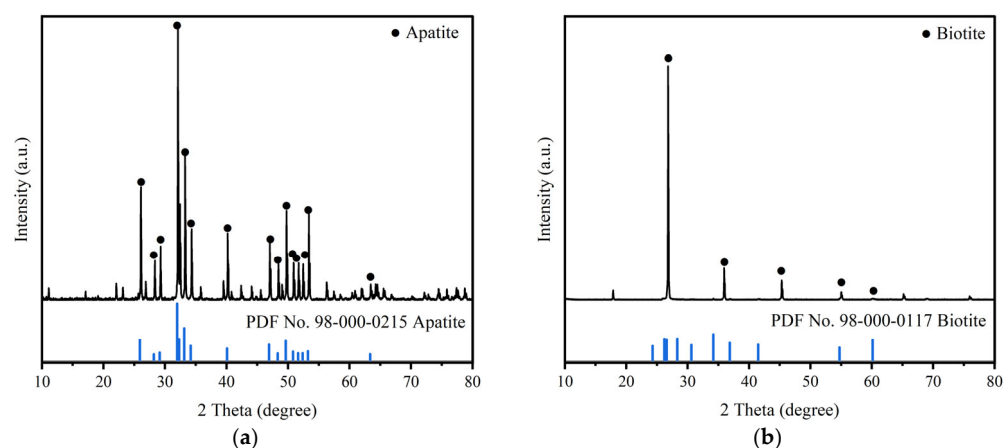


Figure 1. XRD patterns of apatite and biotite: (a) Apatite; (b) Biotite.

The collector used in this study was a proprietary mixed collector developed in our laboratory and composed of analytical-grade sodium oleate, oxidized paraffin soap, and sodium fatty acid methyl ester sulfonate. Its specific composition was not disclosed for reasons of technical confidentiality. Because the collector formulation was not an experimental variable, a single batch with a fixed composition was used throughout all tests, following an identical preparation and addition procedure. The collector dosage is reported as the total mass concentration of the three components in the pulp. Analytical-grade CMCS, Tau, LS-Na, CS, and HPDSP were used as depressants. Deionized water with a resistivity greater than 18.2 MΩ·cm was used for all solution preparation and flotation tests.

2.2. Experimental Methods

2.2.1. Flotation Tests

Single-mineral and artificial-mixture flotation tests were conducted using an XFG-II laboratory hanging-trough flotation machine (Wuhan Exploration Machinery Co., Ltd., Wuhan, China) equipped with a 50 mL flotation cell. For each test, 2.0 g of mineral sample was mixed with 40 mL of deionized water and agitated for 2 min at an impeller speed of 1992 r/min. Reagent dosages are primarily reported in mg/L because fixed-volume pure-mineral microflotation tests were employed. Under the present conditions of 2.0 g mineral in 40 mL of initial liquid, 1 mg/L corresponds to 20 g/t of dry mineral. The reported mg/L values represent nominal reagent concentrations calculated on the basis of the initial 40 mL liquid volume. The experiments were conducted at approximately 25 °C. The pulp pH was adjusted to 9 using a dilute NaOH solution. Preliminary pH-screening tests conducted in the absence of depressant are provided in Figure S1 and were used to select pH 9 for the subsequent flotation experiments. The depressant and collector were then added sequentially, with a conditioning time of 3 min after each addition. During flotation, the aeration rate was controlled using a flowmeter set at 0.1 m³/h, and the froth

product was manually scraped for 3 min. The collected froth product was filtered, dried to constant weight, and weighed. Artificial mineral mixtures were prepared by mixing apatite and biotite at a mass ratio of 1:1. For artificial-mixture tests, the feed P_2O_5 grade was determined by chemical analysis, while concentrate yield and mass-balance closure were calculated from the dry masses of the feed, concentrate, and tailings. Unless otherwise stated, flotation tests, adsorption measurements, and zeta potential measurements were independently performed in triplicate. The results are reported as the mean $\pm$ standard deviation (SD), and the error bars represent the SD of the three independent measurements. Statistical differences in the recovery difference (ΔR) among the tested depressants at their selected dosages were evaluated by one-way ANOVA followed by Tukey's multiple-comparison test, with $p < 0.05$ considered statistically significant. The CMCS dosage used in the interfacial characterization tests was selected from the single-mineral flotation results for the -0.023 mm fraction. For single-mineral tests, the selected dosage was determined from apatite recovery and the recovery difference between apatite and biotite ($\Delta R = R_{Ap} - R_{Bi}$), whereas for artificial-mixture tests it was selected by jointly considering P_2O_5 grade and recovery; therefore, the term "selected dosage" is used rather than "optimum dosage".

2.2.2. Contact Angle Measurements

Apatite and biotite samples from the -0.023 mm fraction were treated under two reagent conditions: collector treatment without CMCS and CMCS pretreatment followed by collector addition. Contact angle measurements were performed using an OCA15Pro video optical contact angle measuring system (DataPhysics Instruments GmbH, Filderstadt, Germany). The reagent dosages and addition sequence were consistent with those used in the single-mineral flotation tests. After reagent conditioning, the solid samples were collected without washing, dried to constant weight, and subsequently pressed into compact pellets with flat surfaces. The pellets were mounted on the sample stage of a contact angle goniometer, and the three-axis stage was adjusted to ensure that the sample surface was horizontal and parallel to the optical axis of the imaging system [17]. An approximately 2 μ L droplet of ultrapure water was gently dispensed onto the pellet surface using a microsyringe, and its profile was recorded using a high-speed imaging system. The apparent contact angle was recorded 5 s after droplet deposition using the same acquisition time for all samples. Therefore, the reported values represent fixed-time apparent contact angles rather than equilibrium contact angles. The apparent contact angle was determined by fitting the droplet profile using the Young–Laplace method and was recorded 5 s after droplet deposition using the same acquisition time for all samples. Time-dependent droplet spreading and penetration into the pressed pellets were not independently quantified; therefore, the reported values are regarded as fixed-time apparent contact angles rather than equilibrium contact angles. To minimize pellet-preparation effects, all samples were prepared under identical pressing conditions and measured at multiple positions. Because surface roughness and porosity may affect pressed pellets, the measured values were used primarily for comparative evaluation among identically prepared samples.

2.2.3. Adsorption Measurements

The adsorption of CMCS on the mineral surfaces was quantified using a total organic carbon (TOC) analyzer. Apatite and biotite samples from the -0.023 mm fraction were tested separately. For each measurement, 2.0 g of mineral sample was dispersed in 40 mL of ultrapure water, and CMCS was added to obtain the required initial concentration following the conditioning procedure used in the single-mineral flotation tests. The suspension was magnetically stirred at 1900 r/min for 4 min at 25 °C to promote contact between CMCS and the mineral surface. After conditioning, the suspension was centrifuged at 2500 r/min

for 20 min. The supernatant was subsequently passed through a disposable 0.45 µm PES syringe filter to minimize interference from residual fine mineral particles before TOC analysis. Residual CMCS concentrations were quantified using a linear TOC calibration ($C_{TOC} = 0.2254C_{CMCS} + 3.2544$, $R^2 = 0.9949$; Figure S2) after correction for the water and mineral blanks. The adsorption amount was calculated using Equation (1) [11]:

$$Q = \frac{(C_i - C_e)V}{m}, \quad (1)$$

where Q is the adsorption amount of CMCS, mg/g; C_i is the background-corrected initial CMCS concentration, mg/L; C_e is the residual CMCS concentration in the supernatant after conditioning, mg/L; V is the liquid volume, L; and m is the mineral mass, g.

2.2.4. Zeta Potential Measurements

The zeta potentials of apatite and biotite were measured using a Zetasizer Nano ZS (Malvern Instruments Ltd., Worcestershire, UK). For each measurement, 1.0 g of mineral sample from the −0.023 mm fraction was dispersed in 20 mL of ultrapure water by magnetic stirring. The suspension pH was adjusted to 7, 8, 9, 10, 11, or 12 using dilute HCl or NaOH solutions. At each target pH, an untreated control and a depressant-treated suspension were prepared. The prescribed dosage of depressant was added to the treated suspension, followed by magnetic stirring for 20 min to allow interaction between the depressant and the mineral surface. An aliquot of the well-mixed suspension was then withdrawn for zeta potential measurement [11].

2.2.5. Fourier Transform Infrared Spectroscopy Measurements

Apatite and biotite samples from the −0.023 mm fraction were tested separately. FTIR spectra were recorded using a Nicolet iS10 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). For each measurement, 1.0 g of mineral sample was dispersed in 20 mL of ultrapure water, after which the prescribed dosage of depressant was added. The suspension was conditioned for a further 20 min and then filtered through medium-speed quantitative filter paper. The collected solid was dried to constant weight at 105 °C. The dried sample was thoroughly ground with spectroscopic-grade KBr at a mass ratio of 1:100 and pressed into a transparent KBr pellet. FTIR spectra were recorded in transmission mode over the wavenumber range of 4000–400 cm^{−1}. Untreated mineral samples were prepared using the same procedure and served as controls [11,12].

2.2.6. X-Ray Photoelectron Spectroscopy Measurements

Apatite and biotite samples from the −0.023 mm fraction before and after CMCS treatment were analyzed by X-ray photoelectron spectroscopy (Thermo Fisher Scientific, East Grinstead, UK) to determine their surface elemental compositions and chemical states. Survey spectra were first acquired to identify the elements present on the mineral surfaces, followed by high-resolution scans of the C 1s, O 1s, Ca 2p, Mg 1s, and other relevant regions. The XPS spectra were processed using Advantage software (Version 6.10.0, Build 00059; Thermo Fisher Scientific, UK). Binding energies were charge-corrected by setting the adventitious C–C/C–H component of the C 1s spectrum to 284.8 eV. Peak fitting was performed using mixed Lorentzian–Gaussian line shapes with a fixed L/G mixing parameter of 30%. A Shirley background was applied during peak deconvolution. Relative surface atomic concentrations were determined from the survey spectra using the corresponding sensitivity factors and are provided in Table S1. All binding energies were calibrated against the C–C component at 284.8 eV [18]. Changes in binding energy, peak shape, and relative peak area before and after CMCS treatment were compared to evaluate

the adsorption behavior and interfacial interactions of CMCS on the apatite and biotite surfaces [11,12].

3. Results and Discussion

3.1. Comparison of the Flotation Performance of Different Depressants

3.1.1. Depressant Dosage Tests for the Intermediate-Size Fraction ($-0.074 + 0.023$ mm)

The effects of carboxymethyl chitosan (CMCS), taurine (Tau), sodium lignosulfonate (LS-Na), chitosan (CS), and hydroxypropyl distarch phosphate (HPDSP) on the flotation behavior of apatite and biotite in the $-0.074 + 0.023$ mm fraction were investigated at pH 9 and a collector dosage of 268 mg/L. The results are presented in Figure 2.

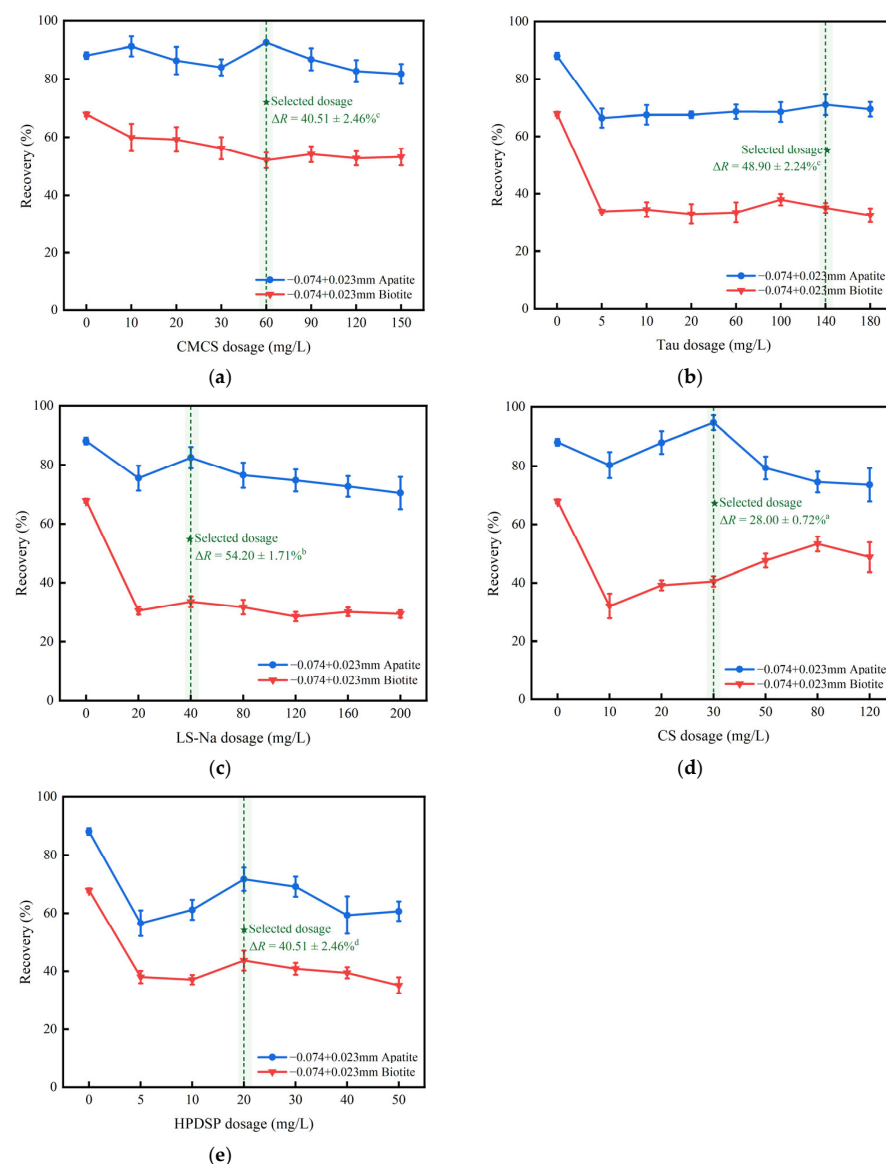


Figure 2. Effects of different depressants on the floatability of apatite and biotite in the $-0.074 + 0.023$ mm fraction: (a) Effect of CMCS on the floatability of apatite and biotite; (b) Effect of Tau on the floatability of apatite and biotite; (c) Effect of LS-Na on the floatability of apatite and biotite; (d) Effect of CS on the floatability of apatite and biotite; (e) Effect of HPDSP on the floatability of apatite and biotite. Different lowercase letters indicate significant differences among depressants according to one-way ANOVA followed by Tukey's multiple-comparison test ($p < 0.05$). The zero-depressant control corresponds to collector-only flotation at pH 9 and a collector dosage of 268 mg/L. The green dashed line indicates the selected depressant dosage.

As shown in Figure 2, at a CMCS dosage of 60 mg/L, the recoveries of apatite and biotite in the $-0.074 + 0.023$ mm fraction were 92.52% and 52.01%, respectively, corresponding to a recovery difference of 40.51 percentage points. Thus, CMCS reduced biotite recovery while maintaining a high apatite recovery. LS-Na and CS also produced pronounced recovery differences in this particle-size fraction. At selected dosages of 40 and 30 mg/L, respectively, LS-Na and CS yielded apatite recoveries of 82.45% and 94.50% and biotite recoveries of 33.55% and 40.50%. By comparison, Tau and HPDSP showed relatively limited selectivity, and the apatite recoveries obtained with these two depressants were generally lower than those achieved with CMCS.

3.1.2. Depressant Dosage Tests for the Fine Fraction (-0.023 mm)

The effects of carboxymethyl chitosan (CMCS), taurine (Tau), sodium lignosulfonate (LS-Na), chitosan (CS), and hydroxypropyl distarch phosphate (HPDSP) on the flotation behavior of apatite and biotite in the -0.023 mm fraction were investigated at pH 9 and a collector dosage of 268 mg/L. The results are presented in Figure 3.

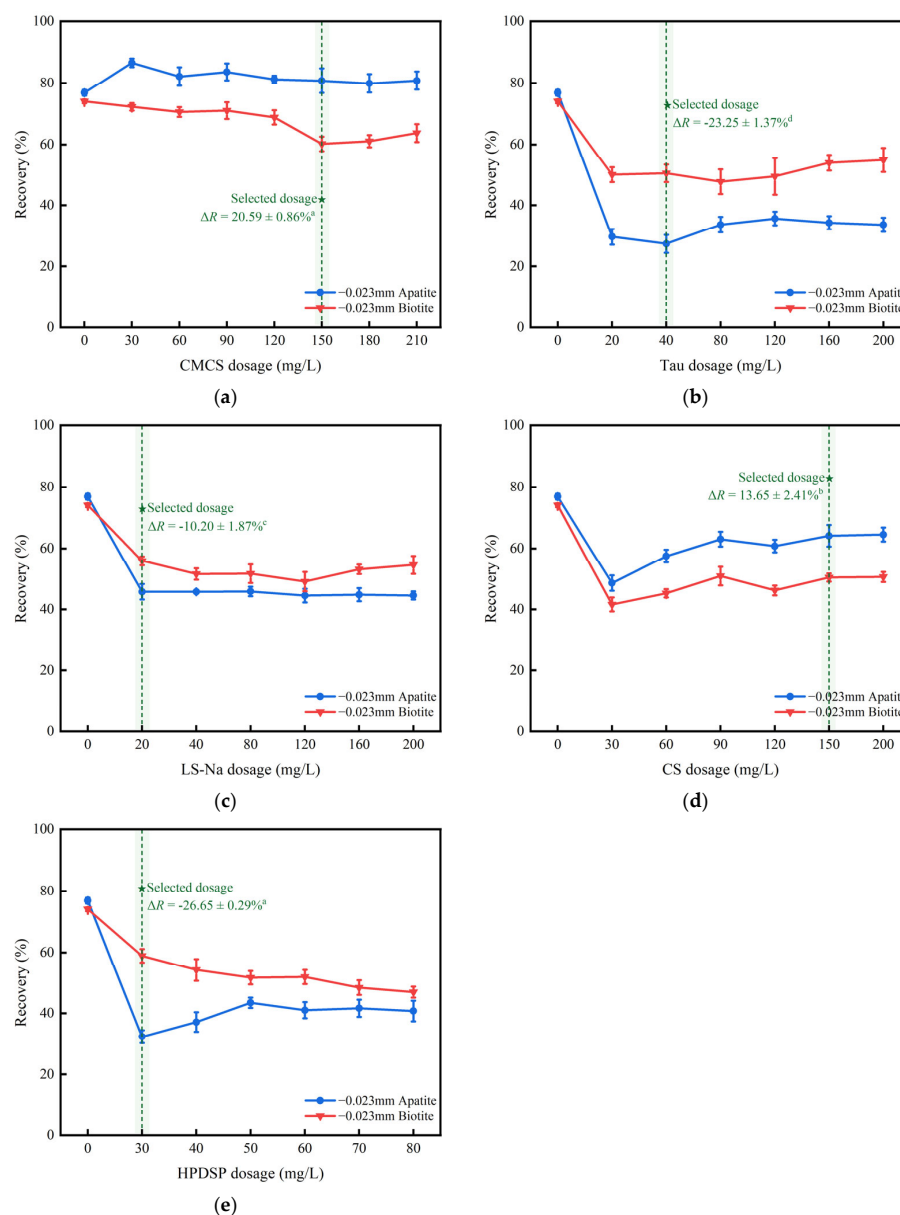


Figure 3. Effects of different depressants on the floatability of apatite and biotite in the -0.023 mm fraction: (a) Effect of CMCS on the floatability of apatite and biotite; (b) Effect of Tau on the floatability of

apatite and biotite; (c) Effect of LS-Na on the floatability of apatite and biotite; (d) Effect of CS on the floatability of apatite and biotite; (e) Effect of HPDSP on the floatability of apatite and biotite. Different lowercase letters indicate significant differences among depressants according to one-way ANOVA followed by Tukey's multiple-comparison test ($p < 0.05$). The zero-depressant control corresponds to collector-only flotation at pH 9 and a collector dosage of 268 mg/L. The green dashed line indicates the selected depressant dosage.

As shown in Figure 3, the selectivity of the tested depressants changed markedly for the -0.023 mm fraction. At a CMCS dosage of 150 mg/L, the apatite and biotite recoveries were 80.77% and 60.18%, respectively, corresponding to a recovery difference of 20.59 percentage points. Thus, preferential recovery of apatite was still maintained. In contrast, Tau, LS-Na, and HPDSP produced lower apatite recoveries than biotite recoveries, indicating reversed selectivity in favor of biotite. CS yielded an apatite recovery of 64.10%, while the biotite recovery remained at 50.45%, resulting in poorer separation than that achieved with CMCS. Although CMCS did not yield the largest recovery difference in the intermediate-size fraction, it produced the largest positive recovery difference among the tested depressants in the fine fraction. CMCS therefore exhibited greater robustness across particle-size fractions and was selected for subsequent investigation. Compared with the collector-only control, CMCS increased the apatite–biotite recovery difference, particularly for the fine fraction, indicating that its role was to improve flotation selectivity rather than simply minimize biotite recovery.

3.2. Effect of CMCS on the Flotation Behavior of Apatite and Biotite

3.2.1. Depressant Dosage Tests for the Coarse Fraction (+0.074 mm)

The effect of CMCS dosage on the flotation behavior of apatite and biotite in the +0.074 mm fraction was investigated at pH 9 and a collector dosage of 268 mg/L. The results are presented in Figure 4.

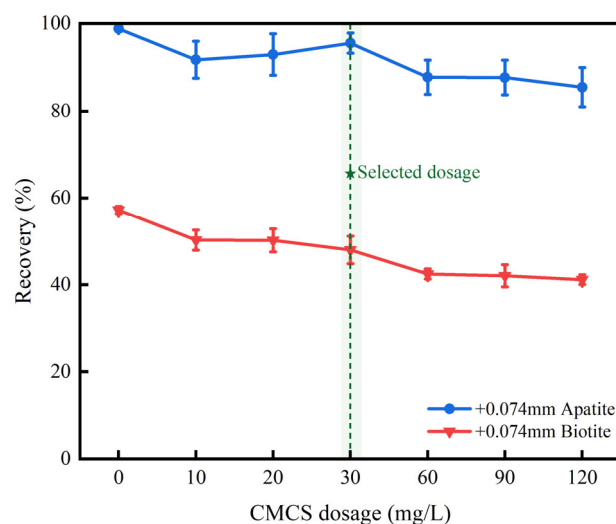


Figure 4. Effect of CMCS dosage on the floatability of apatite and biotite in the +0.074 mm fraction. The zero-depressant control corresponds to collector-only flotation at pH 9 and a collector dosage of 268 mg/L. The green dashed line indicates the selected CMCS dosage.

As shown in Figure 4, at a CMCS dosage of 30 mg/L, the apatite and biotite recoveries were 95.53% and 47.96%, respectively, corresponding to a recovery difference of 47.57 percentage points. With increasing CMCS dosage, the biotite recovery generally decreased and then stabilized at approximately 41%–43% over the range of 60–120 mg/L.

However, the apatite recovery also decreased to approximately 85%–88%, indicating that an excessive CMCS dosage caused some non-selective depression of apatite.

3.2.2. Artificial-Mixture Flotation Tests

The effect of CMCS dosage on the separation of apatite and biotite was further investigated using artificial mineral mixtures prepared at a mass ratio of 1:1 for different particle-size fractions. The tests were conducted at pH 9 and a collector dosage of 268 mg/L, and the results are presented in Figure 5.

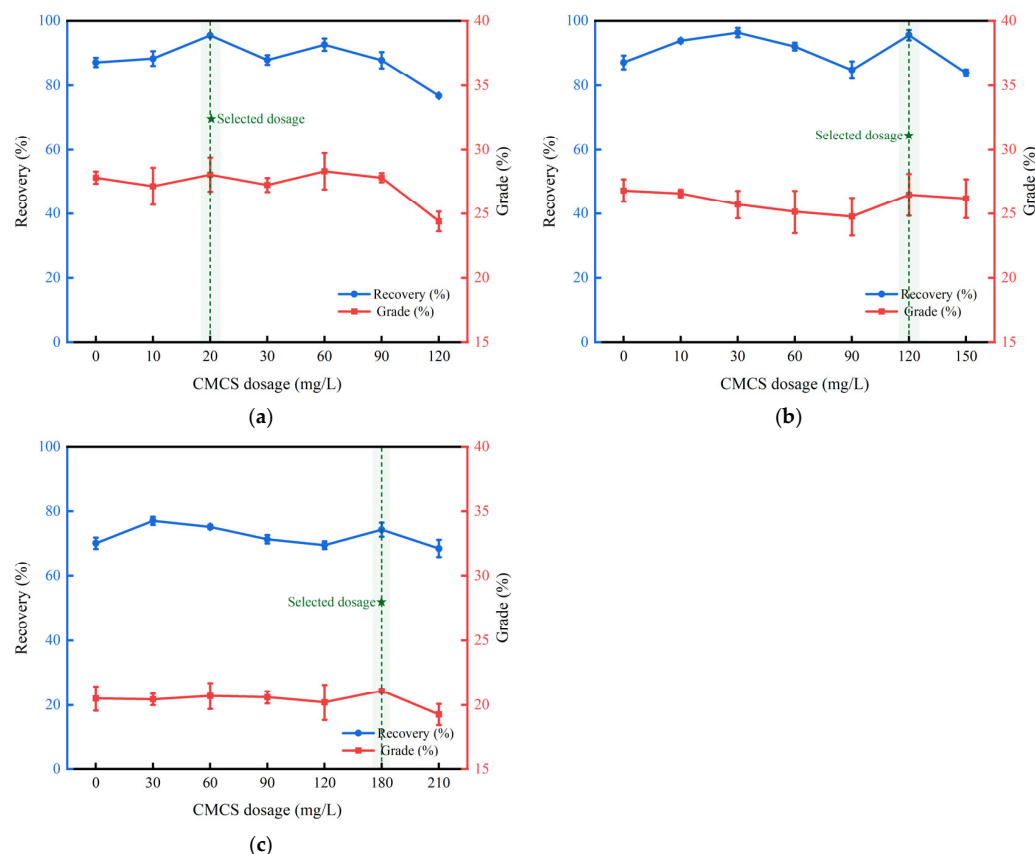


Figure 5. Effect of CMCS dosage on the flotation performance of artificial apatite-biotite mixtures in different particle-size fractions: (a) +0.074 mm fraction; (b) −0.074 + 0.023 mm fraction; (c) −0.023 mm fraction. The data at 0 mg/L CMCS represent collector-only flotation controls at pH 9 and a collector dosage of 268 mg/L. The green dashed line indicates the selected CMCS dosage.

As shown in Figure 5, for the +0.074 mm fraction, a CMCS dosage of 20 mg/L yielded a concentrate with a P_2O_5 recovery of 95.50% and a grade of 28.02%. For the −0.074 + 0.023 mm fraction, the selected CMCS dosage increased to 120 mg/L, producing a P_2O_5 recovery of 95.58% and a grade of 26.47%. For the −0.023 mm fraction, a further increase in CMCS dosage to 180 mg/L resulted in a P_2O_5 recovery of 74.37% and a grade of 21.10%. Compared with the zero-CMCS controls, the selected CMCS dosages produced a more favorable overall grade–recovery response for all three particle-size fractions, although the extent and form of improvement differed with particle size. As the particle size decreased, the required CMCS dosage increased. The concentrate grade decreased progressively, whereas the P_2O_5 recovery remained essentially unchanged from the coarse to the intermediate-size fraction and then declined markedly in the fine fraction. The deterioration in fine-particle separation may be related to several phenomena commonly reported in fine-particle flotation, including the increased surface area per unit mass and associated reagent demand [4,19], particle aggregation [5,20], slime coating, and enhanced mechanical

entrainment [21–23]. However, these effects were not directly quantified in the present study and are therefore considered possible contributing factors rather than experimentally confirmed mechanisms. Overall, CMCS maintained selective separation between apatite and biotite, although the separation performance decreased with decreasing particle size. The difference in reagent demand between the two systems may additionally reflect competitive adsorption and the larger total mineral surface area in the artificial-mixture system, although these effects were not independently quantified in this study. The measured P_2O_5 feed grades were 20.20%, 17.20%, and 17.50% for the +0.074, $-0.074 + 0.023$, and -0.023 mm fractions, respectively. At the selected CMCS dosages, the corresponding concentrate yields were $73.27 \pm 5.55\%$, $67.33 \pm 4.65\%$, and $64.33 \pm 5.20\%$, respectively.

3.3. Contact Angle Measurements

The apparent water contact angles of apatite and biotite under collector-only and CMCS-pretreated + collector conditions are presented in Figure 6.

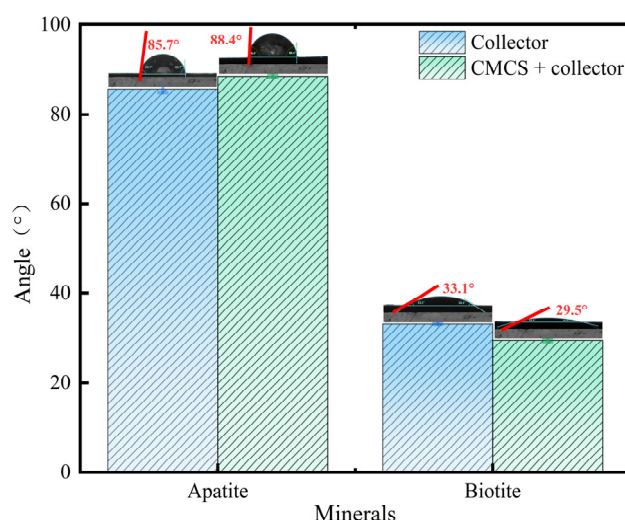


Figure 6. Apparent water contact angles of apatite and biotite after collector treatment in the absence and presence of CMCS. Data are presented as mean $\pm$ SD ($n = 3$).

As shown in Figure 6, in the absence of CMCS, collector-treated apatite and biotite exhibited apparent water contact angles of $85.7^\circ \pm 0.90^\circ$ and $33.1^\circ \pm 0.20^\circ$, respectively, indicating a substantially stronger collector-induced hydrophobic response on apatite than on biotite. After CMCS pretreatment followed by collector addition, the apparent contact angle of apatite remained high at $88.4^\circ \pm 0.40^\circ$, whereas that of biotite decreased slightly to $29.5^\circ \pm 0.70^\circ$. Accordingly, the contact-angle difference between apatite and biotite increased from 52.6° to 58.9° . These results suggest that CMCS had little adverse effect on the collector-induced hydrophobicity of apatite but weakened the hydrophobic response of biotite to some extent, thereby increasing the wettability contrast between the two minerals. This behavior is consistent with the flotation results, in which apatite retained high floatability while biotite was preferentially depressed by CMCS [24].

3.4. Adsorption Behavior of CMCS

The adsorption of CMCS on apatite and biotite was investigated at pH 9 over a range of initial CMCS concentrations, and the results are presented in Figure 7.

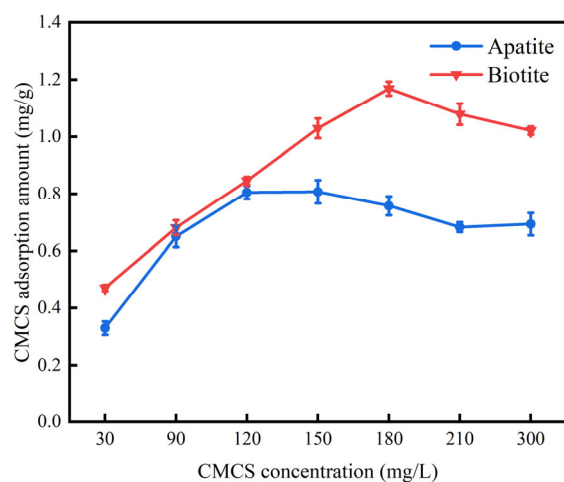


Figure 7. Adsorption of CMCS on apatite and biotite as a function of initial CMCS concentration.

As shown in Figure 7, measurable adsorption of CMCS occurred on both minerals throughout the tested concentration range. However, the adsorption amount on biotite was consistently higher than that on apatite, and the difference generally widened with increasing CMCS concentration. As the initial CMCS concentration increased from 30 to 150 mg/L, the adsorption amount on apatite increased from 0.33 to 0.81 mg/g. It subsequently decreased slightly and fluctuated within approximately 0.68–0.76 mg/g. In contrast, the adsorption amount on biotite increased progressively from 0.47 to 1.03 mg/g over the same concentration range. At 180 mg/L CMCS, biotite exhibited the highest adsorption amount observed within the tested range, reaching 1.17 mg/g, whereas the adsorption amount on apatite was 0.76 mg/g. The resulting adsorption difference between the two minerals was 0.41 mg/g. At higher CMCS concentrations, adsorption on biotite decreased slightly but remained substantially greater than that on apatite. These results indicate that CMCS exhibited a stronger apparent adsorption affinity for biotite than for apatite [11,21,25,26].

3.5. Zeta Potential Analysis

The zeta potentials of apatite and biotite as a function of pH before and after CMCS treatment are presented in Figure 8, and the CMCS-induced zeta potential changes are summarized in Table 3.

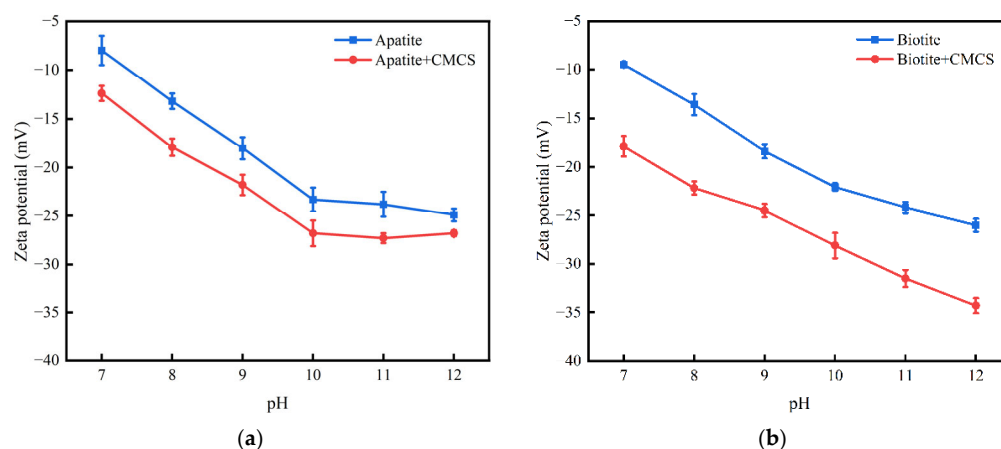


Figure 8. Zeta potentials of apatite and biotite as a function of pH before and after CMCS treatment: (a) Apatite; (b) Biotite.

Table 3. Zeta Potential Shifts induced by CMCS Adsorption ($\Delta\zeta^1$, mV).

pH	7	8	9	10	11	12
$\Delta\zeta$ (Apatite)	−4.4	−4.7	−3.8	−1.5	−3.5	−1.9
$\Delta\zeta$ (Biotite)	−8.4	−8.6	−6.1	−6.0	−7.3	−8.3

¹ $\Delta\zeta = \zeta_{\text{CMCS-treated}} - \zeta_{\text{untreated}}$.

As shown in Figure 8, both minerals exhibited negative zeta potentials over the pH range of 7–12, and their potentials generally became more negative with increasing pH. CMCS treatment induced a further negative shift in the zeta potential of both minerals. The magnitude of this shift ranged from 1.5 to 4.7 mV for apatite and from 6.0 to 8.6 mV for biotite. The substantially larger shift observed for biotite indicates that CMCS exerted a stronger influence on its interfacial electrokinetic properties. This behavior was consistent with the greater CMCS adsorption on biotite observed in the adsorption measurements and suggests more extensive CMCS coverage of the biotite surface than of the apatite surface [7,27,28].

3.6. Fourier Transform Infrared Spectroscopy Analysis

The FTIR spectra of apatite and biotite before and after CMCS treatment are presented in Figure 9.

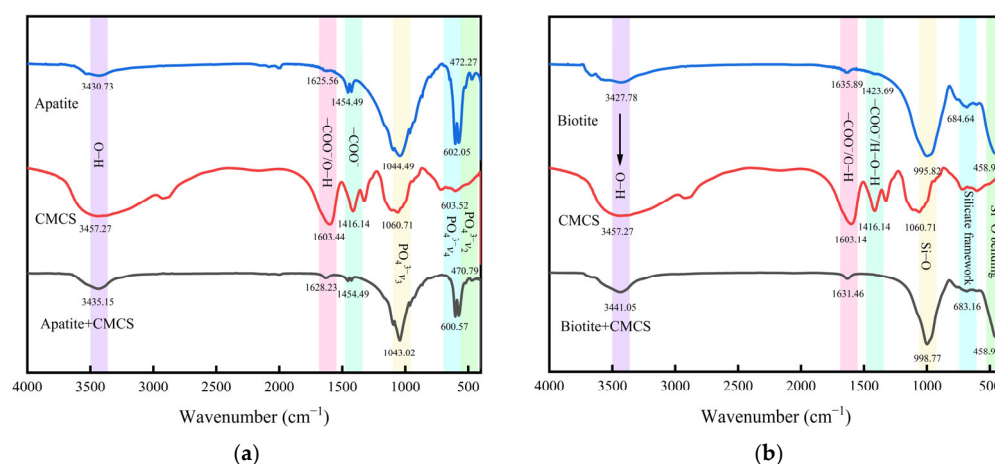


Figure 9. FTIR spectra of apatite and biotite before and after CMCS treatment: (a) Apatite; (b) Biotite. The arrows indicate the positions of selected characteristic absorption bands discussed in the text.

As shown in Figure 9, CMCS treatment shifted the O–H band of apatite from 3430.73 to 3435.15 cm^{-1} . The characteristic bands assigned to the ν_3 asymmetric stretching, ν_4 bending, and ν_2 bending vibrations of PO_4^{3-} [29] shifted from 1044.49, 602.05, and 472.27 cm^{-1} to 1043.02, 600.57, and 470.79 cm^{-1} , respectively. These relatively small shifts indicate that CMCS caused only limited perturbation of the apatite surface functional groups, suggesting relatively weak interfacial interactions potentially involving hydrogen bonding, electrostatic interactions, and van der Waals forces [27,30]. In comparison, the O–H band of biotite shifted from 3427.78 to 3441.05 cm^{-1} , while the Si–O stretching band and silicate framework band shifted from 995.82 and 684.64 cm^{-1} to 998.77 and 683.16 cm^{-1} , respectively [31]. More pronounced changes in the absorption profile near 1600 cm^{-1} were also observed after CMCS treatment. These spectral changes suggest that the carboxyl and hydroxyl groups of CMCS participated in its interaction with the biotite surface through hydrogen bonding and electrostatic interactions. Weak coordination between CMCS functional groups and exposed surface metal sites may also have contributed to the adsorption process.

3.7. X-Ray Photoelectron Spectroscopy Analysis

3.7.1. XPS Survey Spectra

The XPS survey spectra of apatite and biotite before and after CMCS treatment are shown in Figure 10. The principal substrate elements detected on apatite were O, Ca, P, F, and C, whereas the biotite surface was mainly characterized by O, Si, Al, Mg, Fe, K, and C. Changes in the relative survey-spectrum intensities were observed after CMCS treatment, indicating modification of the surface chemical composition. Because survey-spectrum intensities are affected by relative elemental sensitivity and surface heterogeneity, the preferential adsorption of CMCS was further evaluated using high-resolution XPS spectra together with the adsorption and zeta-potential results.

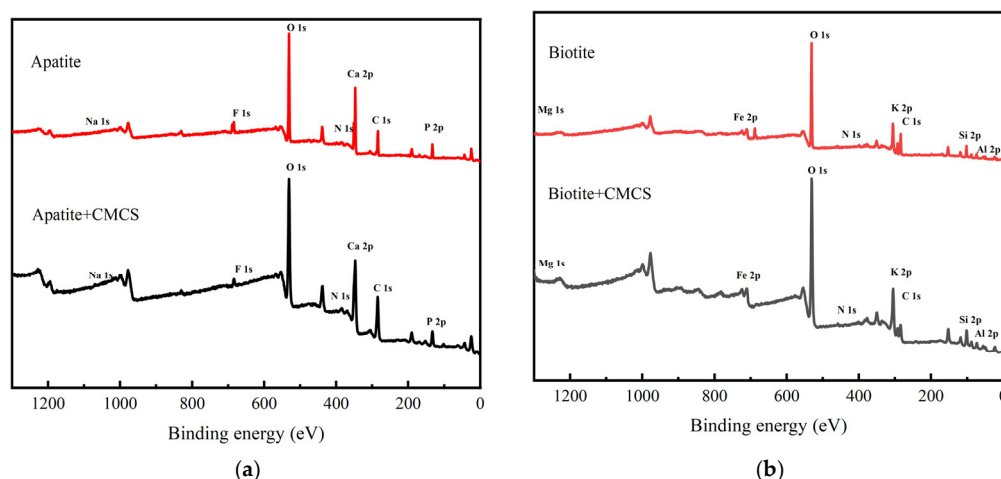


Figure 10. XPS survey spectra of apatite and biotite before and after CMCS treatment: (a) apatite before and after CMCS treatment; (b) biotite before and after CMCS treatment.

3.7.2. High-Resolution XPS Spectra of Apatite

The peak-fitted C 1s, O 1s, and Ca 2p spectra of apatite before and after CMCS treatment are presented in Figure 11. As shown in Figure 11a,b, the relative contributions of the C–O–C and O–C=O components increased markedly after CMCS treatment [32]. Their binding energies shifted from 286.57 and 289.27 eV to 286.50 and 288.95 eV, respectively. The enrichment of these oxygenated carbon species was consistent with the presence of CMCS on the apatite surface [18]. The relatively small binding-energy shifts suggest that CMCS caused only limited perturbation of the surface chemical environment, with adsorption likely dominated by relatively weak non-covalent interactions, including hydrogen bonding, electrostatic interactions, and van der Waals forces.

As shown in Figure 11c,d, the O 1s components at 531.41 and 533.20 eV were assigned primarily to lattice P–O and to surface hydroxyl groups, adsorbed water, and oxygen-containing organic species, respectively [32]. After CMCS treatment, these components shifted to 531.04 and 532.99 eV, while the relative contribution of the higher-binding-energy component increased. This increase was consistent with the introduction of oxygen-containing functional groups from CMCS onto the apatite surface. Nevertheless, the limited overall spectral changes indicate that the interaction was relatively weak and was likely governed mainly by hydrogen bonding and electrostatic interactions. Weak interactions between CMCS oxygen-containing groups and surface Ca sites may also have contributed.

As shown in Figure 11e,f, the Ca 2p spectrum of untreated apatite exhibited the characteristic spin–orbit–split Ca 2p_{3/2} and Ca 2p_{1/2} components at 347.48 and 351.03 eV, respectively [33]. After CMCS treatment, the corresponding peaks were located at 347.46 and 350.83 eV. The Ca 2p binding energies therefore changed only marginally, and no

additional resolvable Ca component was observed. These results suggest that the electronic environment of the surface Ca sites was only weakly perturbed. Accordingly, CMCS adsorption on apatite was dominated by relatively weak interfacial interactions, with only a limited possible contribution from electrostatic interactions or weak coordination involving surface Ca sites.

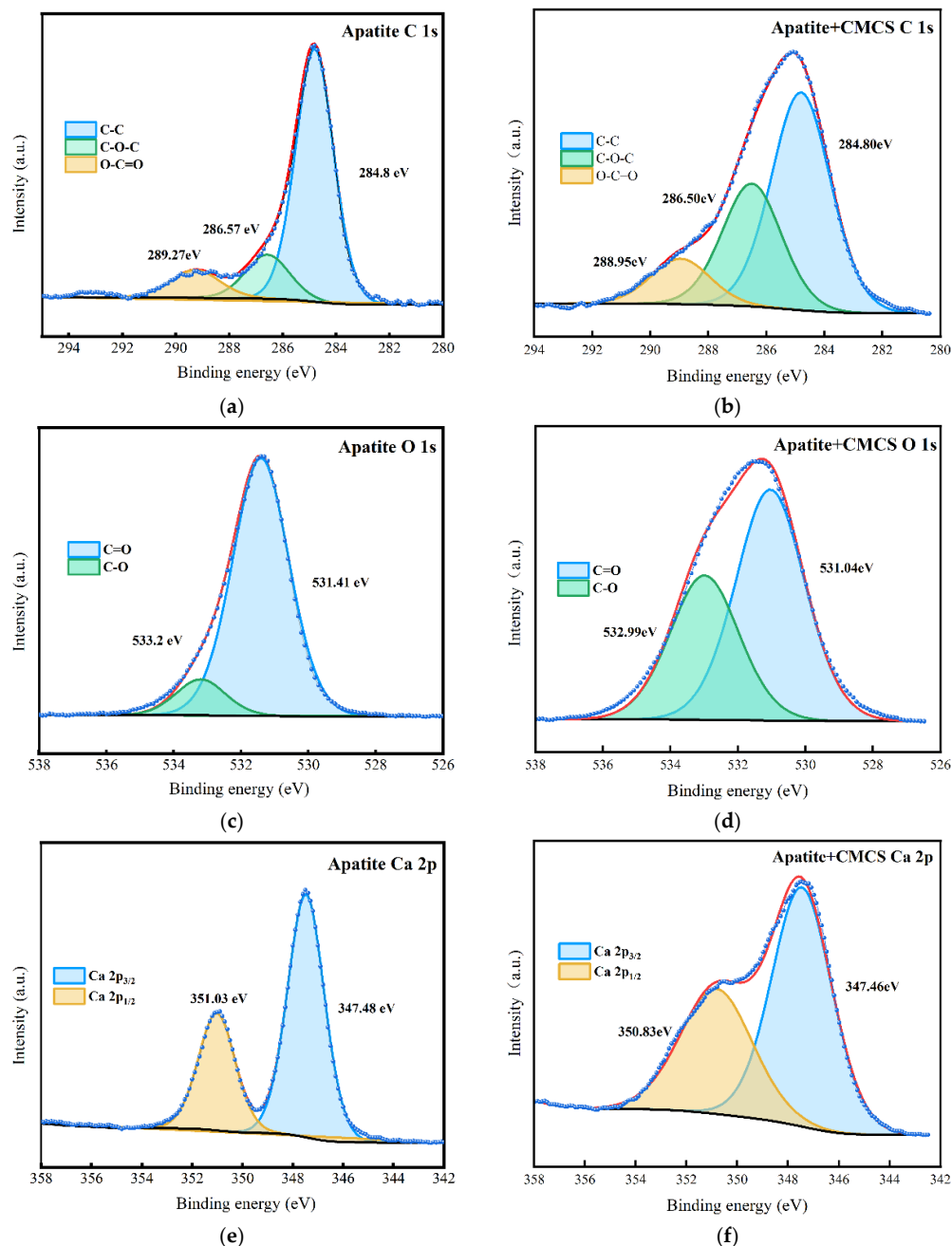


Figure 11. Peak-fitted C 1s, O 1s, and Ca 2p spectra of apatite before and after CMCS treatment: (a) Apatite; (b) Apatite + CMCS; (c) Apatite; (d) Apatite + CMCS; (e) Apatite; (f) Apatite + CMCS. Symbols and colored lines denote the experimental data, fitted envelope, individual fitted components, and background, respectively.

3.7.3. High-Resolution XPS Spectra of Biotite

The peak-fitted C 1s, O 1s, and Mg 1s spectra of biotite are presented in Figure 12. As shown in Figure 12a,b, the C–O–C component shifted slightly from 286.45 to 286.35 eV after CMCS treatment. For untreated biotite, the higher-binding-energy com-

ponent at 289.01 eV was assigned to O–C=O species, whereas after CMCS treatment, an oxygen-containing carbon component was observed at 287.65 eV and was conservatively assigned to C=O/O–C–O related species. Considering the possible overlap among oxygen-containing carbon components, the change from 289.01 to 287.65 eV was not interpreted as a direct binding-energy shift in the same O–C=O chemical state. Together with the changes in the relative contributions of the oxygen-containing components, these spectral variations indicate modification of the surface carbon chemical environment following CMCS adsorption.

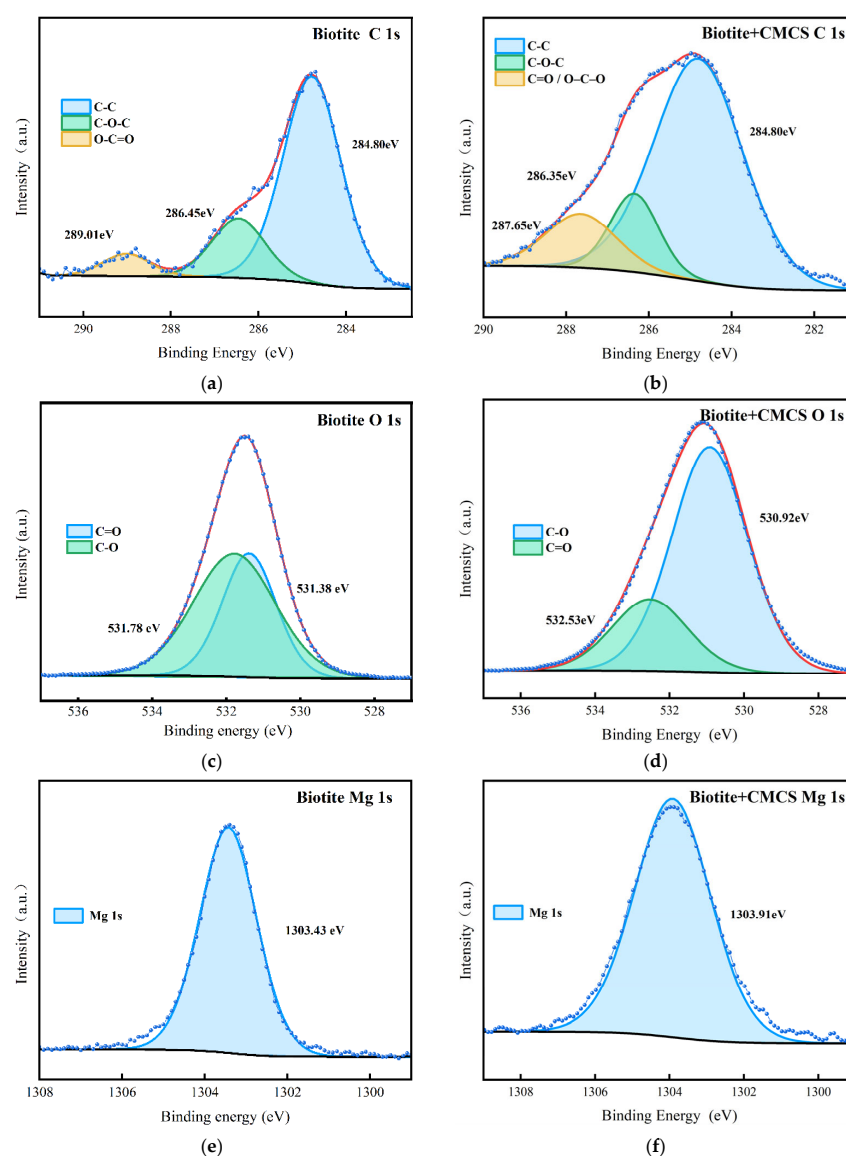


Figure 12. Peak-fitted C 1s, O 1s, and Mg 1s spectra of biotite before and after CMCS treatment: (a) Biotite; (b) Biotite + CMCS; (c) Biotite; (d) Biotite + CMCS; (e) Biotite; (f) Biotite + CMCS. Symbols and colored lines denote the experimental data, fitted envelope, individual fitted components, and background, respectively.

As shown in Figure 12c,d, the lower-binding-energy component of the biotite O 1s spectrum was mainly assigned to lattice oxygen in Si–O, Al–O, and Mg–O environments, whereas the higher-binding-energy component was associated with surface hydroxyl groups, adsorbed water, and oxygen-containing functional groups derived from CMCS. After CMCS treatment, these two components were located at 530.92 and 532.53 eV, respectively, accompanied by pronounced changes in their line shapes and relative peak

areas. These changes indicate that the carboxyl and hydroxyl groups of CMCS altered the local electronic environment of oxygen species on the biotite surface. The adsorption process likely involved hydrogen bonding and electrostatic interactions, together with specific chemical interactions between the oxygen-containing functional groups of CMCS and exposed surface metal sites.

As shown in Figure 12e,f, the Mg 1s peak shifted from 1303.43 to 1303.91 eV after CMCS treatment, corresponding to a positive binding-energy shift of 0.48 eV, accompanied by noticeable peak broadening. These spectral changes indicate an alteration in the local chemical environment of Mg-related surface sites after CMCS treatment. The observed Mg 1s shift is consistent with the possible participation of Mg-related sites in interactions with the oxygen-containing groups of CMCS [26,34,35]; however, the XPS results alone are insufficient to establish a specific coordination structure.

3.8. Interfacial Interaction of CMCS with Apatite and Biotite Under Fine-Particle Conditions

CMCS adsorbed on both apatite and biotite, but its adsorption amount and its influence on the surface chemical environment of apatite were relatively limited. The CMCS chains likely interacted with the apatite surface predominantly through relatively weak non-covalent interactions, including hydrogen bonding, possible electrostatic interactions, and van der Waals forces. These limited surface interactions were consistent with the relatively high floatability retained by apatite. In contrast, CMCS exhibited substantially greater adsorption on biotite. Its carboxyl and hydroxyl groups may interact with surface hydroxyl groups and other oxygen-containing sites through hydrogen bonding and electrostatic interactions, while the Mg 1s shift suggests possible participation of Mg-related surface sites in the interfacial interaction. Contact-angle measurements further showed that CMCS pretreatment preserved the collector-induced hydrophobicity of apatite while slightly weakening that of biotite. As particle size decreases, increased surface area per unit mass, greater reagent demand, and fine-particle phenomena such as aggregation, slime coating, and mechanical entrainment may collectively contribute to poorer separation; these effects were not directly quantified in the present work. Based on the combined flotation, adsorption, wettability, zeta potential, FTIR, and XPS results, a proposed interfacial interaction model highlighting the roles of the -COO^- and -OH groups of CMCS was developed, as illustrated in Figure 13.

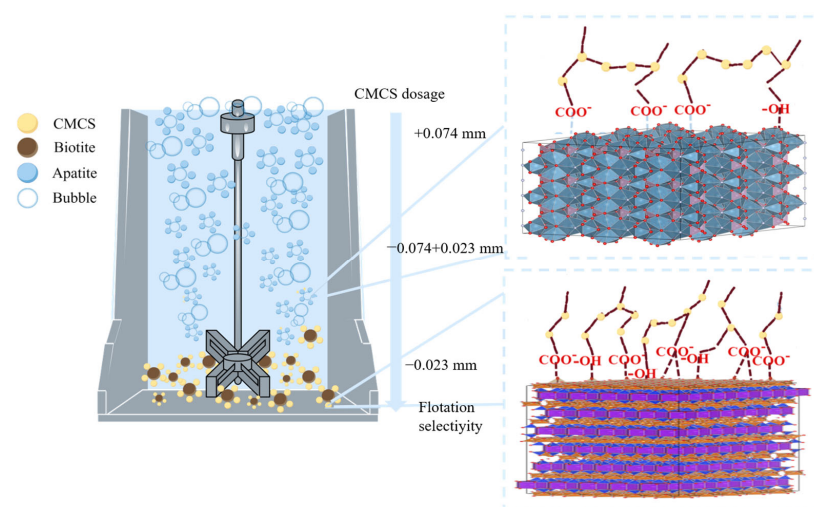


Figure 13. Schematic illustration of the particle-size-dependent flotation response and proposed CMCS–mineral interfacial interactions in the apatite–biotite system. Symbols for CMCS, biotite, apatite, and bubbles are defined in the figure legend; the upper-right and lower-right structural models schematically represent apatite and biotite surfaces, respectively.

4. Conclusions

- (1) Among the five depressants evaluated, CMCS consistently maintained a higher apatite recovery than biotite recovery in both the $-0.074 + 0.023$ and -0.023 mm fractions. Although CMCS did not yield the largest recovery difference in the intermediate-size fraction, it retained selectivity in favor of apatite in the fine fraction, demonstrating greater robustness across particle-size fractions than Tau, LS-Na, CS, and HPDSP.
- (2) CMCS-assisted apatite-biotite separation exhibited a pronounced particle-size dependence. The apatite-biotite recovery differences were 47.57, 40.51, and 20.59 percentage points for the $+0.074$, $-0.074 + 0.023$, and -0.023 mm fractions, respectively. In artificial-mixture flotation tests, the required CMCS dosage increased with decreasing particle size. The P_2O_5 grade decreased progressively, while the recovery remained nearly unchanged from the coarse to the intermediate-size fraction but declined markedly in the fine fraction. The poorer separation of the fine fraction may be associated with increased surface area per unit mass, greater reagent demand, and fine-particle phenomena such as aggregation and mechanical entrainment.
- (3) CMCS adsorption was consistently greater on biotite than on apatite. At an initial CMCS concentration of 180 mg/L, the adsorption amounts on biotite and apatite were approximately 1.17 and 0.76 mg/g, respectively. Contact-angle measurements showed that CMCS pretreatment exerted little adverse effect on the collector-induced hydrophobicity of apatite, whereas the apparent water contact angle of biotite decreased from 33.1° to 29.5° . CMCS also induced a larger negative zeta-potential shift for biotite, collectively supporting its preferential interaction with the biotite surface.
- (4) FTIR and XPS analyses indicated that CMCS adsorbed on both minerals but caused more pronounced changes in the functional groups and local chemical environments of biotite. Its interaction with apatite was relatively weak and was likely dominated by non-covalent forces, including hydrogen bonding, electrostatic interactions, and van der Waals forces. On biotite, these interactions may have been accompanied by additional interactions involving the carboxyl and hydroxyl groups of CMCS, while Mg-related surface sites may participate in the interfacial interaction. The greater adsorption of CMCS on biotite, as supported by the adsorption measurements, likely contributed to its preferential depression and enhanced separation from apatite.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations13100278/s1>, Figure S1: Effect of pulp pH on the flotation behavior of apatite and biotite in different particle-size fractions at a collector dosage of 268 mg/L (5360 g/t) in the absence of depressant: (a) apatite; (b) biotite; Figure S2: Calibration curve between CMCS concentration and TOC concentration; Table S1: Relative surface atomic concentrations (at.%) derived from XPS survey spectra of apatite and biotite before and after CMCS treatment.

Author Contributions: Z.Y. (Zixuan Yang): Investigation, data curation, conceptualization, methodology, writing—review and editing, Writing—original draft; Z.Y. (Zurong Yi): Data curation, validation; L.Z.: Resources, writing—review and editing, funding acquisition; M.L.: Data curation, validation; J.H.: Data curation, validation; B.G.: Resources, funding acquisition; M.H.: Resources, funding acquisition; W.L.: Resources, funding acquisition; Y.L.: Resources, funding acquisition; C.W.: Resources, funding acquisition; X.G.: Resources, Supervision; F.L.: Resources, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Natural Science Foundation of China Youth Program (No. 51804123) and the Technology Development Entrusted Project of HBIS Group Co., Ltd. (Contract No. HG2022116).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: Bin Guo, Ming Han, Wantao Li, Youbang Lai, and Chuntao Wu are employees of HBIS Group Mining Co., Ltd. Fengliang Liu is an employee of Huate Magnet Group Co., Ltd. The authors declare that this study received funding from HBIS Group Co., Ltd. The funder was not involved in the study design, collection, analysis, interpretation of data, the writing of this article or the decision to submit it for publication. The authors declare no other financial or non-financial competing interests related to this work.

Abbreviations

The following abbreviations are used in this manuscript:

CMCS	Carboxymethyl chitosan
Tau	Taurine
LS-Na	Sodium lignosulfonate
CS	Chitosan
HPDSP	Hydroxypropyl distarch phosphate

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