Physicochem. Probl. Miner. Process., 61(5), 2025, 211353 | Physicochemical Problems of Mineral Processing

http://www.journalssystem.com/ppmp | ISSN 1643-1049

Ultrasound-assisted shear flocculation of quartz tailings with dodecylamine hydrochloride (DAH)

Can Gungoren [1], Mine Maide Vay [1], Ismail Demir [1], Mert Terzi [1], Ilgin Kursun [1], Orhan Ozdemir [2]

[1] Istanbul University-Cerrahpasa, Engineering Faculty, Mining Engineering Department, 34500, Buyukcekmece, Istanbul, Türkiye

[2] Istanbul Technical University, Faculty of Mines, Department of Mineral Processing Engineering, 34485, Sariyer, Istanbul, Türkiye

Corresponding authors: can@iuc.edu.tr (Can Gungoren), orhanozdemir@itu.edu.tr (Orhan Ozdemir)

Abstract: Ultrasound creates extreme conditions such as acoustic streaming and acoustic cavitation in the liquid it propagates, depending on its frequency. Due to these extreme conditions, it is beneficial in various operations in the mineral processing industry. This study aims to improve the efficiency of shear flocculation of quartz mineral in the presence of dodecylamine hydrochloride (DAH), a common collector for quartz, by ultrasound application. The outcomes of this study indicated that the interface height decreased by 18% with shear flocculation compared to free-settling conditions at the 3% (w/w) solids ratio in 120 min sedimentation time. Moreover, the interface height between the turbid and supernatant phases of the quartz pulp could be reduced considerably by 70.33% with conventional shear flocculation at the conditions of 3% solids ratio, 3 min conditioning time, 1×10^{-4} mol/dm^3 DAH concentration, and 1500 rpm mixing speed. Under these conditions, the turbidity of the supernatant was 377 NTU. This study also revealed that the interface height could be decreased by 80% by using ultrasound-assisted shear flocculation. However, in this case, the turbidity increased by 100-400% depending on the ultrasound power due to the dispersion effect of ultrasonic cavitation on ultrafine particles.

Keywords: amine, quartz, shear flocculation, solid-liquid separation, ultrasound

1. Introduction

The increase in raw material consumption creates a need to exploit finer and lower-grade ores, and flotation is the most commonly used method for the recovery of liberated particles below 200 µm (Kohmuench et al., 2018; Mankosa et al., 2018). In the mineral processing industry, the fine-sized tailings resulting from the flotation process are discharged into tailings dams containing significant amounts of water. And, the flocculation process is widely applied in the management of the tailings to reuse the process water and extend the life of the tailings dam (Demir et al., 2021). This process uses flocculants, which generally consist of long-chain polymeric structures (Forbes, 2011). Most commercial polymeric flocculants used in industry are based on polyacrylamides (PAM), and their molecular weight, charge, and dosage play a crucial role in the success of the flocculation process (Strandman et al., 2017; Gungoren et al., 2020; Moud, 2022; Slöetjes and Soares, 2025).

Meanwhile, another flocculation technique called shear flocculation uses surfactants, specifically flotation collectors, instead of polymers. This method is mainly based on the interaction between the repulsive force of the electrical double layer (EDL) around the particles and the hydrophobic interaction potential. In the presence of a sufficiently large EDL repulsive force, the particles will not be able to come close enough to each other to form flocs. Therefore, it is necessary to impart kinetic energy to the particles to overcome this potential barrier between them and provide particle collision, which is usually achieved in high shear conditions during high-speed mixing. If these particles become sufficiently hydrophobic through the adsorption of collector molecules on their surfaces, these hydrophobic

DOI: 10.37190/ppmp/211353

particles will bind to each other via the hydrophobic tails of the collector molecules, causing the particles to flocculate (Yin et al., 2011; Esmeli and Ozkan, 2023). For this reason, shear flocculation is also called hydrophobic flocculation, especially when hydrophobic minerals are studied (Song and Valdivieso, 1998; Song and Lu, 2000; Esmeli, 2024). Particle size, hydrophobicity, charge, and concentration of particles, type, and design of shear devices and impeller, shear rate, and flocculation time are among the important parameters that affect the results of the shear flocculation process (Warren, 1992; Spicer et al., 1996; Serra et al., 2008).

In the shear flocculation technique, it is possible to selectively agglomerate fine particles (0.5-10 μm) of a certain mineral using an adequate collector and mixing speed, while other mineral particles remain dispersed in the aqueous solution. In most applications, the aggregates formed by shear flocculation are generally strong enough to withstand the turbulences that occur in mineral processing operations. Even in some processes where larger and more robust flocs are required, the shear flocculation product can be re-flocculated in a two-stage shear flocculation process (Ucbeyiay and Ozkan, 2014; Yang et al., 2025).

As is known from the literature, the separation efficiency of ultrafine particles called slime is not at an acceptable level in many beneficiation processes. Meanwhile, the particles flocculated by shear flocculation provide the opportunity to work with larger flocs that can be separated from other minerals by selective flocculation. In addition, the hydrophobicity of the surfaces of the flocs formed in this way becomes hydrophobic thanks to the collector used, and if desired, they can be separated from other minerals that remain hydrophilic by the flocculation-flotation method. In a previous study, Ni et al. (2022) compared the flocculation-flotation kinetics of shear flocculation with the conventional flotation process for ultrafine microcrystalline graphite. As a result of this study, smaller-sized kerosene droplets were obtained by shear flocculation, and the hydrophobicity of graphite particles increased, thus allowing the formation of larger graphite aggregates, and consequently, the efficiency of the flocculation-flotation process increased.

Ultrasound application is one of the methods used to improve mineral processing operations in the presence of fine particles at a certain stage appropriate to the nature of the process. Ultrasound is a sound wave with a frequency above 20 kHz, beyond the perception capability of humans (Gungoren et al., 2024). When ultrasound travels in the form of rarefaction and compression waves in a liquid medium, it creates two effects called acoustic streaming and cavitation, depending on its frequency. The dominant mechanism at high ultrasound frequencies (>100 Hz) is acoustic streaming (Ambedkar et al., 2011). Acoustic streaming is the phenomenon where the liquid flows due to the pressure waves of the ultrasound. As the ultrasound frequency decreases (<100 Hz), cavitation occurs in addition to acoustic streaming. During the propagation of ultrasound, the liquid molecules move away from each other and approach each other in the rarefaction and compression phases, respectively. If the negative pressure during the rarefaction phase is strong enough, the liquid molecules are separated from each other, and the gases dissolved in the liquid fill the resulting space, forming a cavitation bubble that is squeezed during the compression phase and may burst immediately. However, most of the time, the surface area of the bubble is larger in the rarefaction phase than in the compression phase; therefore, the gas that enters the bubble is greater than the gas that comes out, and the bubble grows for several cycles before bursting (Chen et al., 2020).

During the bursting of cavitation bubbles, very high temperatures (5000 K) and pressure values (1000 atm) are reached locally (Suslick et al., 1999). However, since these hot spots are very small and short-lived compared to the bulk phase of the liquid, the released temperatures dissipate in a very short time. Furthermore, since the adhesion force of the liquid around a solid decrease, cavitation bubbles form more easily in the presence of a solid particle in the system. When bubbles burst near a solid particle, the liquid pressure around the bubble is disrupted, and a high-speed liquid jet is formed, moving towards the solid (Suslick, 1989).

Thanks to the extreme conditions ultrasound creates, it has been used in various operations of mineral processing, including solid-liquid separation. In flotation and flocculation, ultrasound is useful in stages such as the cleaning of particle surfaces, emulsifying and dispersing the reagent molecules in the pulp, increasing the activity of surfactant molecules, and spreading them more homogeneously on the particle surface (Gungoren et al., 2019; Esmeli, 2024). Therefore, ultrasound treatment can change the adsorption of surfactant molecules on particle surfaces and, hence, particle hydrophobicity, which can lead to shear flocculation. As a result, the process efficiency and product quality can be improved with the application of ultrasound by increasing the solids ratio of the dense phase in the pulp and reducing the turbidity of the clean phase.

While quartz is a mineral beneficiated by flotation and whose flotation behavior with cationic collectors such as DAH is well-established, studies on shear flocculation of quartz with DAH are extremely scarce. In this context, this study aimed to investigate the shear flocculation behavior of fine-sized (-38 µm) quartz tailings found as gangue material in many ores. To the authors' knowledge, this is the first study to investigate the effect of ultrasound on the shear flocculation of quartz with DAH. Therefore, the selection of quartz as a mineral and DAH as a surfactant in this study is to investigate the shear flocculation process by utilizing the well-known relationship between these two factors in flotation, allowing us to better define the effects of ultrasound. Furthermore, because quartz is present as a gangue mineral in many ores, the results of this study have a broader impact. The use of hydrodynamic shear forces generated by ultrasound in shear flocculation, either as a substitute for or in addition to high-energy mechanical mixing, can provide energy efficiency. Using surfactants instead of polymers and producing concentrates and tailings with lower water content will contribute to technical, economic, and environmental sustainability.

For this purpose, several experimental studies based on various flocculation parameters, including the solids ratio, conditioning time, collector concentration, and mixing speed, were carried out in the presence of dodecylamine hydrochloride (DAH), which is a widely used collector for quartz. Furthermore, the effect of ultrasound was revealed by applying ultrasound with an ultrasonic probe at different stages of the shear flocculation process at various ultrasound power levels and application times.

2. Materials and methods

2.1. Materials

The quartz tailing sample used in this study was obtained from a quartz processing plant located in Istanbul, Türkiye. Chemical analysis of the sample was carried out by the X-ray fluorescence (XRF) (Perform'X, Thermo Scientific, USA), and mineralogical analysis was conducted by the X-ray diffraction (XRD) (D/Max-2200, Rigaku, Japan) techniques. The results of the XRF and XRD of the sample are presented and shown in Table 1 and Fig. 1, respectively.

Table 1. Chemical composition of the quartz tailing sample (%)

Compounds	SiO_2	Al_2O_3	K_2O	Fe_2O_3	TiO_2	Na_2O	MgO	LOI*
Content (%)	85.9	9.1	1.7	0.5	0.4	0.2	0.2	1.6

*LOI: Loss on ignition

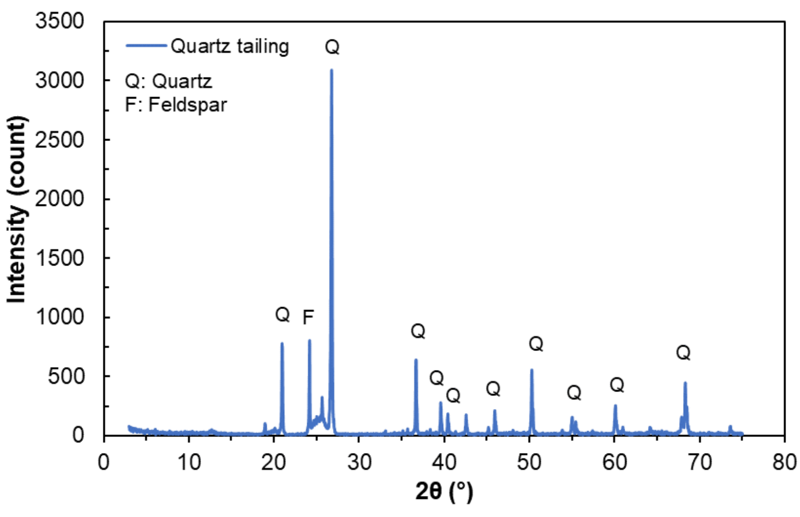

Fig. 1. The XRD spectrum of the sample

As presented in Table 1, the quartz content of the sample is 85.9%. And, the contents of other major oxides not shown in the table are each below 0.1%. The XRD results shown in Fig. 1 also indicated that the main mineral of the sample was quartz. Meanwhile, a peak of feldspar, which is the source of the K and Na content seen in the chemical analysis, is also present in the XRD spectrum of the sample.

The particle size distribution of the sample was measured with a particle size analyzer (Mastersizer 2000, Malvern, UK), and the results are given in Fig. 2. The frequency and cumulative undersize curves given in Fig. 2 show that the particles in the sample were mostly between 6 and 26 µm. Additionally, the d_{50} and d_{80} sizes of the samples were determined as 11 and 26 µm, respectively.

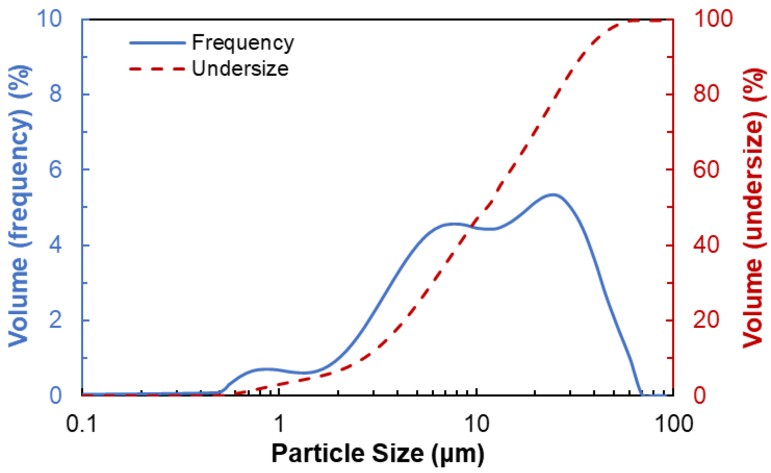

Fig. 2. Particle size distribution of the sample

Analytical dodecylamine hydrochloride (DAH) (98% $CH_3(CH_2)_{11}NH_2 \cdot HCl$, TCI, Japan) was used as a surfactant (collector) in the experiments. Collector solutions were prepared at room temperature (23±1°C) using pure water with a total dissolved solid (TDS) content below 3 ppm (~5 µS/cm).

2.2. Methods

2.2.1. Shear flocculation experiments

Shear flocculation experiments were carried out using 100 cm^3 aqueous quartz suspensions. The shear flocculation methods applied in this study are shown in Fig. 3. The parameter levels used in this study were determined by using the literature. From the results obtained in the study conducted by Gungoren et al. (2019), it is known that the flotation recovery of quartz in the presence of 1×10^{-5}–1×10^{-4} mol/dm^3 DAH varies between 22% and 96%. Meanwhile, amine can exhibit flocculation properties between 100 and 2000 rpm (Akdemir, 1997). However, since relatively high mixing speeds are required in shear flocculation, a mixing speed of 1000–2000 rpm was applied in this study (Nogueira, 2023). According to previous studies, 30-150 W ultrasound power, 0-5 min ultrasonic application time, and 0-5 min mechanical condition time are reasonable parameter levels (Esmeli and Ozkan, 2023; Ozkan and Esmeli, 2023). Shear flocculation experiments were carried out at lower solids ratios as reported in the literature (Ucbeyiay and Ozkan, 2014).

In laboratory studies, sedimentation experiments are often performed at relatively low solids ratios (~ 5%) to study the sample sedimentation and understand the fundamental mechanisms governing the settling behaviour of particles and the initial formation of flocs. Under such dilute conditions, the system is generally in the free-settling regime in which particle–particle interactions are minimal. On the contrary, high solids ratios (commonly ≥15%) are preferred in flocculation processes for industrial applications such as thickeners and clarifiers. At such a higher solids ratio, hindered and compressive settling regimes dominate the system, causing significant floc compaction, particle–particle interactions, and sludge bed formation. Therefore, laboratory studies at low solids ratios provide fundamental aspects that are a valuable starting point for understanding the physics and chemistry of the settling process. For this reason, the results obtained from these studies should not be considered as direct industrial applications, but should be carefully confirmed at pilot-scale tests to optimize the performance of large-scale sedimentation processes. In short, although high solids ratios are preferred in flocculation processes in industrial applications (Nogueira et al., 2023), in this study, shear flocculation experiments were carried out at lower solids ratios with the help of ultrasound.

In conventional shear flocculation experiments, the conditioning process was carried out through an overhead stirrer (RW20, IKA, Germany). Immediately after the conditioning process, the suspension was transferred to a graduated cylinder to measure the interface height in the flocculation stage as a function of time (Figure 3a). At the end of the flocculation stage, a sample was taken from the clear phase (supernatant) of the suspension with a Pasteur pipette, and its turbidity was measured using an optical turbidimeter (AQUAfast II, Thermo Scientific, USA). The experiments were carried out two or three times, considering the experimental conditions. The average errors of the interface height and turbidity measurements were below ±5% and ±4%, respectively.

The effect of ultrasound on shear flocculation was investigated by experiments in which ultrasonic conditioning was carried out in the absence and presence of mechanical mixing (Figs. 3b and 3c). The applied shear flocculation parameters are given in Table 2.

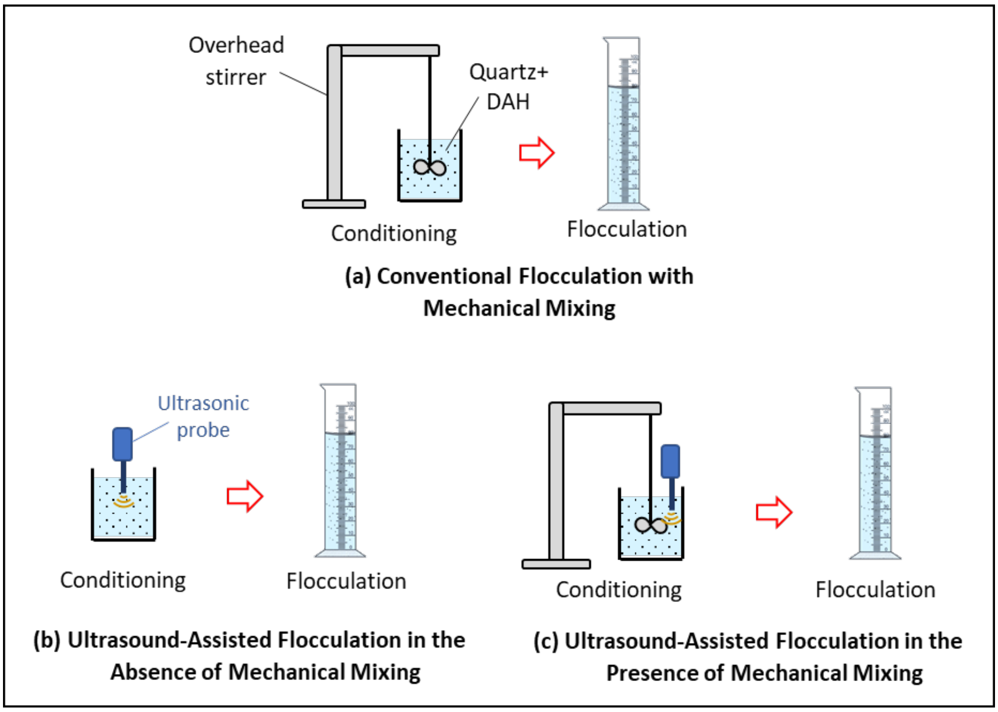

Fig. 3. Applied shear flocculation methods

Table 2. Applied shear flocculation parameters

Parameter	Level
Solids ratio (%) (w/w)	1, 3, and 5
Conditioning time (min)	0.5, 1, 3, and 5
DAH concentration (mol/dm^3)	1×10^{-5}, 5×10^{-5}, 1×10^{-4}, and 5×10^{-4}
Mixing speed (rpm)	1000, 1500, and 2000
Ultrasound power level (W)	30, 90, and 150
Ultrasound conditioning time (s)	15, 30, and 300

3. Results and discussion

3.1. Conventional shear flocculation experiments

In this study, the flocculation results were evaluated based on the interface height between the turbid and supernatant phases and the turbidity of the supernatant. First, the effect of the solids ratio on flocculation was investigated under free-settling conditions in the absence of a collector (DAH), and the results are given in Fig. 4.

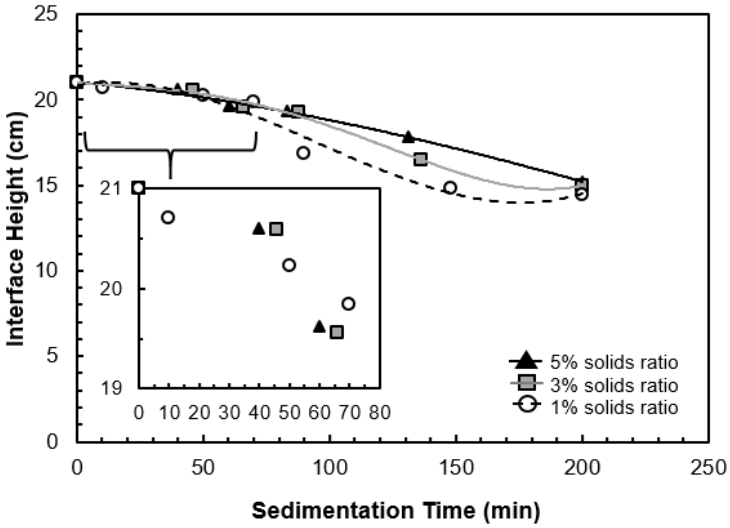

Fig. 4. Free-settling results in the absence of DAH (3 min conditioning time, 1000 rpm mixing speed)

As seen in Fig. 4, the quartz tailing sample did not settle effectively under free-settling conditions. In 200 min, the height of the interface decreased from the initial suspension height of 21.0 cm to ~15.0 cm. Since there were fewer particles per unit volume at lower solids ratios, slightly lower interface heights were obtained at the same sedimentation times as the solids ratio decreased. From the experimental data, it can be estimated that more time is required for particles to settle at higher solids ratios due to the hindered settling conditions.

Since there were no significant differences in the flocculation behavior of the sample as a function of solids concentration, as seen in Fig. 4, further experiments were carried out with the suspensions at a 3% solids ratio to investigate the effect of shear flocculation on the quartz in the presence of the collector of DAH. The comparison of the free-settling and shear flocculation results is given in Fig. 5. As seen in Figure 5, the particles settled down better in the case of shear flocculation compared to the free-settling at a 3% solids ratio. For instance, the interface height at 200 min sedimentation time was 12.5 cm, which was slightly lower than that obtained under free-settling conditions.

The results for conventional shear flocculation at various conditioning times are given in Fig. 6. The high interface heights at 0.5 min seen in Fig. 6 indicate that this conditioning time was not sufficient for the adsorption of DAH molecules onto quartz particles. The flocculation was slightly improved when

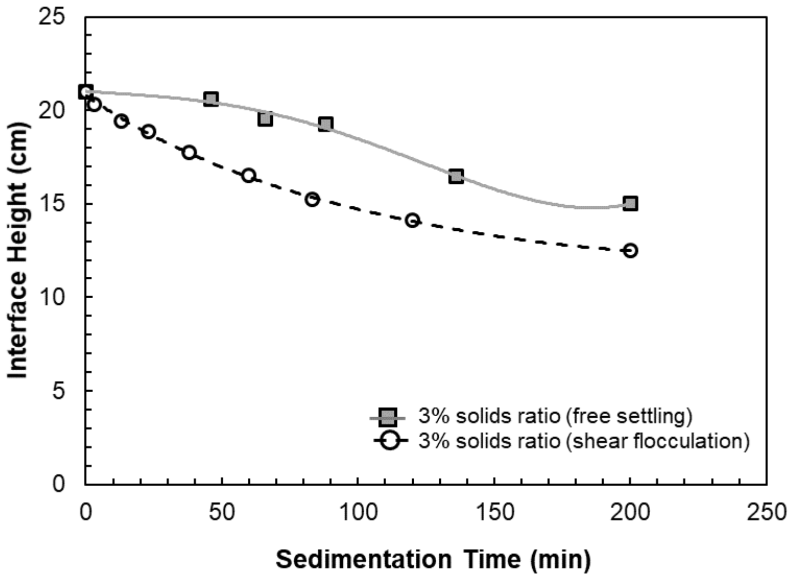

Fig. 5. Conventional shear flocculation results at various solids ratios (1×10^{-4} mol/dm^3 DAH concentration, 3 min conditioning time, 1000 rpm mixing speed)

the conditioning time was increased to 3 min. Under this condition, the interface height at 60 min was 16.5 cm. However, when the conditioning time was increased to 5 min, sedimentation was negatively affected because of the breakage of the formed flocs during the prolonged mixing time. The increase in the turbidity values from 375 to 963 NTU at 5 min conditioning time supports this opinion. Therefore, the further experiments were carried out at 3 min conditioning time.

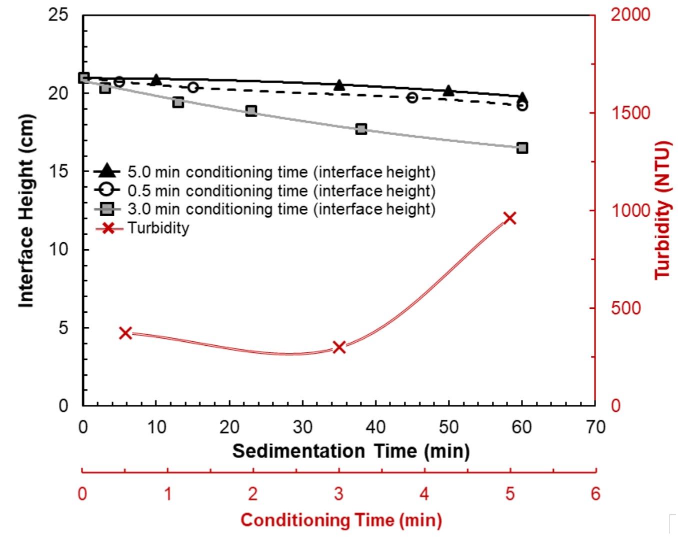

Fig. 6. Conventional shear flocculation results at various conditioning times (3% solids ratio, 1×10-4 mol/dm3 DAH concentration, 1000 rpm mixing speed)

The results for conventional shear flocculation at various DAH concentrations are given in Fig. 7. As seen from the high interface height values in Fig. 7, 5×10-5 mol/dm3 DAH concentration was not sufficient to flocculate the particles. When the DAH concentration increased to 1×10-4 mol/dm3, the interface height decreased to 14.1 cm at 120 min sedimentation time. Furthermore, at 5×10-4 mol/dm3 DAH concentration, the interface height reached a plateau of 6.6 cm in approximately 2 min of sedimentation time. Meanwhile, the turbidity of the supernatant, which was 1305 NTU at 5×10-5 mol/dm3 DAH, decreased considerably and reached a plateau at 220 NTU in the presence of 1×10-4 mol/dm3 DAH. From the results in Fig. 7, it is predicted that slightly lower interface height and turbidity values can be obtained by further increasing the DAH concentration. In light of these results, further experiments were carried out at 1×10-4 mol/dm3 DAH concentration to investigate the possible positive or negative effects of the investigated parameters.

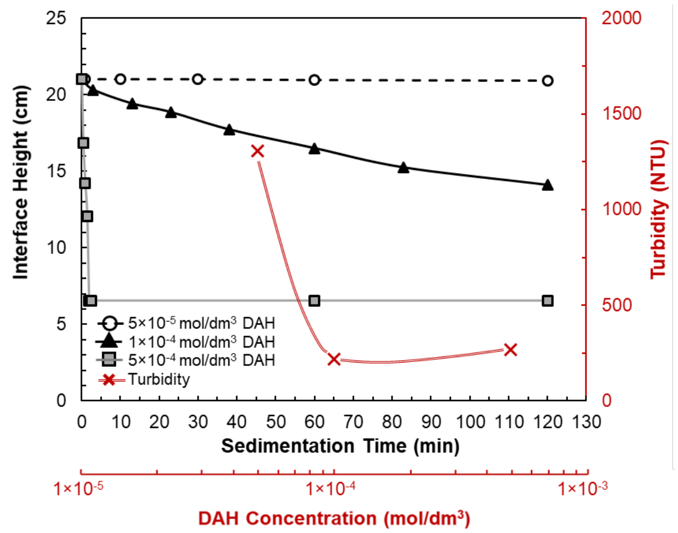

Fig. 7. Conventional shear flocculation results at various DAH concentrations (3% solids ratio, 3 min conditioning time, 1000 rpm mixing speed)

The results for shear flocculation at various mixing speeds are given in Fig. 8. As seen in Fig. 8, the interface height obtained at 1000 rpm mixing speed was higher than at excessive mixing speeds, and the sedimentation continued at the end of 120 min sedimentation time. On the other hand, in the presence of 1500 and 2000 rpm mixing speeds, the interface height reached a plateau of about 7.0 cm in ~2.5 min of sedimentation time. The reason for the improved flocculation at higher mixing speeds was the defeat of the electrostatic repulsion force between the particles more easily at high shearing forces; therefore, the particles could collide more easily. Consequently, larger flocs could be formed, and sedimentation accelerated. Meanwhile, it is also seen in Fig. 8 that the lowest turbidity value of 220 NTU was reached at 1000 rpm mixing speed. Supernatants became more turbid at excessive mixing speeds as it took longer for fine particles to settle.

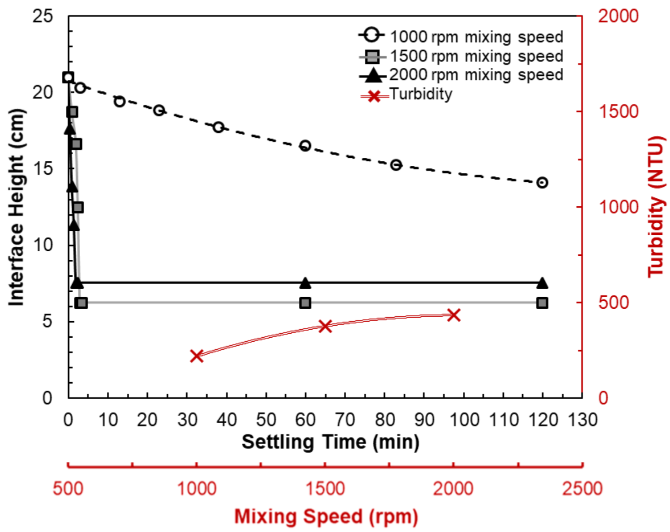

Fig. 8. Conventional shear flocculation results at various mixing speeds (3% solids ratio, 3 min conditioning time, 1×10^{-4} mol/dm^3 DAH concentration)

3.2. Ultrasound-assisted shear flocculation experiments

The effect of ultrasound on shear flocculation was investigated by experiments in which conditioning was carried out with ultrasound application alone and in which ultrasound was used in addition to mechanical mixing.

The results for the ultrasound-assisted shear flocculation experiments without mechanical mixing at various ultrasound power levels are given in Fig. 9. As seen in Fig. 9, lower interface heights were obtained as the ultrasound power increased in the conditioning stage. While the interface height was 7.6 cm in 6 min at 30 W ultrasound power, this value became 4.4 cm in 4 min at 150 W ultrasound power. Furthermore, the turbidity values in Fig. 9 indicate that the lowest turbidity value of 314 NTU was obtained at 30 W ultrasound power. When the ultrasound power increased to 90 W, the turbidity increased to 482 NTU. The increase in turbidity was due to the increase in cavitation as the ultrasound power increased, and thus the ultra-fine particles coated on the particle surfaces were detached and remained suspended in the suspension. The slight decrease in turbidity observed in the presence of 150 W was due to the improvement of flocculation with the increase in shear force.

The results for the ultrasound-assisted shear flocculation in the presence of mechanical mixing at various ultrasound power levels are given in Fig. 10. As seen in Fig. 10, lower interface heights were obtained at lower ultrasound power levels. While the interface height reached 13.0 cm in 20 min at 150 W ultrasound power, this value decreased to 4.2 cm in 8 min at 30 W. Fig. 10 indicates that the turbidity of the supernatant, which was 811 NTU at 30 W, increased considerably with ultrasound power and reached 1447 NTU at 150 W as a result of the breakage of the aggregates and dispersion of the particles.

Comparing the results in Fig. 9 and Fig. 10, it is seen that the effect of ultrasound power on the sedimentation distance is completely reversed in the presence of mechanical mixing. In the absence of mechanical mixing, the only effective force in the medium was ultrasonic cavitation and acoustic streaming. In other words, the shear force required for surfactant adsorption on the particle and the

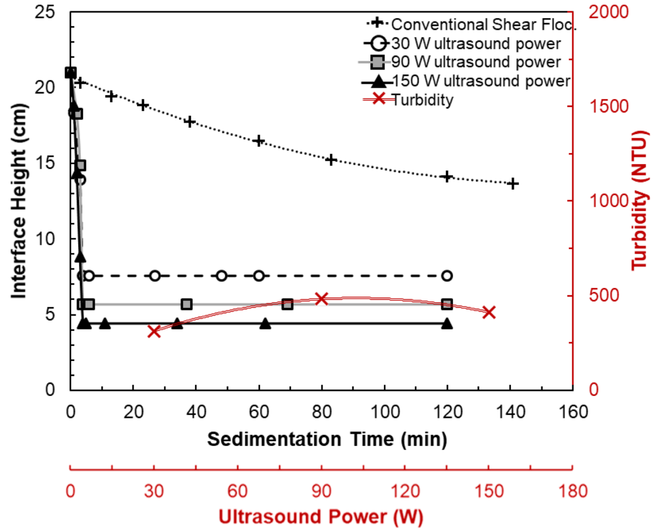

Fig. 9. Ultrasound-assisted shear flocculation results in the absence of mechanical mixing at various ultrasound power levels (3% solids ratio, 3 min conditioning time, 1×10^{-4} mol/dm^3 DAH concentration)

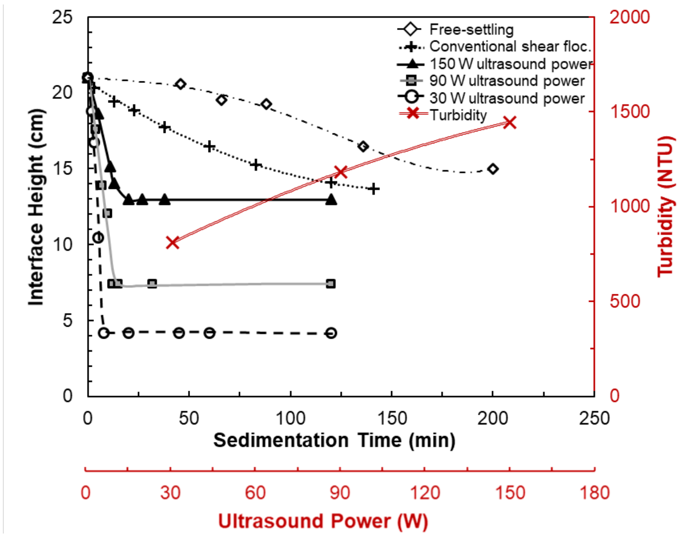

Fig. 10. Ultrasound-assisted shear flocculation results in the presence of mechanical mixing at various ultrasound power levels (3% solids ratio, 3 min conditioning time, 1×10^{-4} mol/dm^3 DAH concentration, 1000 rpm mixing speed)

collision of the particles (floc formation) was created only by ultrasound. Therefore, it is natural that flocculation was improved with the power of ultrasound, which increased the shear forces. On the other hand, in the presence of mechanical mixing, the generation of shear forces could already be provided by mechanical mixing. In this case, the use of ultrasound at excessive power levels increased the turbulence in the medium, making the floc formation difficult and causing the flocs formed to break apart. For this reason, flocculation was negatively affected in terms of both sedimentation and turbidity.

The results for the ultrasound-assisted shear flocculation at various conditioning times in the presence of mechanical mixing are given in Fig. 11. As seen in Fig. 11, lower interface heights could be achieved as the conditioning time increased. While the interface height reached 14.4 cm in 16 min sedimentation time for 15 s conditioning time, this value became 4.2 cm in 8 min sedimentation time for 180 s conditioning time. The turbidity results in Fig. 11 show that the turbidity value was measured as 1089 NTU because the 15 s conditioning time was not sufficient for effective sedimentation. With an increase in the conditioning time to 30 s, the surfactant adsorption on the particle surfaces and the floc formation due to shearing increased, and the turbidity decreased to 599 NTU. However, as a result of the disintegration of the flocs formed at excessive mixing times, the turbidity value increased to 811 NTU at 180 s conditioning time.

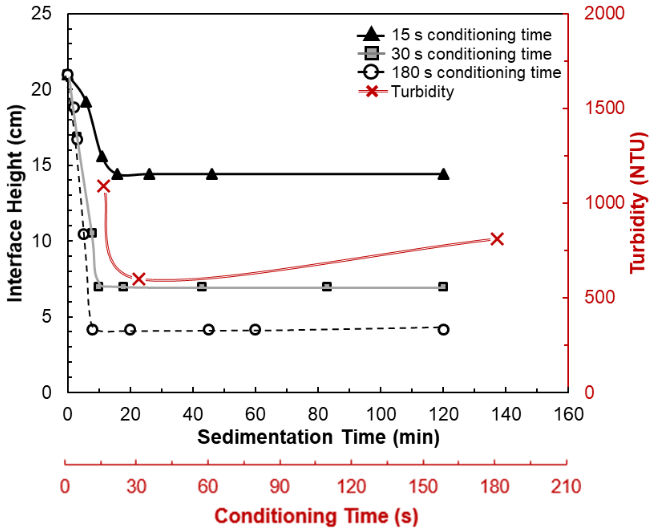

Fig. 11. Ultrasound-assisted shear flocculation results in the presence of mechanical mixing at various conditioning times (3% solids ratio, 1×10^{-4} mol/dm^3 DAH concentration, 1000 rpm mixing speed, 30 W ultrasound power)

3.3. General discussion

Since no previous work was on the effect of ultrasound on shear flocculation, the results of this study are discussed under this section in a general aspect. As it is known from the literature, there is a strong relationship between the shear flocculation efficiency and the hydrophobicity of the particles. In a previous study, Akdemir (1997) reported that the shear flocculation efficiency of hematite particles increased with the hydrophobicity of the particles determined by contact angle measurements. Similarly, Duzyol and Ozkan (2010) stated that higher degrees of hydrophobicity and surface tension levels were required to reach high aggregation efficiencies in the oil agglomeration of magnesite fines. In addition, the results of Nogueira et al. (2023) showed that particle hydrophobicity was the most effective parameter in the process of shear flocculation. Similarly, the most successful flocculation results of the present study were obtained at the highest DAH concentration of 5×10^{-4} mol/dm^3 due to the increased hydrophobicity, and hence the easier flocculation of highly hydrophobic particles.

Mixing speed is another important parameter affecting the shear flocculation results. Song and Lu (2000) reported that the maximum degree of aggregation occurred at 1000 rpm mixing speed and decreased at higher mixing speeds due to the possible breakage of the aggregates and the strong shear forces. This effect was also observed in the shear flocculation of coal particles by Ofori et al. (2011). Patil et al. (2001) studied the mathematical model of the shear flocculation and reported that the flocculation rate decreased with increasing shear speed and the breakage rate is proportional to the ~0.70 power of floc volume. Meanwhile, Serra et al. (2008) reported that aggregation was greater than breakup at low mixing speeds (<20 s^{-1}). At medium mixing speeds (20-30 s^{-1}), flocculation rate and floc size are maximized. At high shear rates (>30 s^{-1}), the formed flocs begin to break up. Additionally, Ucbeyiay Sahinkaya and Ozkan (2011) investigated the shear flocculation of colemanite in the presence of the anionic surfactants of sodium oleate (NaOL) and sodium dodecyl sulfate (SDS). Their result indicated that mixing speeds lower than 500 rpm were not sufficient for adequate particle collision, while higher mixing speeds caused particle breakage. Meanwhile, in the present study, the shear flocculation of the quartz particles was not at the desired level at a lower mixing speed of 1000 rpm. However, when the mixing speed was increased to 1500 and 2000 rpm, the shear flocculation was enhanced.

In the literature, several positive effects of ultrasound on shear flocculation were reported by researchers working in this field. For example, Ozkan and Esmeli (2022) investigated the effect of ultrasound on the shear flocculation of colemanite mineral and stated that ultrasound application increased the collector adsorption on colemanite particles; and therefore, increased the contact angle of the particles. This increase in particle hydrophobicity resulted in increased flocculation efficiency. They also reported that the low collision probability of the ultrafine particles can be enhanced by ultrasound application. In another study focusing on the improvement of shear flocculation of galena by ultrasound application in the presence of xanthates, it was reported that the shear flocculation was improved by ultrasound at high ultrasound power (150 W) by promoting the adsorption of surfactant molecules onto the galena surfaces (Esmeli and Ozkan, 2023). Furthermore, it was reported by Esmeli (2024) that tiny (micro/nano) bubbles formed by cavitation were able to improve the bubble-particle attachment by forming a bridge between the mineral surface and the collector molecules. This phenomenon has also been observed in the presence of quartz and amine systems (Calgaroto et al., 2015; Nazari et al., 2018). It has also been reported by Zhu et al. (2020) that low-frequency ultrasound (20 kHz) could break the polymer flocculant chains into shorter chains, hence promoting the compaction of tailings and the release of water. Additionally, high-speed collisions of particles in the presence of ultrasound can cause overheating at the collision point, resulting in melting and agglomerate formation (Suslick, 1989; Prozorov et al., 2004).

Recent studies in the literature have indicated that the functionality of ultrasound in shear flocculation depends on application conditions. For example, Biggs and Lant (2000) reported that the ultrasound application disrupted flocs due to the cavitation effect. Similarly, the results of Sauter et al. (2008) showed that quartz particles were de-agglomerated with ultrasound application. Ultrasound enhances the dispersion of particles and inhibits agglomeration, specifically for large-sized agglomerate particles. In a study on the flocculation of borate tailings in the presence of ultrasound, Demir et al. (2021) mentioned that the use of ultrasound negatively affected the settling rate of particles, mostly because it caused the flocs to break. However, lower sediment bed heights were obtained with ultrasound application. Ozkan and Esmeli (2023) investigated the effect of ultrasound on the shear flocculation of celestite. They reported that low duration (2 min) and high power (150 W) ultrasound application in the absence of chemicals caused coagulation by decreasing the zeta potential of the celestite mineral particles. When ultrasound was applied as a pre-treatment in the presence of a collector, it was also beneficial to the flocculation process by decreasing the zeta potential of the mineral and increasing its contact angle. However, when ultrasound was applied during the flocculation stage, the aggregation of celestite particles was negatively affected. They stated that the effective mechanism of ultrasound might be that the tiny bubbles formed by cavitation attached to particle surfaces, increasing their hydrophobicity, thus facilitating the hydrophobic aggregation of the particles. Cavitation bubbles act as a bridge between the hydrocarbon chains of the collector molecules adsorbed on the particle surfaces during collisions, facilitating the adherence of collector molecules to each other from their hydrocarbon chains. This eased the formation and growth of the flocs, which increased the shear flocculation efficiency. However, an excessive increase in the number of these air-filled cavitation bubbles might cause a decrease in the total density of the aggregate, which has the potential to reduce the settling rate of the formed flocs. Therefore, the application of ultrasound should be optimized for each flocculation process.

Furthermore, Esmeli (2023b) and Esmeli (2023c) studied the improvement of coal flocculation by the application of ultrasound and reported that the flocculation could be enhanced by using ultrasound as a pre-treatment by reducing the magnitude of the zeta potential of coal with anionic polymer. However, the results also showed that flocculation did not occur when the ultrasound alone was used in the flocculation process. The author emphasized that the power level and application time of ultrasound are important parameters affecting the success of the flocculation and need to be optimized. In another study, the oil agglomeration of barite was enhanced using ultrasound. The results showed that the ultrasound as a pre-treatment caused a decrease in the reagent (oleate and kerosene) consumption. However, the use of ultrasound at the agglomeration stage affected the process negatively (Esmeli, 2023a). Similar results were obtained in the ultrasound-assisted hydrophobic flocculation of coal in the presence of kerosene by Esmeli (2024).

Meanwhile, the results of the ultrasound-assisted experiments of the present study indicated that when the shear force required for the surfactant adsorption and the particle collision was provided only with ultrasound in the absence of mechanical mixing, flocculation was improved with the power of ultrasound, which increased the shear forces. On the other hand, since the required shear forces for these sub-processes were provided by mechanical mixing, an increase in the power level of the simultaneous ultrasound application made the floc formation difficult because of the increased turbulence of the medium at high shear conditions.

4. Conclusions

In this study, the effect of various flocculation parameters, such as solids ratio, conditioning time, collector concentration, and mixing speed, on the shear flocculation of the fine-sized (-38 μm) quartz tailings was investigated in the presence of dodecylamine hydrochloride (DAH), a widely used collector for quartz. In addition, the influence of ultrasound on the shear flocculation efficiency was studied in terms of ultrasound power level and application time by applying ultrasound using an ultrasonic probe at the different stages of the shear flocculation process to benefit from its acoustic streaming and acoustic cavitation effects.

In conclusion, the results of this study indicated that the fine quartz particles that did not settle efficiently under free-settling conditions could be flocculated with shear flocculation. The interface height of the pulp at the 3% solids ratio reduced by 18% in 120 min sedimentation time with shear flocculation compared to free-settling conditions. In addition, the interface height decreased by 70.33% with conventional shear flocculation at the conditions of 3% solids ratio, 3 min conditioning time, 1×10^{-4} mol/dm^3 DAH concentration, and 1500 rpm mixing speed with 377 NTU supernatant turbidity.

When 30 W ultrasound was applied in addition to the mechanical mixing during the conditioning stage at the same solids ratio, conditioning time, DAH concentration, and 1000 rpm mixing speed, the interface height decreased by 80% in 8 min sedimentation time. Under these conditions, the turbidity of the supernatant was 811 NTU. If ultrasound was applied alone during the conditioning stage, much higher ultrasound power levels (>90 W) are required to obtain similar flocculation results.

As seen from the overall experimental results, solids ratio, conditioning time, collector concentration, and mixing speed are effective parameters on the shear flocculation of quartz. In addition, the application of ultrasound could be a beneficial supporting method depending on the power level, application stage, and time. Therefore, these effective parameters should be optimized with empirical investigations for a successful solid-liquid separation process.

It should also be noted that if the clarified water from the shear flocculation with DAH is returned to the flotation system, DAH molecules remaining in solution, even at relatively low concentrations, can adsorb onto quartz surfaces during pulp conditioning, thus increasing the overall hydrophobicity of the particles and significantly affecting the subsequent flotation performance. Therefore, while water recycling is important from an economic and environmental perspective, residual collector concentrations must be carefully monitored to prevent uncontrolled reagent addition and maintain optimal flotation performance. For this, it is necessary to control this effect by optimizing reagent dosages during the shear flocculation process, controlling recycled water, applying water treatment processes such as coagulation, activated carbon, etc., and most importantly, by continuously monitoring DAH to maintain flotation efficiency.

Acknowledgments

This study was supported by The Scientific and Technological Research Council of Türkiye (TUBITAK), grant number: 1919B012326653.

References

AKDEMIR, U., 1997. *Shear flocculation of fine hematite particles and correlation between flocculation, flotation and contact angle*. Powder. Technol. 94, 1-4.

AMBEDKAR, B., CHINTALA, T.N., NAGARAJAN, R., JAYANTI, S., 2011. *Feasibility of using ultrasound-assisted process for sulfur and ash removal from coal*. Chem. Eng. Process.: Process. Intensif. 50, 236-246.

BIGGS, C.A., LANT, P.A., 2000. *Activated sludge flocculation: On-line determination of floc size and the effect of shear*. Wat. Res. 34, 2542-2550.

CALGAROTO, S., AZEVEDO, A., RUBIO, J., 2015. *Flotation of quartz particles assisted by nanobubbles*. Int. J. Miner. Process. 137, 64-70.

CHEN, Y., TRUONG, V.N.T., BU, X., XIE, G., 2020. *A review of effects and applications of ultrasound in mineral flotation*. Ultrason. Sonochem. 60, 104739.

DEMIR, I., GUNGOREN, C., BAKTARHAN, Y., YUCEL, M., KURSUN, I., CINKU, K., OZKAN, S.G., 2021. *Ultrasound supported flocculation of borate tailings with differently charged flocculants*. J. Boron 6, 348 - 358.

DUZYOL, S., OZKAN, A., 2010. *Role of hydrophobicity and surface tension on shear flocculation and oil agglomeration of magnesite*. Sep. Purif. Technol. 72, 7-12.

ESMELI, K., 2023a. *The effect of ultrasound treatment on oil agglomeration of barite*. Miner. Process. Extr. Metall. Rev. 44, 189-200.

ESMELI, K., 2023b. *Improvement of lignite flocculation by ultrasound pre-treatment and performance optimization using Box-Behnken design*. Int. J. Coal Prep. Util. 43, 1335-1357.

ESMELI, K., 2023c. *Improvement of lignite oil agglomeration by ultrasound process using waste engine oil*. Part. Sci. Technol. 41, 544-554.

ESMELI, K., 2024. *The influence of ultrasound treatment on the hydrophobic flocculation of lignite*. Int. J. Coal Prep. Util. 44, 1-18.

ESMELI, K., OZKAN, A., 2023. *Enhancement of shear flocculation of a galena suspension by ultrasonic treatment*. J. South Afr. Inst. Min. Metall. 123, 365-370.

FORBES, E., 2011. *Shear, selective and temperature responsive flocculation: A comparison of fine particle flotation techniques*. Int. J. Miner. Process. 99, 1-10.

GUNGOREN, C., KURSUN, I., OZDEMIR, O., 2020. *Investigation of flocculation properties and floc structure of coal processing plant tailings in the presence of monovalent and divalent ions*. Physicochem. Probl. Miner. Process. 56, 747-758.

GUNGOREN, C., OZDEMIR, O., WANG, X., OZKAN, S.G., MILLER, J.D., 2019. *Effect of ultrasound on bubble-particle interaction in quartz-amine flotation system*. Ultrason. Sonochem. 52, 446-454.

GUNGOREN, C., OZKAN, S.G., OZDEMIR, O., 2024. *Use of ultrasound in physical and chemical mineral processing operations*. Advances in Minerals Research. S. J. Ikhmayies. Switzerland, Springer Nature: 25-54.

KOHMUENCH, J.N., MANKOSA, M.J., THANASEKARAN, H., HOBERT, A., 2018. *Improving coarse particle flotation using the HydroFloat™ (raising the trunk of the elephant curve)*. Miner. Eng. 121, 137-145 https://doi.org/10.1016/j.mineng.2018.03.004.

MANKOSA, M.J., KOHMUENCH, J.N., CHRISTODOULOU, L., YAN, E.S., 2018. *Improving fine particle flotation using the StackCell™ (raising the tail of the elephant curve)*. Miner. Eng. 121, 83-89.

MOUD, A.A., 2022. *Polymer based flocculants: Review of water purification applications*. J. Water Process. Eng. 48, 102938.

NAZARI, S., SHAFAEI, S.Z., SHAHBAZI, B., CHEHREH CHELGANI, S., 2018. *Study relationships between flotation variables and recovery of coarse particles in the absence and presence of nanobubble*. Coll. Surf. A Physicochem. Eng. Asp. 559, 284-288.

NI, C., ZHANG, Q., JIN, M., XIE, G., PENG, Y., YU, H., BU, X., 2022. *Effect of high-speed shear flocculation on the flotation kinetics of ultrafine microcrystalline graphite*. Powder Technol. 396, 345-353.

NOGUEIRA, F., RODRIGUES, K., PEREIRA, C., SILVA, A.C., SILVA, E.M.S., AZIZI, A., HASSANZADEH, A., 2023. *Quartz fine particle processing: Hydrophobic aggregation by shear flocculation*. Minerals 13, 1208.

OFORI, P., NGUYEN, A.V., FIRTH, B., MCNALLY, C., OZDEMIR, O., 2011. *Shear-induced floc structure changes for enhanced dewatering of coal preparation plant tailings*. J. Chem. Eng. 172, 914-923.

OZKAN, A., ESMELI, K., 2022. *Improvement of colemanite flocculation with collectors by ultrasound treatment*. Particul. Sci. Technol., 1-9.

OZKAN, A., ESMELI, K., 2023. *Use of ultrasonic treatment as a pre-phase in the shear flocculation process*. Ultrasonics 134, 107052.

PATIL, D.P., ANDREWS, J.R.G., UHLHERR, P.H.T., 2001. *Shear flocculation—kinetics of floc coalescence and breakage*. Int. J. Miner. Process. 61, 171-188.

PROZOROV, T., PROZOROV, R., SUSLICK, K.S., 2004. *High velocity interparticle collisions driven by ultrasound*. J. Am. Chem. Soc. 126, 13890-13891.

SAUTER, C., EMIN, M.A., SCHUCHMANN, H.P., TAVMAN, S., 2008. *Influence of hydrostatic pressure and sound amplitude on the ultrasound induced dispersion and de-agglomeration of nanoparticles*. Ultrason. Sonochem. 15, 517-523 .

SERRA, T., COLOMER, J., LOGAN, B.E., 2008. *Efficiency of different shear devices on flocculation*. Water Res. 42, 1113-1121.

SLÖETJES, K., SOARES, J.B.P., 2025. *Controlling polymer addition flowrate to improve the flocculation of kaolinite suspensions as models for oil sands mature fine tailings*. Can. J. Chem. Eng., 1-17 https://doi.org/10.1002/cjce.25665.

SONG, S., LU, S., 2000. *Theory and applications of hydrophobic flocculation technology*. Developments in Mineral Processing. P. Massacci. 13**:** C5-31-C35-38.

SONG, S., VALDIVIESO, A.L., 1998. *Hydrophobic flocculation flotation for beneficiating fine coal and minerals*. Sep. Sci. Technol. 33, 1195-1212.

SPICER, P., KELLER, W., PRATSINS, S.E., 1996. *The effect of impeller type on floc size and structure during shear-induced flocculation*. J. Colloid Interface Sci. 184, 112-122.

STRANDMAN, S., VACHON, R., DINI, M., GIASSON, S., ZHU, X.X., 2017. *Polyacrylamides revisited: flocculation of kaolin suspensions and mature fine tailings*. Can. J. Chem. Eng. 96, 20-26.

SUSLICK, K.S., 1989. *The Chemical Effects of Ultrasound*. Sci. Am. 260, 80-87.

SUSLICK, K.S., DIDENKO, Y., FANG, M.M., HYEON, T., KOLBECK, K.J., MCNAMARA III, W.B., MDLELENI, M.M., WONG, M., 1999. *Acoustic cavitation and its chemical consequences*. Phil. Trans. R. Soc. Lond. A 357, 335-353.

UCBEYIAY, H., OZKAN, A., 2014. *Two-stage shear flocculation for enrichment of fine boron ore containing colemanite*. Sep. Purif. Technol. 132, 302-308.

UCBEYIAY SAHINKAYA, H., OZKAN, A., 2011. *Investigation of shear flocculation behaviors of colemanite with some anionic surfactants and inorganic salts*. Sep. Purif. Technol. 80, 131-139.

WARREN, L.J., 1992. *Shear flocculation*. Colloid chemistry in mineral processing. J. S. Laskowski and J. Ralston. New York, USA, Elsevier**:** 309–329.

YANG, Y., LIU, X., ZHANG, L., GUO, M., 2025. *Two-step shear flocculation for high-efficiency dewatering of ultra-fine tailings*. Minerals 15, 176.

YIN, W., YANG, X., ZHOU, D., LI, Y., LU, Z., 2011. *Shear hydrophobic flocculation and flotation of ultrafine Anshan hematite using sodium oleate*. Trans. Nonferrous. Met. Soc. China 21, 652-664.

ZHU, L., LYU, W., YANG, P., WANG, Z., 2020. *Effect of ultrasound on the flocculation-sedimentation and thickening of unclassified tailings*. Ultrason. Sonochem. 66, 104984.