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The effect of the composite grinding aid PEG/TIPA on the flotation behavior of quartz in a TTAC system

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Abstract: Incorporation of grinding aid into mineral comminution has been demonstrated to promote energy utilization and potentially optimize the flotation response of the resulting products. The present work undertook a comprehensive, systematic examination of quartz particle flotation behavior under TTAC collector conditions, specifically focusing on the modulatory effects exerted by a binary grinding aid system composed of PEG and TIPA. The findings demonstrate that introducing grinding additives can effectively enhance the comminution efficiency and flotation response of quartz. Moreover, the composite grinding aid exhibited superior performance compared with individual additives, indicating a synergistic effect between the components. At a dosage of 0.06% for the PEG/TIPA composite grinding aid, with a PEG:TIPA ratio of 2:1, the -0.074 mm particle size fraction reached 86.09%, and the flotation recovery reached 94.17%. Microstructural examination via SEM indicated that introducing the grinding aid generated supplementary fractures across quartz surfaces while concomitantly diminishing particulate agglomeration. Spectroscopic investigations employing FT-IR and XPS demonstrated that the composite grinding aid functioned synergistically with TTAC to alter interfacial properties of the mineral. Specifically, TTAC adhered to quartz primarily via physical adsorption mechanisms, whereas the composite additive established surface attachment through both hydrogen bonding and electrostatic adsorption. Importantly, no antagonistic adsorption behavior was observed between the composite reagent and TTAC. Zeta potential measurements further confirm that -OH groups in the solution undergo ionization, and the grinding aid and collector work synergistically to enhance the flotation performance of quartz.

Keywords: grinding, grinding aids, quartz, PEG/TIPA

1. Introduction

Within mineral processing operations, comminution represents one of the most energy-demanding stages, typically responsible for 30-70% of overall electricity consumption at mining facilities while additionally requiring substantial grinding media replacement (Matsanga et al., 2023). The introduction of chemical additives exhibiting grind-enhancing characteristics during milling operations constitutes a critical approach for the extractive industry to boost operational throughput, curtail power requirements, and minimize consumable resource utilization. Previous studies have demonstrated that incorporating grinding aids can effectively promote material comminution, inhibit particle aggregation, and improve the transport and flowability of materials during the milling process (Yang et al., 2025). Under specific operational conditions, the incorporation of chemical grinding aids can induce surface defects and microcracks of mineral particulates, thereby promoting more efficient ore disintegration throughout the milling stage. Consequently, comminution effectiveness improves while the specific power requirement of the process declines correspondingly (Camalan and Hoşten, 2019). Early grinding aids were primarily inorganic substances such as hydrochloric acid (HCl), calcium chloride ($CaCl_2$), and lime, which had poor adaptability and

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produced only modest grinding effects. With the growing demand for sustainable resource development, organic grinding aids, particularly ethylene glycol and triethanolamine (TEA), have been increasingly used in the cement industry. These aids not only enhance material dispersion and improve grinding efficiency but also enhance hydration properties (Ji et al., 2024; Kang et al., 2024). Grinding aids have also been used in the processing of bauxite, iron ore, quartz, and other minerals.

The application of grinding aids provides an effective approach to increasing grinding efficiency and reducing energy consumption without the need for additional equipment investment or modifications to current processing flowsheets. Nevertheless, their addition during grinding requires careful evaluation of their potential effects on downstream mineral processing, especially flotation. Since mineral flotation performance is largely governed by mineral surface properties and reagent adsorption behavior, these critical factors may be altered by the preceding grinding process (M. Yang et al., 2026). Within the integrated grinding-flotation process, comminution represents a complex physicochemical process involving mechanical, chemical, and interfacial interactions. This operation can induce significant variations in mineral surface characteristics, crystal structure, particle size distribution, elemental composition, and the chemical environment of the pulp (Tong et al., 2025).

In the grinding-flotation system, the flotation behavior of quartz is significantly influenced by changes in surface properties, particle-size distribution, and the chemical environment of the slurry induced by grinding, elucidating the mechanisms underlying these effects is of great significance for the efficient separation and purification of quartz. Among the diverse silicate phases constituting the Earth's crust, quartz ranks as the most abundant, distinguished by its widely distributed in diverse geological environment and its exceptional structural and chemical stability. High-purity, high-purity quartz crystals is colorless and transparent, with excellent light transmission and a vitreous luster (Ren et al., 2023). Quartz is primarily composed of SiO_2, making it an abundant and widely available non-metallic mineral resource (Guo et al., 2024). Driven by the accelerated growth of advanced materials and renewable energy fields, the utilization of quartz has expanded beyond conventional applications, including construction and glass production, and has increasingly become important in various strategic emerging industries (Xie et al., 2024). Quartz containing more than 99.9% SiO_2 is generally classified as high-purity quartz, which serves as a critical raw material for advanced technological applications (Zhang et al., 2024). It is extensively utilized in fields such as semiconductor manufacturing, photovoltaic technologies, and aerospace engineering (Li et al., 2023).

In this work, high-purity quartz ore was selected as the feed material, while polyethylene glycol (PEG) and triisopropanolamine (TIPA) were introduced as grinding aids. The study aimed to evaluate the influence of a polymer–alkanolamine composite grinding aid on the flotation behavior of quartz under a tetradecyltrimethylammonium chloride (TTAC) flotation system. An extensive suite of analytical methodologies was utilized to systematically examine how grinding aids influence the particle-size distribution, surface properties, and adsorption behavior of quartz particles. Additionally, the underlying mechanisms by which composite grinding aids modulate the flotation response of this mineral were elucidated, thereby furnishing a theoretical foundation for rational selection of grinding aids and the refinement of separation processes.

2. Materials and methods

2.1. Materials

High-purity quartz was selected as the feed material for the grinding experiments. Prior to testing, the raw quartz was subjected to a systematic sample-preparation procedure involving coarse crushing, manual sorting, grinding, and particle-size classification by sieving, yielding a prepared sample with a particle size of <2 mm. The mineralogical composition of the prepared sample was characterized by X-ray diffraction (XRD), and the corresponding XRD pattern is presented in Fig. 1. The chemical composition of the sample is summarized in Table 1. The SiO_2 content was determined to be 99.62%, indicating that the prepared sample had a sufficiently high quartz content for the subsequent grinding and flotation experiments.

Polyethylene glycol 4000 (PEG 4000, $HO(CH_2CH_2O)_nH$) and triisopropanolamine (TIPA, $C_9H_{21}NO_3$) were employed as grinding aids, while tetradecyltrimethylammonium chloride (TTAC, $C_{17}H_{38}ClN$) was used as the cationic flotation collector. Hydrochloric acid (HCl) and sodium hydroxide (NaOH)

aqueous solutions were used to adjust the slurry pH. All reagents were of analytical grade, and deionized water was used throughout the experiments.

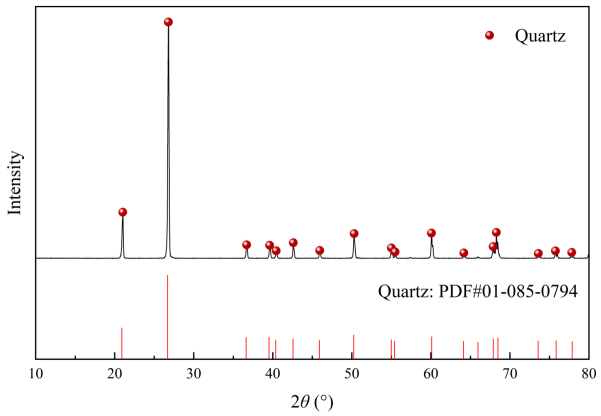


Fig. 1. XRD pattern of quartz

Table 1. Results of multi-element analysis by quartz XRF

Ingredients	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	TFe	Other
Content/%	99.62	0.11	0.10	0.05	0.04	0.02	0.02	0.04

2.2. Grinding test

Grinding experiments were conducted using a planetary ball mill with a working volume of 100.00 mL. Prior to the grinding-aid experiments, preliminary optimization experiments were performed to establish the baseline grinding conditions for quartz in the absence of grinding aids. The wet milling protocol employed zirconia spheres of mixed diameters (Φ15 mm: 10 mm: 6 mm = 11:2:1) as the grinding medium. The baseline grinding conditions were a grinding-media-to-quartz mass ratio of 0.8, a solid concentration of 50 wt%, and a grinding time of 10 min. For each experiment, 20.00 g of quartz was loaded into the mill with 20.00 mL of deionized water, and the grinding aid was subsequently added at a predetermined dosage based on the mass of quartz.

2.3. Flotation test

To minimize interference from impurity ions during flotation, zirconia grinding balls were used during the grinding process to prepare the flotation feed samples. Different grinding aids were added at predetermined dosages, and the grinding time was varied according to the experimental design. After co-grinding quartz with the selected grinding aids, the resulting products were dried under ambient conditions and collected for subsequent flotation experiments.

Flotation experiments were conducted at room temperature using an XFGII5-35 flotation machine equipped with a 40 mL flotation cell. For each test, 2.00 g of the pretreated sample was added to the flotation cell, followed by the addition of deionized water to form the pulp. The pulp pH was adjusted with HCl or NaOH solution for 1 min. Subsequently, TTAC was added as the cationic flotation collector, and the pulp was conditioned for an additional 2 min. The froth product was continuously collected until froth formation ceased. The flotation concentrate and tailings were then separately collected, dried, and weighed, and the quartz flotation recovery was calculated accordingly. The effect of the grinding aids on quartz floatability was evaluated by comparing the flotation recovery obtained under different grinding-aid conditions. A schematic illustration of the experimental procedure is presented in Fig. 2.

2.4. Particle size analysis

The particle-size distribution of the quartz samples was determined using an NTK600-D laser diffraction particle-size analyzer. A small amount of quartz sample was gradually added to the

sample cell until the light obscuration reached 15-20%. Before measurement, the sample suspension was subjected to ultrasonic treatment for 30 s to ensure adequate particle dispersion. Particle-size measurements were performed using a quartz refractive index of 1.51 and a dispersing-medium refractive index of 1.33 (Wei et al., 2026).

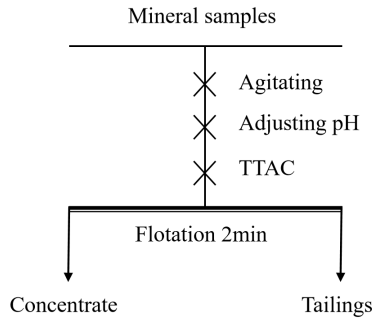


Fig. 2. Flotation test procedure

2.5. Surface topography analysis

The microstructural morphology of the samples was characterized using a field-emission scanning electron microscope (FE-SEM; Scios, Thermo Scientific) to investigate the surface morphology and microstructural features of the quartz particles. The quartz powder was uniformly dispersed onto conductive adhesive carbon tape mounted on an SEM sample stub, followed by conductive coating prior to observation. The sample height was adjusted to ensure that the upper surface remained below the 7 mm yellow reference line displayed in the CCD imaging window. SEM observations and micrographs were acquired under a chamber pressure below 9×10^{-3} Pa, an accelerating voltage of 1–30 kV, and a beam current of 1.6 pA–1.6 nA (Tian et al., 2022).

2.6. FT-IR measurement

Fourier-transform infrared (FT-IR) spectroscopy was performed using an FTIR-8400 spectrometer to characterize the quartz samples. For sample preparation, 2.00 g of quartz was dispersed in 50 mL of deionized water in a glass vessel. The suspension was first adjusted to neutral pH, after which the PEG/TIPA composite grinding aid and TTAC were added separately. To ensure sufficient interaction between the quartz surface and the added reagents, the suspension was continuously stirred for 5 min. After conditioning, the solid phase was recovered by filtration and subsequently dried under vacuum. For FT-IR analysis, 1.00 mg of the dried sample was thoroughly mixed with potassium bromide (KBr) at a sample-to-KBr mass ratio of 1:100. The resulting mixture was compressed into transparent pellets using an FW-4A pellet press at an applied pressure of 2.00×10^{-5} MPa. The prepared pellets were then placed in the spectrometer, and FT-IR spectra were recorded in the mid-infrared region from 500 to 4000 cm^{-1} (Ozun and Raimov, 2025).

2.7. XPS measurement

The elemental composition and chemical states of the outermost atomic layers of the quartz samples were characterized by X-ray photoelectron spectroscopy (XPS) to investigate the surface chemical interactions and adsorption behavior of the reagents. For sample preparation, 2.00 g of quartz was dispersed in 40 mL of deionized water, followed by the sequential addition of the PEG/TIPA composite grinding aid and TTAC as the cationic flotation collector. The suspension was magnetically stirred for 5 min to facilitate interaction between the reagents and the quartz surface. After conditioning, the solid samples were recovered by filtration and dried under vacuum before XPS analysis. The XPS spectra were processed using Advantage software, including background subtraction and peak fitting. The binding energy scale was calibrated by assigning the C 1s peak to 284.80 eV. The binding energies and chemical-state-related peak components of the surface elements were subsequently compared to identify treatment-induced changes in the surface chemical environment. (Mao et al., 2022).

2.8. Zeta potential detection

The electrokinetic properties of the quartz surface before and after reagent conditioning were characterized using a Zetasizer Nano ZS90 instrument. For each measurement, the quartz sample was dispersed in 20 mL of deionized water in a glass vessel. The suspension pH was adjusted as required by dropwise addition of HCl or NaOH solution, both at a concentration of 5%. Subsequently, predetermined amounts of the PEG/TIPA composite grinding aid and TTAC were added sequentially to the suspension. The resulting suspension was magnetically stirred for 5 min to facilitate interaction between the reagents and the quartz surface. After conditioning, the suspension was allowed to stand, and an aliquot of the supernatant was carefully withdrawn and transferred to the electrophoretic cell for zeta potential measurement. Each experimental condition was measured in triplicate, and the arithmetic mean was reported as the final value (Fan et al., 2026).

3. Results and discussion

3.1. Results of the grinding test

3.1.1. The single grinding aid

The particle-size distribution of mineral particles plays a critical role in determining their subsequent flotation behavior. Moreover, the proportion of fine particles generated after a given grinding time provides an important indicator of grinding performance and comminution efficiency (Xu et al., 2025). To evaluate the effects of different grinding aids on grinding performance, the experimental results are presented in Fig. 3. Specifically, Fig. 3 shows the proportion of quartz particles with a particle size below 0.074 mm obtained after grinding with different grinding-aid formulations.

As shown in Fig. 3, when a single grinding aid was used, the yield of the -0.074 mm size fraction increased markedly from 66.35% to 82.75% as the PEG dosage increased to 0.06%, followed by a gradual decrease with further increases in dosage. At an appropriate dosage, grinding aids can improve the contact conditions between the grinding media and quartz particles, thereby promoting particle breakage and enhancing grinding efficiency. However, excessive addition of grinding aids may result in the formation of a dense adsorbed layer on the mineral surface, which can partially hinder direct contact between the grinding media and quartz particles and consequently reduce grinding efficiency. This behavior was observed at a PEG dosage of 0.1%, where the yield of the -0.074 mm size fraction decreased to 70.97%. Similarly, increasing the TIPA dosage from 0 to 0.06% resulted in a pronounced increase in the yield of the -0.074 mm size fraction, from 66.35% to 79.58%. However, further increases in the grinding-aid dosage led to a gradual decrease in the proportion of fine particles. Comparison of the two grinding aids indicates that PEG exhibited slightly greater effectiveness than TIPA in promoting quartz breakage under the investigated conditions.The superior grinding performance of PEG and TIPA can be attributed to their distinct interactions with the quartz surface. PEG may form an adsorbed polymer layer on the quartz surface, providing steric stabilization that suppresses the re-agglomeration of fine particles and thereby facilitates the generation and retention of fine particles during grinding. In contrast, adsorption of the amine-containing grinding aid TIPA may modify the surface chemical environment and reduce the interfacial free energy of quartz, thereby facilitating deformation and crack propagation under mechanical stress. These interfacial effects can promote crack initiation and propagation and ultimately enhance the breakage of quartz particles during grinding.

3.1.2. The composite grinding aids

To comprehensively evaluate the effectiveness of the composite grinding aid, the relative proportions of its two components were systematically varied. PEG and TIPA were formulated at three different mass ratios, namely 1:1, 1:2, and 2:1, and their effects on the generation of the -0.074 mm size fraction were evaluated under otherwise identical grinding conditions. The corresponding results are presented in Fig. 4.

After the addition of the composite grinding aid at different PEG/TIPA mass ratios, the yield of the −0.074 mm size fraction exhibited a non-monotonic variation, increasing initially and subsequently

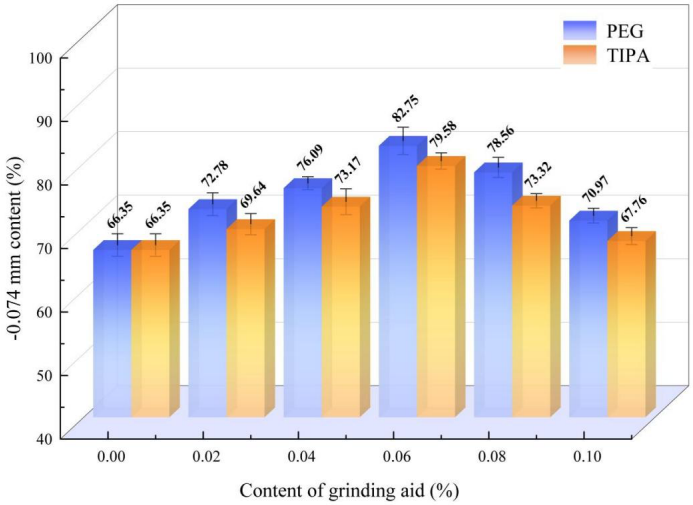


Fig. 3. The effect of single grinding aid content on particle size

decreasing with increasing grinding-aid dosage. This trend was consistent with that observed for the individual grinding aids; however, the composite systems consistently yielded a higher proportion offine particles than the individual PEG- or TIPA-based systems. As the PEG proportion in the composite grinding aid increased, the yield of the −0.074 mm size fraction gradually increased. The optimum grinding performance was obtained at a PEG/TIPA mass ratio of 2:1 and a total grinding-aid dosage of 0.06 wt%, resulting in a −0.074 mm size-fraction yield of 86.09%.The superior grinding performance of the PEG/TIPA composite system may arise from the complementary and synergistic effects of the two components. PEG may provide steric stabilization against the re-agglomeration of fine particles, whereas TIPA may modify the quartz surface and facilitate crack initiation and propagation under mechanical stress. The combined interfacial and steric effects may therefore promote particle breakage and improve the overall grinding efficiency of quartz.

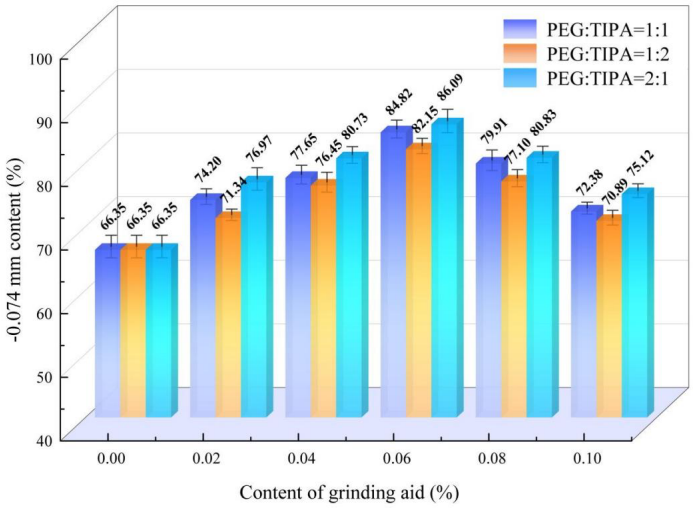


Fig. 4. The effect of composite grinding aid content on particle size

3.2. Results of the flotation test

3.2.1. Optimization of flotation parameters

TTAC was selected as the cationic collector because of its molecular structure, which consists of a C14 hydrophobic alkyl chain and a positively charged quaternary ammonium headgroup $[NR_4]^+$(Shi et al., 2025). This amphiphilic structure can facilitate electrostatic attraction between TTAC and the

negatively charged quartz surface at pH 7. In the absence of grinding aids, the effects of TTAC dosage and pulp pH on the flotation behavior of quartz were systematically investigated.

As shown in Fig. 5(a), the quartz flotation recovery increased markedly from approximately 70.25% to 91.44% with increasing TTAC concentration from 4 to 16 mg/L. The enhanced flotation recovery can be attributed to the increased availability of TTAC for interaction with the quartz surface, which may promote surface hydrophobicity and consequently improve quartz floatability. Upon further increasing the TTAC concentration, the increase in flotation recovery became progressively smaller and approached a plateau, with the recovery reaching approximately 93.50% at around 40 mg/L. This result indicates that increasing the collector concentration beyond 16 mg/L provided only a limited improvement in quartz flotation recovery. Therefore, considering the flotation performance and collector consumption, 16 mg/L TTAC was selected as the optimum collector concentration for the subsequent experiments. Further investigation of the effect of pH showed that the quartz flotation recovery reached a maximum of 91.44% at pH 7, as shown in Fig. 5(b). The flotation recovery decreased markedly under both acidic and alkaline conditions. At neutral pH, partial deprotonation of surface silanol groups can generate negatively charged siloxide sites (≡Si-O$^-$), which favor electrostatic attraction with the cationic collector TTAC and thereby promote the hydrophobization of the quartz surface. In strongly acidic media, protonation of surface silanol groups increases the positive charge of the quartz surface, making electrostatic attraction with cationic TTAC unfavorable and consequently reducing TTAC-quartz interfacial interactions. The resulting decrease in surface hydrophobicity may account for the lower flotation recovery under strongly acidic conditions. The residual flotation recovery under these conditions may arise, at least in part, from non-selective processes such as bubble entrainment rather than efficient TTAC adsorption. On the basis of the flotation recovery and collector consumption, 16 mg/L TTAC at pH 7 was selected as the baseline condition for subsequent flotation experiments.

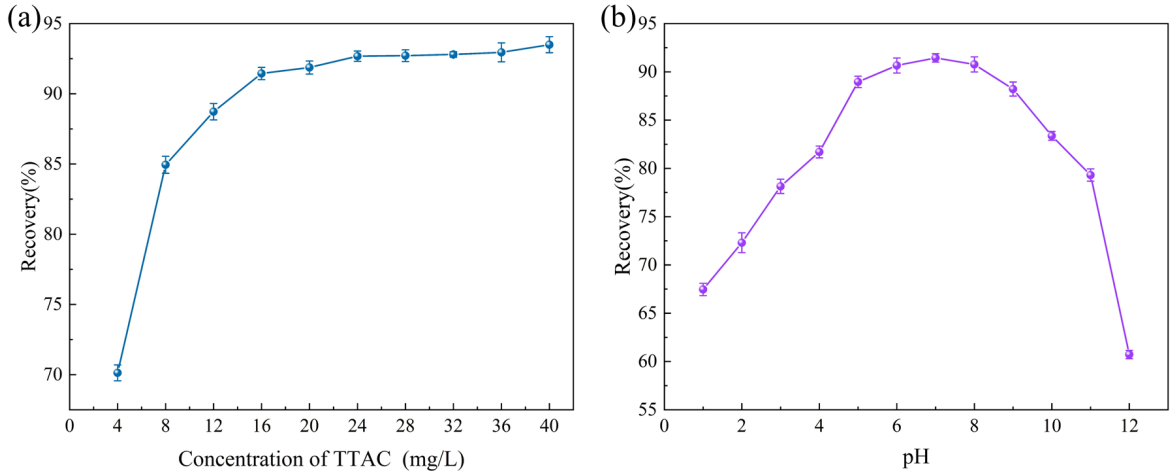


Fig. 5. Effects of TTAC concentration and pH on quartz flotation. (a) TTAC concentration, (b) pH

3.2.2. The effect of a single grinding aid on flotation

Under the optimized flotation conditions (16 mg/L TTAC and pH 7), PEG and TIPA were separately added as grinding aids during the grinding process to investigate the effects of grinding-aid dosage on the flotation behavior of quartz. The corresponding flotation results are presented in Fig. 6.

The results show that both grinding aids improved the quartz flotation recovery, which initially increased and subsequently decreased with increasing grinding-aid dosage. This behavior was generally consistent with the dosage-dependent trend observed in the grinding experiments. Specifically, at a PEG dosage of 0.06%, the quartz flotation recovery reached a maximum of 93.32%, corresponding to an increase of 1.88 percentage points compared with the grinding-aid-free system. In contrast, when TIPA was used as the grinding aid, the flotation recovery reached a maximum of 92.73% at a dosage of 0.06%, representing an increase of 1.29 % to the grinding-aid-free system.The grinding results indicate that the addition of grinding aids improved the grinding fineness of quartz and

increased the yield of the -0.074 mm size fraction. This shift toward finer particles increased the proportion of quartz particles within the size range favorable for flotation and thereby increased the fraction of particles available for effective flotation. In addition, the increased generation of fine particles may improve the contact conditions between quartz particles and flotation reagents, thereby contributing to enhanced quartz flotation recovery.However, excessive addition of grinding aids may promote the generation of ultrafine particles and particle agglomeration, which can reduce the probability of effective particle-bubble collision and attachment and consequently impair flotation recovery. At the same time, excessive grinding-aid molecules may interfere with the adsorption of the flotation collector TTAC on the quartz surface, thereby reducing surface hydrophobicity and ultimately leading to a decrease in quartz flotation recovery.

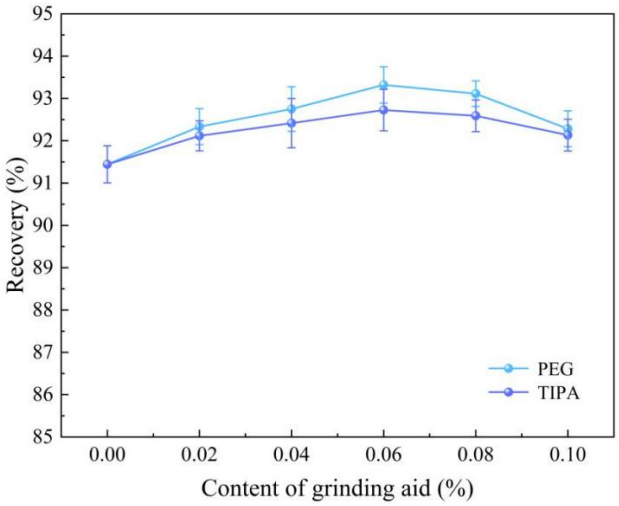


Fig. 6. The effect of a single grinding aid on quartz flotation

3.2.3. The effect of composite grinding aids on flotation

To investigate the effect of composite grinding aids on the flotation performance of quartz, PEG and TIPA were formulated at PEG/TIPA mass ratios of 1:1, 1:2, and 2:1 and added during grinding. Flotation experiments were subsequently conducted under the optimized conditions of 16 mg/L TTAC and pH 7, and the corresponding flotation results are presented in Fig. 7.

The results show that, regardless of the PEG/TIPA mass ratio, the quartz flotation recovery initially increased and subsequently decreased with increasing total grinding-aid dosage. Within an appropriate dosage range, the addition of grinding aids improved the grinding fineness of quartz and increased the yield of the −0.074 mm size fraction, thereby increasing the proportion of quartz particles within the size range favorable for flotation and consequently enhancing flotation recovery. However, excessive addition of grinding aids may promote the generation of ultrafine particles and particle agglomeration, which can reduce the probability of effective particle–bubble collision and attachment, ultimately resulting in a decrease in flotation recovery.At a constant total dosage of the composite grinding aid, the quartz flotation recovery increased with increasing PEG proportion in the PEG/TIPA composite grinding aid. The highest flotation recovery of 94.17% was achieved at a PEG/TIPA mass ratio of 2:1 and a total grinding-aid dosage of 0.06%, corresponding to an increase of 2.73% compared with the grinding-aid-free system. The enhanced flotation performance of the PEG/TIPA composite system may be associated with the complementary effects of the two grinding aids on the quartz surface. Their combined action may modify the surface chemical environment of quartz and facilitate the subsequent interaction of the quartz surface with the cationic collector TTAC, thereby contributing to the enhanced flotation recovery of quartz.

3.3. Surface morphology analysis

The surface morphology and microstructural features of quartz grinding products obtained under different grinding-aid conditions were characterized using scanning electron microscopy (SEM). The

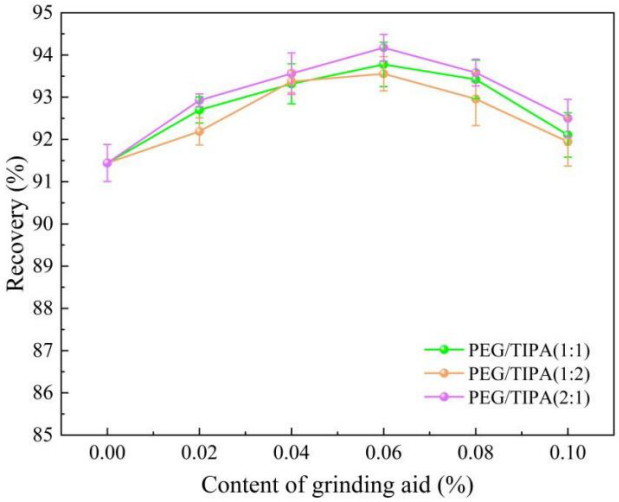


Fig. 7. The effect of composite grinding aids on quartz flotation

objective was to elucidate the effects of PEG, TIPA, and their composite grinding aid on the surface morphology and structural characteristics of quartz particles and to provide insights into the mechanisms by which grinding aids regulate the quartz grinding process.Fig. 8 shows the surface morphology and microstructural features of the quartz grinding products obtained under different grinding-aid conditions. As shown in Fig. 8(a), in the absence of grinding aids, the quartz particles exhibited irregular block-like morphologies with relatively smooth and dense surfaces. Pronounced particle agglomeration was observed, whereas relatively few obvious cracks and fragmentation features were present, indicating limited particle breakage under the grinding conditions.After the addition of PEG, as shown in Fig. 8(b), more distinct cracks and fragmentation features appeared on the particle surfaces, suggesting that PEG facilitated particle breakage during grinding. Nevertheless, a certain degree of particle agglomeration remained in some regions. After the addition of TIPA, as shown in Fig. 8(c), the particle edges became more irregular, accompanied by an increased number of flaky and fragmented structures. Distinct cracks were also observed, although particle agglomeration remained evident, suggesting that TIPA contributed to the breakage of quartz particles. In contrast,

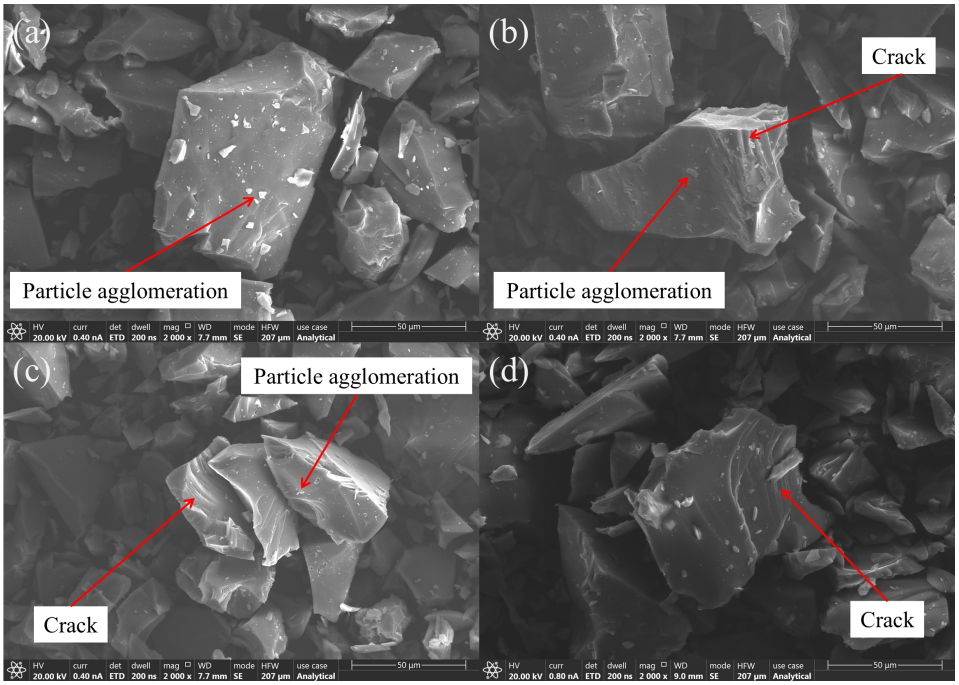


Fig. 8. Changes in the Morphology of Quartz. (a) Without grinding aid, (b) With PEG, (c) With TIPA, (d) With PEG/TIPA

the quartz particles treated with the PEG/TIPA composite grinding aid exhibited more pronounced fragmentation and crack features, while particle agglomeration was visibly reduced, as shown in Fig. 8(d). This indicates that the composite grinding aid promoted particle breakage while suppressing the re-agglomeration of fine particles. The enhanced grinding performance of the PEG/TIPA system may be attributed to the complementary effects of the two grinding aids. Their combined action may modify the surface chemical environment of quartz and reduce interparticle interactions, thereby facilitating crack development and particle breakage during grinding (Song et al., 2025; Wang et al., 2023).

3.4. FT-IR analysis

To elucidate the mechanism by which the PEG/TIPA composite grinding aid (PEG/TIPA mass ratio of 2:1) enhances quartz floatability, FT-IR spectroscopy was performed to characterize the composite grinding aid and the cationic collector TTAC before and after interaction with the quartz surface. The corresponding FT-IR spectra are presented in Fig. 9.

FT-IR spectroscopy indicates that both the PEG/TIPA composite grinding aid and TTAC can modify the local chemical environment of the quartz surface. As shown in Fig. 10, quartz exhibits characteristic vibrational bands associated with Si-O-Si bonds at 692.2 cm^{-1}, 776.9 cm^{-1}, and 1079.5 cm^{-1}. After conditioning with TTAC, these bands shifted to 693.1 cm^{-1}, 777.5 cm^{-1}, and 1081.3 cm^{-1}, respectively. Following grinding with the PEG/TIPA composite grinding aid, the corresponding bands shifted further to 693.3 cm^{-1}, 778.2 cm^{-1}, and 1082.9 $cmcm^{-1}$, respectively. In the PEG/TIPA – TTAC system, these bands exhibited further shifts to 693.6 cm^{-1}, 778.7 cm^{-1}, and 1084.7 cm^{-1}, respectively. These progressive shifts suggest that the interaction of the grinding aid and collector modifies the local chemical environment of the Si-O-Si structure on the quartz surface. The broad absorption band centered at approximately 3420.7 cm^{-1} is assigned to O-H stretching vibrations associated with surface hydroxyl groups and interfacial water molecules. After conditioning with TTAC, PEG/TIPA, and PEG/TIPA-TTAC, this band shifted to 3419.1 cm^{-1}, 3417.6 cm^{-1}, and 3414.9 cm^{-1}, respectively. The progressive shift toward lower wavenumbers indicates changes in the hydrogen-bonding environment of the hydroxylated quartz surface and its interfacial hydration layer, suggesting enhanced hydrogen-bonding interactions (Chipakwe et al., 2022). Taken together, the changes in the characteristic Si-O-Si and O-H vibrational bands indicate that the PEG/TIPA composite grinding aid modifies the surface hydroxylation and hydration environment of freshly generated quartz surfaces. These changes may provide a more favorable interfacial environment for the subsequent interaction and adsorption of TTAC, thereby facilitating the hydrophobization of the quartz surface and contributing to the enhanced flotation recovery observed experimentally.

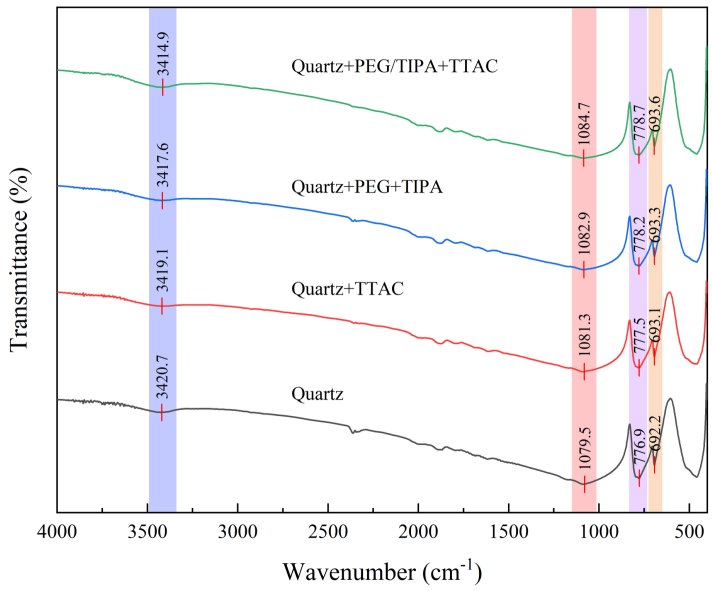


Fig. 9. FT-IR measurement results

3.5. XPS analysis

To further investigate the surface chemical interactions responsible for the enhanced quartz flotation performance, XPS was employed to characterize the elemental composition and chemical states of the quartz surface before and after conditioning with TTAC and the PEG/TIPA composite grinding aid at a PEG/TIPA mass ratio of 2:1. The corresponding XPS spectra are presented in Fig. 10.

The XPS survey spectra of the quartz samples are presented in Fig. 10. The untreated quartz surface was primarily composed of carbon, oxygen, and silicon. After conditioning with TTAC, the carbon atomic concentration increased markedly from 20.24% to 28.91%, whereas the atomic concentrations of oxygen and silicon decreased from 54.05% to 49.72% and from 25.71% to 21.37%, respectively. These changes in surface elemental composition support the enrichment of carbon-containing species on the quartz surface, consistent with the adsorption of TTAC. When quartz was first treated with the PEG/TIPA composite grinding aid at a PEG/TIPA mass ratio of 2:1 during grinding, followed by conditioning with TTAC, the carbon atomic concentration increased further to 51.41%, while the oxygen and silicon concentrations decreased to 36.76% and 11.83%, respectively. The pronounced enrichment of surface carbon suggests that pretreatment with the PEG/TIPA composite grinding aid facilitates the subsequent interaction and adsorption of TTAC at the quartz–solution interface, thereby contributing to the enhanced quartz flotation recovery.

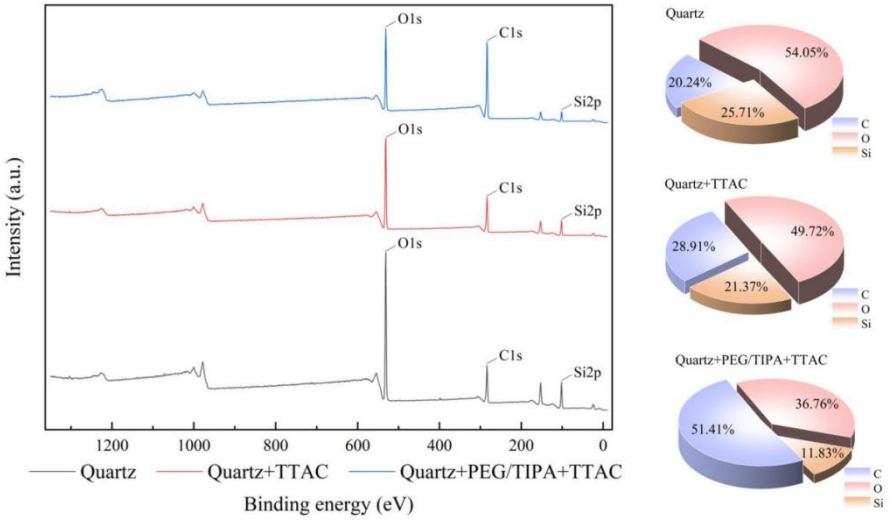


Fig. 10. Full spectrum of quartz XPS

Fig. 11 presents the high-resolution O 1s XPS spectra. For the untreated quartz, peak deconvolution identified three O 1s components centered at 531.18, 531.30, and 531.72 eV, assignable to bridging oxygen (Si-O-Si), non-bridging oxygen (Si-O), and hydroxyl oxygen (Si-OH). The surface hydroxyls arise from hydration of mechanically generated defects during particle fracture (Jiang et al., 2022). After TTAC treatment, no new O 1s peak appeared on the quartz surface, but all three characteristic peaks shifted, indicating that TTAC primarily interacts with oxygen-containing sites on the quartz surface through electrostatic and interfacial interactions involving quaternary ammonium groups, thereby altering the electronic environment of the oxygen atoms and causing changes in binding energy; no new O 1s component attributable to a new oxygen-containing chemical species was observed. (Liu et al., 2023). Under PEG/TIPA modification, the peaks relocated to 530.89, 530.95, and 531.97 eV. This additional perturbation reflects hydrogen-bonding between PEG ether oxygens and either surface silicon atoms or TTAC-associated hydrogens, which redistributes electron density around interfacial oxygen nuclei. The TIPA component further contributes through its hydroxyl-rich structure and pronounced coordinating ability. Since the pH during grinding is lower than the pKa of TIPA (approximately 8.06), the degree of protonation of TIPA increases. The hydroxyl groups in TIPA molecules can form hydrogen bonds with oxygen-containing sites on the quartz surface and, through electrostatic and other interfacial interactions, alter the electronic environment of the quartz surface. This causes a change in the O 1s binding energy, while simultaneously forming a hydration layer and

increasing steric hindrance, thereby inhibiting the agglomeration of fine particles and improving particle dispersion and grinding efficiency(B. Yang et al., 2026a).

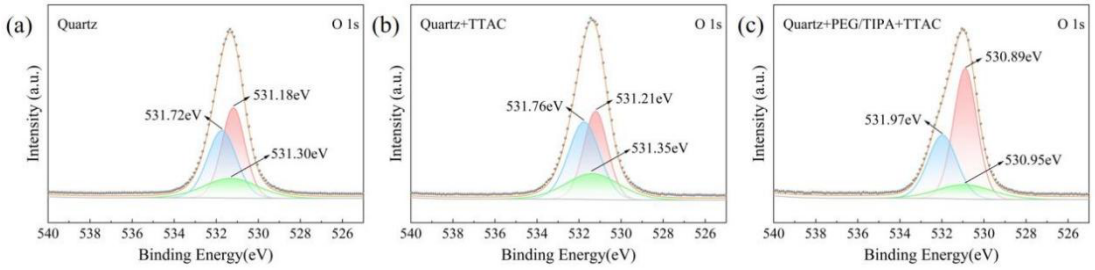


Fig. 11. Narrow XPS spectra of quartz O 1s. (a) Quartz, (b) Quartz + TTAC, (c) Quartz + TTAC + PEG/TIPA

The high-resolution Si 2p XPS spectra presented in Fig. 12 provide further evidence for the modification of the quartz surface by the PEG/TIPA composite grinding aid during grinding. Peak deconvolution revealed changes in the relative contributions of different Si chemical environments, which can be associated with Si–O–Si, deprotonated silanol (≡Si–O$^-$), and silanol (≡Si–OH) species. Quartz surfaces in aqueous media contain abundant surface silanol groups. Under near-neutral to moderately alkaline conditions, these groups can undergo partial deprotonation, generating negatively charged ≡Si–O$^-$ sites on the quartz surface.The ether oxygen atoms and terminal hydroxyl groups of PEG, together with the hydroxyl groups of TIPA, may interact with these oxygen-containing surface sites through hydrogen bonding and other interfacial interactions. Such interactions can modify the local chemical environment and electronic structure of surface Si–O bonds, resulting in measurable changes in the Si 2p binding energies. These surface interactions may promote the adsorption of the PEG/TIPA composite grinding aid onto freshly generated quartz surfaces, thereby contributing to the suppression of fine-particle re-agglomeration and the enhancement of quartz grinding efficiency (Mao et al., 2025).

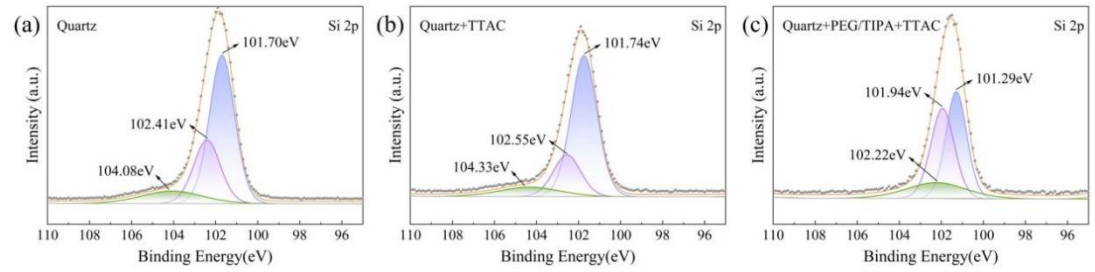


Fig. 12. Narrow Si 2p XPS spectra of quartz. (a) Quartz, (b) Quartz + TTAC, (c) Quartz + PEG/TIPA + TTAC

3.6. Zeta potential analysis

Changes in zeta potential are widely used to evaluate changes in surface charge and interfacial interactions associated with reagent adsorption at solid-liquid interfaces. The adsorption or accumulation of charged or polar species on a mineral surface can modify the structure of the electrical double layer, thereby altering the measured zeta potential (Chipakwe et al., 2023). Based on this principle, the surface interaction mechanisms between the reagents and quartz were further investigated under the optimized experimental conditions, namely, a PEG/TIPA mass ratio of 2:1, a total grinding-aid dosage of 0.06 wt%, and a TTAC concentration of 16 mg/L.

The electrokinetic data presented in Fig. 13 show that the zeta potential of untreated quartz became increasingly negative with increasing suspension pH. Upon conditioning with the cationic collector TTAC, the zeta potential shifted toward more positive values, increasing from -15.3 to -8.99 mV at pH 7. This shift suggests that TTAC interacted with the quartz surface and is consistent with the adsorption of positively charged quaternary ammonium species. The surface charge of quartz in aqueous media is closely related to the protonation and deprotonation of surface silanol groups. During grinding, freshly fractured quartz surfaces contain reactive oxygen-containing sites that can undergo hydration and protonation/deprotonation reactions, leading to the formation of surface

silanol groups (≡Si–OH) and negatively charged siloxide sites (≡Si-O$^-$) (Mao et al., 2024). Under near-neutral conditions, the partial deprotonation of surface silanol groups generates negatively charged sites, which can favor electrostatic attraction with the quaternary ammonium groups ($[NR_4]^+$) of TTAC (B. Yang et al., 2026b). This interfacial interaction is consistent with the enhanced flotation response of quartz observed under the corresponding conditions. When the PEG/TIPA composite grinding aid was introduced during grinding, an additional shift of the zeta potential toward more positive values was observed. This result suggests that PEG/TIPA modified the surface charge and interfacial chemical environment of quartz, potentially facilitating the subsequent interaction and adsorption of TTAC on the quartz surface.

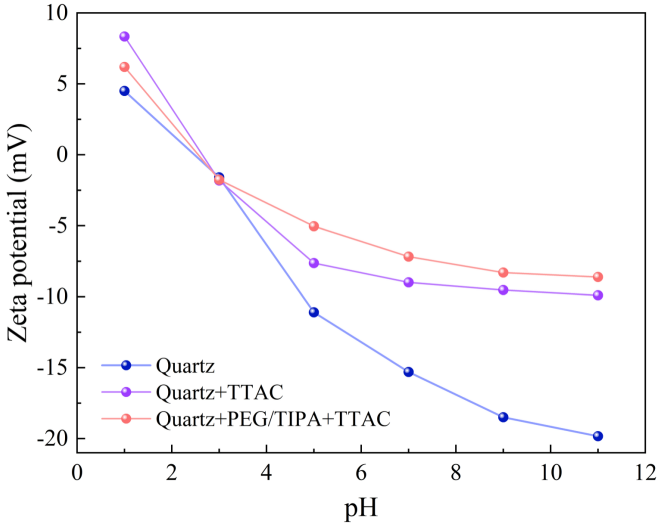


Fig. 13. Zeta potential map of a quartz surface

3.7. Mechanism of floatation enhancement by composite grinding aids

The proposed mechanism of PEG/TIPA-enhanced quartz flotation is illustrated in Fig. 14. During grinding, the PEG/TIPA composite grinding aid promotes crack initiation and propagation, enhances particle breakage, and increases the proportion of fine quartz particles within the favorable flotation size range. Simultaneously, PEG and TIPA interact with freshly generated quartz surfaces, modifying their interfacial chemical environment and suppressing fine-particle re-agglomeration. In the subsequent TTAC flotation stage, these newly generated and modified surface sites facilitate the

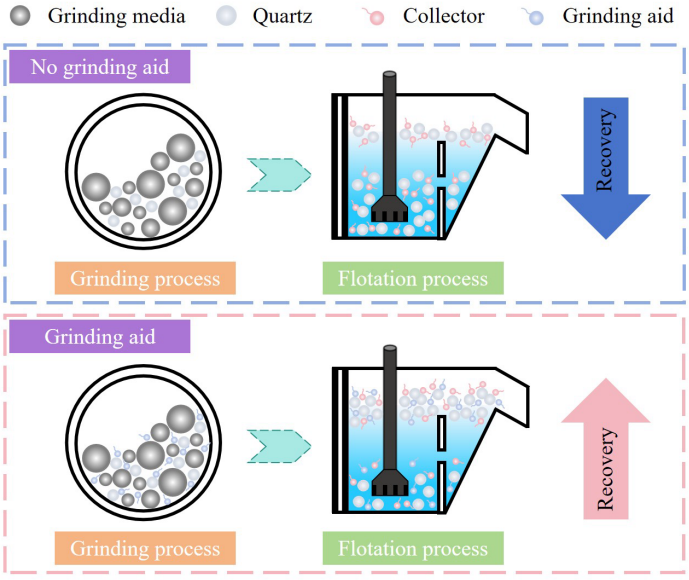


Fig. 14. Schematic diagram of the mechanism by which composite grinding aids enhance flotation behavior

interaction and adsorption of cationic TTAC species, promoting surface hydrophobicity and increasing the probability of particle-bubble attachment. The combined effects of enhanced particle breakage, improved dispersion, and favorable interfacial interactions ultimately lead to higher quartz flotation recovery. Thus, the synergistic regulation of particle size and surface properties by PEG/TIPA provides the principal basis for the enhanced flotation response of quartz.

4. Conclusions

The current work provides a systematic inquiry into the consequences of incorporating chemical additives into the quartz grinding circuit, with particular attention to their dual impact on particle breakage kinetics and flotation performance. The salient conclusions distilled from the experimental results are enumerated as follows.

(1) The present findings demonstrate that chemical grinding aids confer advantageous modifications to both the communition behavior and the flotation response of quartz. The binary PEG/TIPA additive system surpasses its single-component counterparts in efficacy. Maximal performance was realized at a composite concentration of 0.06% with a constituent mass ratio of 2:1, yielding an optimal fine particle fraction (sub-0.074 mm) of 86.09% and a peak flotation recovery of 94.17%.

(2) SEM analysis demonstrates that PEG and TIPA exhibit a synergistic influence on the quartz surface, facilitating the generation of abundant cracks and defects in particle fracture regions. Meanwhile, the composite grinding aid inhibits particle agglomeration, modifies surface characteristics, and weakens interparticle interactions, thereby improving the overall grinding performance.

(3) According to the FT-IR and XPS characterization results, the PEG/TIPA composite interacts with quartz surfaces through hydrogen bonding and electrostatic interactions, modifying their chemical and interfacial environments. These interactions facilitate subsequent adsorption of cationic TTAC through electrostatic attraction between quaternary ammonium groups and negatively charged quartz sites. The exposed hydrophobic alkyl chains promote quartz surface hydrophobization, while PEG/TIPA suppresses fine-particle re-agglomeration, thereby enhancing particle – bubble attachment and quartz flotation recovery.

(4) The zeta potential measurement results confirm that the -OH groups in the grinding solution become ionized, causing the quartz surface to become negatively charged. Consequently, the positively charged $[NR_4]^+$ species of TTAC can be effectively attached to the quartz interface through electrostatic attraction. Moreover, the incorporation of the grinding aid induces a further positive displacement of the quartz zeta potential, which facilitates the adsorption of TTAC molecules on the mineral surface.

Acknowledgments

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