

Review Article

A Brief Review of Pulp and Froth Rheology in Mineral Flotation

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In mineral flotation, rheological problems have limited the efficient upgrading of low-grade and complex ores. Since pulp and froth rheology are deemed to play different roles in influencing the separation performance, in this paper, a brief review on pulp and froth rheology in flotation is provided, with an objective of developing a basic understanding of rheology in flotation. The essential variables that affect the rheology of a flotation pulp and froth are discussed. The methods for measuring pulp and froth rheology are presented. The correlations of pulp and froth rheological properties to flotation performance are reviewed. Strategies that are currently used to mitigate the deleterious effects of problematic ores in flotation are also provided for flotation optimization. Research gaps are also proposed to highlight the need of further exploration of flotation rheology in future.

1. Introduction

Rheology is a science related to the deformation and flow of a material under applied stress, and it is widely applied to industrial, geological, and biological materials [1]. In mineral processing industries, it has witnessed a dramatic influence of the rheological behaviour of mineral particles in mineral slurry transportation, ore grinding, and mineral separation such as dewatering and flotation [2, 3]. In the past, investigations on the rheological effect of mineral particles mainly focused on slurry transportation and ore grinding [4]. As low-grade and complex ores such as clayey and fibrous ores in large quantities are being processed due to the depletion of high-grade ores (both metallic and nonmetallic) on a world scale, the fine/ultrafine grinding for the liberation of valuable minerals often leads to rheological difficulties and complexities in the subsequent separation process, namely, flotation [5, 6]. Thus, attention has been increasingly aroused as to the importance of flotation rheology.

Flotation is a useful technique for ore upgrading by exploiting differences in surface properties to separate valuable minerals from gangue, which is typically carried out in a flotation cell that contains both a pulp and froth zone

(see Figure 1). Flotation pulp and froth zone are well known to play different roles in determining flotation performance due to their different compositions and characteristics [8]. In the pulp zone, hydrophobic particles collide with air bubbles to form particle-bubble aggregates moving upwards against gravity to the froth zone while most hydrophilic gangue mineral particles report to the tailings. The froth zone further concentrates the collected particles by reducing the recovery of entrained gangue mineral particles to the concentrate stream, leading to an improved selectivity and recovery of the flotation process. In general, variations in flotation conditions could result in different rheological behaviours of mineral particles in the pulp and froth, thereby influencing the separation performance.

In the literature, Boger [9] has provided a review on the significance of rheology in mineral processing with detailed rheological behaviours of nonsettling mineral slurries and the relevant measuring methods. Farrokhpay [4] has reviewed the importance of rheology in mineral flotation with a focus on the correlation of flotation rheology to froth stability and flotation recovery. Cruz and Peng [10] and Cruz et al. [3] also offered reviews on flotation rheology particularly associated with rheology measurements of flotation

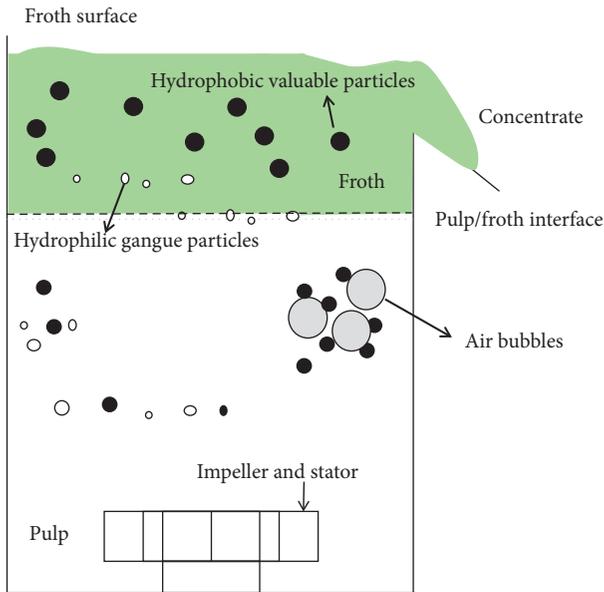


FIGURE 1: Processes of true flotation and entrainment in a flotation cell (after [7]).

pulps with a high clay content. In general, in mineral flotation, studies on flotation rheology have been detailed in many aspects including rheological effects on flotation response, influencing variables and rheological measurement techniques, in both the pulp and froth zone. In recent years, progress in flotation rheological investigations, especially the froth rheology, has been greatly advanced. However, no work is available yet that updates this progress to improve the understanding of rheology in mineral flotation.

In this paper, flotation pulp and froth rheology are reviewed in brief. The essential variables that affect flotation rheological behaviours, the techniques for rheology measurements, and the correlation of rheological characteristics to flotation performance are reviewed with respect to the pulp and the froth zone. Strategies that are currently attempted to mitigate the deleterious effects of problematic ores in flotation are also presented. Research gaps are also proposed to highlight the need of further exploration of flotation rheological effects in the future.

2. Rheology in Froth Flotation

The rheological behaviour of a material is often presented by a “flow curve” or “rheogram” obtained by plotting the shear stress against the shear rate obtained from a rheometer. Figure 2 shows five typical rheograms representing the Newtonian and the non-Newtonian behaviours including dilatant, plastic, pseudoplastic, and Bingham that a material could exhibit [11]. Yield stress and apparent viscosity are two important rheological parameters, of which the former represents the stress at which a material begins to deform plastically and the latter measures the resistance of a material to gradual deformation by shear stress. In flotation, mineral slurries made of good quality ores often display a Newtonian behaviour, whereas complex and low-grade ore slurries

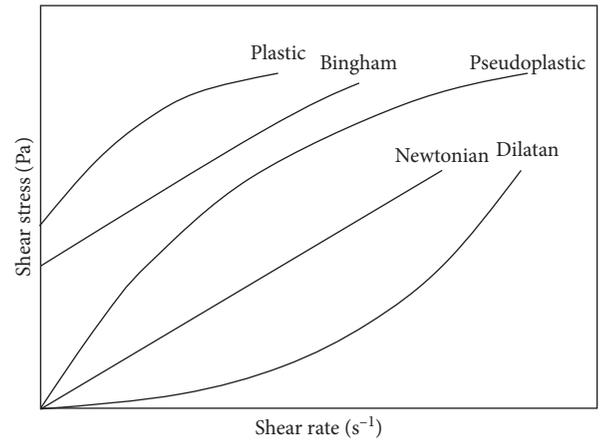


FIGURE 2: Flow curves or rheograms representing the rheological behaviour of different flow types (after [11]).

normally exhibit a pseudoplastic or Bingham behaviour [4]. Flotation froths, as indicated from the literature, exhibit pseudoplastic characteristics, similar to air-liquid foams [12–14].

The information regarding the rheological behaviour of flotation pulps and froths as exhibited in Figure 2 is usually incorporated in relationships between yield stress and viscosity using rheological models such as the Bingham, the Casson, and the Herschel–Bulkley model [15]. Among these models, the Herschel–Bulkley model is the most widely used one in flotation rheology characterisation, which is given as [15]

$$\tau = \tau_0 + K\dot{\gamma}^n, \quad (1)$$

where τ is the shear stress, τ_0 is the yield stress, $\dot{\gamma}$ represents the shear rate, and n and K are the parameters representing the flow index and consistency index, respectively. When flow index is lower than 1, the fluid material behaves as pseudoplastic or plastic flow; if flow index is greater than 1, the material is dilatant flow. When n is 1, the viscosity of the fluid material is constant, suggesting a Newtonian flow or Bingham flow. When the consistency index is high, the fluid material is more viscous.

3. Rheology of Flotation Pulp

3.1. Variables Affecting Pulp Rheology. The rheology of flotation pulp is a complex function of the physical properties of the continuous and discrete phases as well as of processes that occur at the scale of mineral particles. The principal factors affecting pulp rheology mainly include solids volume fraction, particle characteristics, and interaction between particles and its associated influencing variables such as shear rate and pulp chemistry. These influencing factors often combine to determine the rheological behaviour of flotation pulps.

3.1.1. Solids Volume Fraction. Solids volume fraction is one of the essential variables that dominate the rheology of mineral suspensions in mineral processing [16–18]. In

flotation, pulp apparent viscosity generally increases with increasing solid concentration of pulp slurries. Figure 3 shows the apparent viscosity of flotation samples with different solids concentrations obtained from processing two different platinum ores (UG2 ore and Great Dyke ore) [19]. Clearly, pulp solid concentration significantly affects the slurry rheological behaviour. And this effect of solid concentration on the pulp apparent viscosity has been widely attributed to the significant energy dissipation resulting from the friction between particles [15, 20].

In most flotation pulps, a low solid concentration is generally used. The more dilute the pulp, the cleaner the separation [21]. As can be seen in Figure 3, when the UG2 and Great Dyke feed solid concentration exceeds 25 vol.%, a discernible increase in the apparent viscosity of the feed samples could be detected, which would result in rheological complexities in the separation process. In mineral flotation, it has been reported that pulp solid concentration generally falls at 5–40 wt.% (11–20 vol.%), with an upper-bound concentration of about 50 wt.% (approximately 27 vol.%) [21, 22]. In this case, flotation pulps with good-quality ores are Newtonian or very close to Newtonian with a low viscosity, but those made of low-grade and complex ores are typically non-Newtonian exhibiting a pseudoplastic or Bingham behaviour, which could cause deleterious rheological effect on flotation, as evidenced in a number of studies [6, 23–25].

3.1.2. Particle Characteristics. Flotation is often employed to float mineral particles with certain size, depending on the floatability of the particles within relevant limits of flotation conditions [26]. Particle size is well known to significantly affect the pulp rheological behaviour, and generally, the apparent viscosity of the pulp slurries increases as particle size decreases. Figure 4 shows the apparent viscosity of a gold ore slurry with high clay contents as a function of particle size [27]. Particle size effect became notable when the pulp solids concentration exceeded 25 wt.%, and the apparent viscosity of the mineral suspension increased with decreasing particle size (P80 of $125\ \mu\text{m} < 106\ \mu\text{m} < 53\ \mu\text{m}$). This clearly shows that the apparent viscosity is affected by particle size, and the interaction of particle size effect with pulp solid concentration is also indicated. In general, a decrease in particle size could result in a more complex rheological property such as shear thickening and aggregation of network structures, which inevitably entails a difficulty in the separation process [17, 27–29].

Pulp rheology is also affected by particle shape, although this effect has never been well studied in flotation [30]. Studies have shown that the rheology of mineral suspensions is associated with particle shape [10, 17, 31–34]. At the same particle volume fraction, the degree of frictions among irregular particles is greater than that among spherical particles [17]. For example, it has been found in the dense medium separation that the suspension of spherical particles of ferrosilicon exhibited lower viscosity than the irregular particles of ground magnetite for a given slurry density and particle size [35].

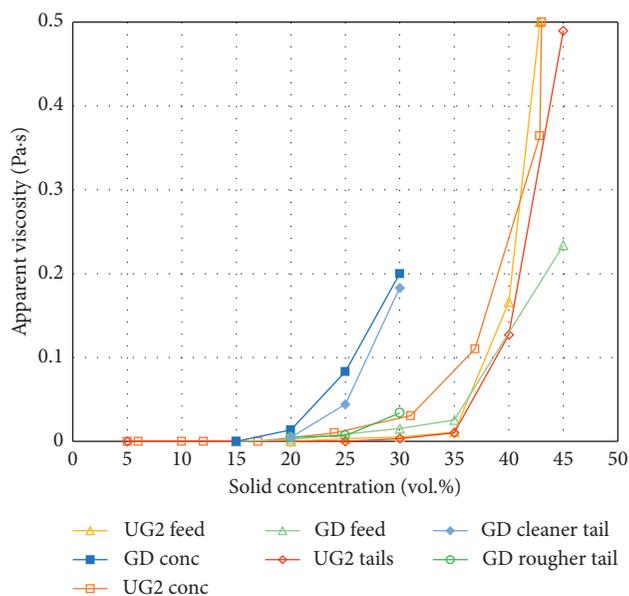


FIGURE 3: The comparison of the apparent viscosity (at $160\ \text{s}^{-1}$) of the UG2 and Great Dyke flotation samples at different solid concentrations (after [19]).

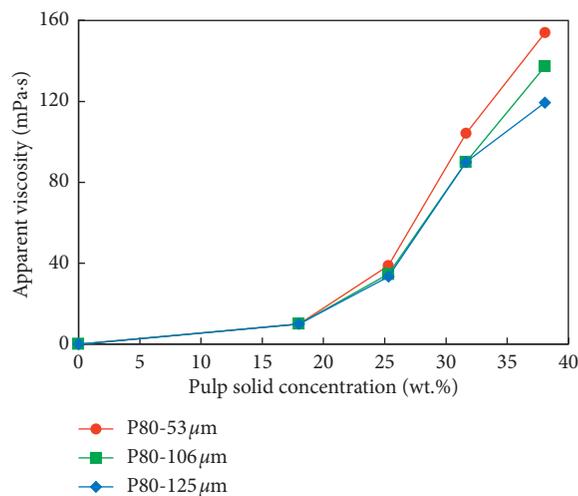


FIGURE 4: Apparent viscosity of the ore as a function of pulp density for different P80 values (after [27]).

Rheological complexities in flotation pulps also originate from the minerals themselves such as mineral surface charge distribution and morphologies. Studies on the correlation of rheological response and mineralogical content have shown that mineral type can significantly vary pulp rheological behaviour [6, 19, 25, 27, 34, 36–39]. Figure 5 shows the difference in the Bingham viscosity of mineral suspensions composed of different clay minerals that usually exist in real ores [6]. Clearly, the rheological behaviour of flotation pulps is closely associated with mineral type, and phyllosilicate minerals, particularly swelling clays and serpentine minerals, can result in higher viscosities compared with non-phyllosilicate minerals such as quartz.

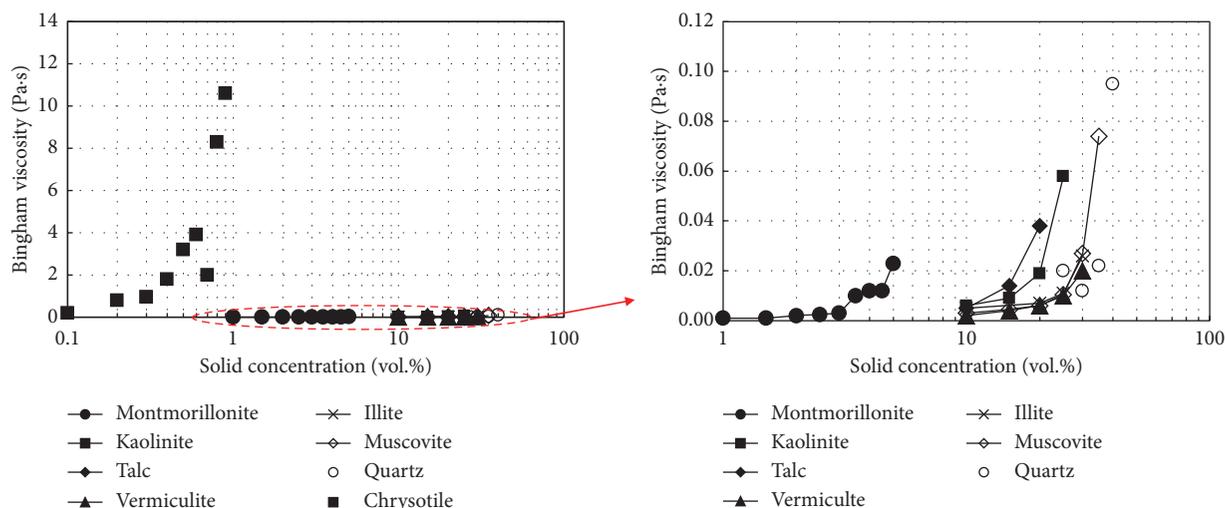


FIGURE 5: Comparison of the Bingham viscosities of different minerals (after [6]).

3.1.3. Interparticle Interaction. Since the presence of numerous fine/ultrafine particles (colloidal particles and clays) is a characteristic of pulps comprising low-grade and complex ores, interparticle interaction force becomes one of the most important aspects to determine the rheological properties of flotation pulps [10, 40]. Various mineral particles with different surface properties and a broad size distribution commonly exist in this type of flotation pulps, and therefore, many interactions can occur. Hard-sphere interaction, electrostatic interaction, steric interaction, and van der Waals attractions have been reported to govern the rheology of flotation pulps [15]. Depending on the complexity of particle surfaces, these interaction forces can be DLVO or non-DLVO [10].

It is known that interparticle interactions can be attractive or repulsive, but they are also susceptible to the shear rate and to pulp chemistry such as medium conditions (ionic strength and pH) and chemical reagents. For non-Newtonian flotation pulps, rheology is strongly dependent on the shear rate in a flotation cell [41, 42]. In several studies on pulp viscosity measurement (e.g., [19, 39, 43, 44]), apparent viscosity was obtained at 100 s^{-1} or 160 s^{-1} which are claimed to represent a typical shear rate in a mechanical flotation cell [19, 45]. Actually, a wide range of apparent viscosities can be displayed for non-Newtonian pulps in a flotation cell as the shear rate varies from high values close to the impeller to very low ones near the froth phase or in the pulp quiescence zone (see Figure 6). Thus, the rheological behaviour of these pulps also varies at different locations in the flotation cell. Since the collecting zone and quiescence zone in the pulp play different roles in the flotation process, it is advisable to obtain the rheological data from both areas to understand the pulp rheological effects.

In mineral flotation, various reagents can be added to facilitate the separation, and these reagents include collector, frother, promoter, depressant, dispersant, and pH modifier [21]. In some operations, seawater is used in regions where fresh water is in shortage [47]. Chemical additives and salt ions could change pulp chemistry, which in turn affect

interparticle interactions and pulp rheology. For example, Cruz et al. [43] studied the effect of flotation reagents including pH modifiers (NaOH, lime, and Na_2CO_3), collector (potassium amyl xanthate), and frother (Interfroth 6500), on the rheological behaviour of kaolinite and bentonite suspensions. All these reagents were found to alter the rheological behaviour of the kaolinite and bentonite suspensions, which was ascribed to the variation in the interparticle interactions in the presence of these reagents. In a different study by Farrokhpay and Zanin [48] where the effect of water quality on froth stability was investigated, the pulp viscosity increased as the concentration of Al^{3+} , Ca^{2+} , and Na^+ in a zinc ore pulp increased (see Figure 7). This change was believed as a result from these salt ions changing the particle interaction to form aggregates.

In summary, pulp rheology is affected by a number of variables in the pulp including solids concentration and particle attributes. Given the nature of flotation pulps made of low-grade and complex ores, the interactions between particles in the pulp also dominate the rheological properties of a flotation pulp. These interactions are not only subject to solids concentration and particle characteristics but also susceptible to shear rate at local regions of a flotation cell, as well as to pulp chemistry such as medium conditions and chemical reagents.

3.2. Pulp Rheology Measurements. Although flotation pulps are a three-phase regime consisting of air bubbles, water, and mineral particles, the viscosity of flotation slurries (water and mineral particles) is generally the subject investigated. It is known that bubbles disperse in the liquid phase without becoming attached when the air volume fraction (air holdup) is less than the critical air holdup point (73%) [49]. In flotation pulps, air holdup was found to range from 2.5% to 15% in laboratory flotation cells and from 6% to 21% in industrial machines, which is far below 73% [50]. In these cases, energy dissipations during pulp flow are thought not

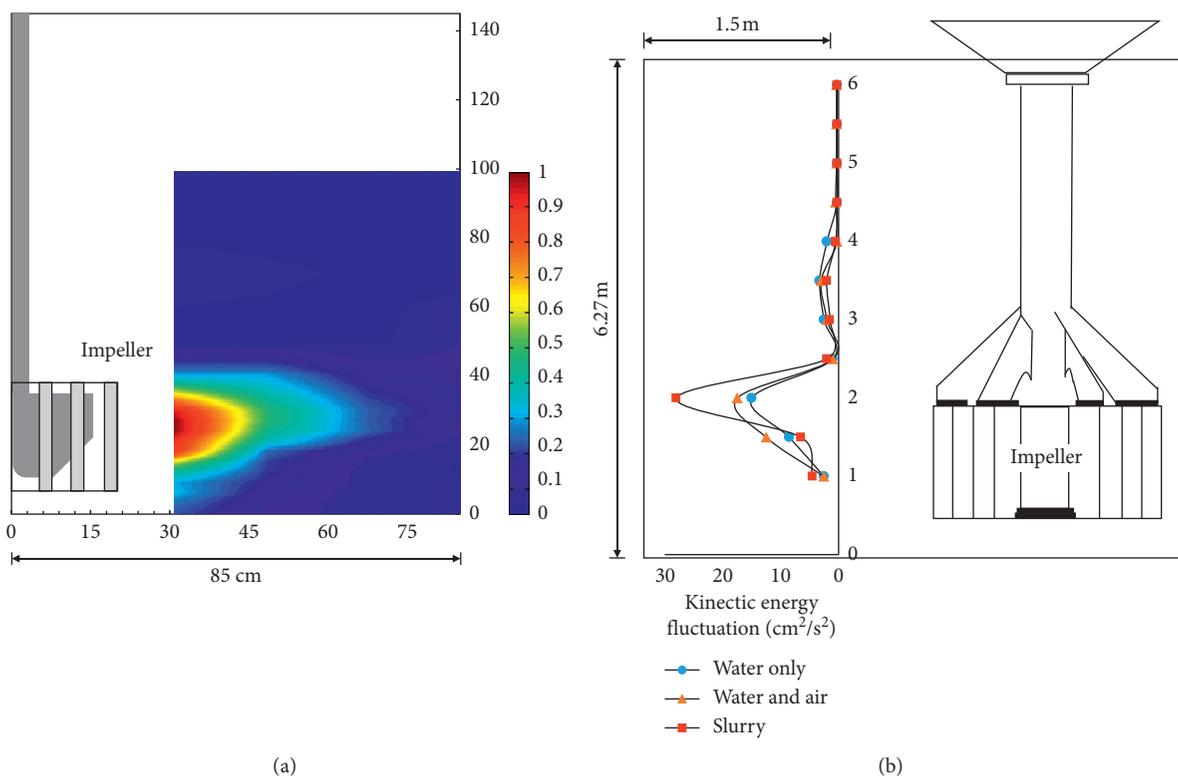


FIGURE 6: Turbulence distribution indicating shear rate distribution in a (a) 3 m³ flotation cell operating with slurry and (b) 300 m³ flotation cell operating with water, water and air, and slurry [46].

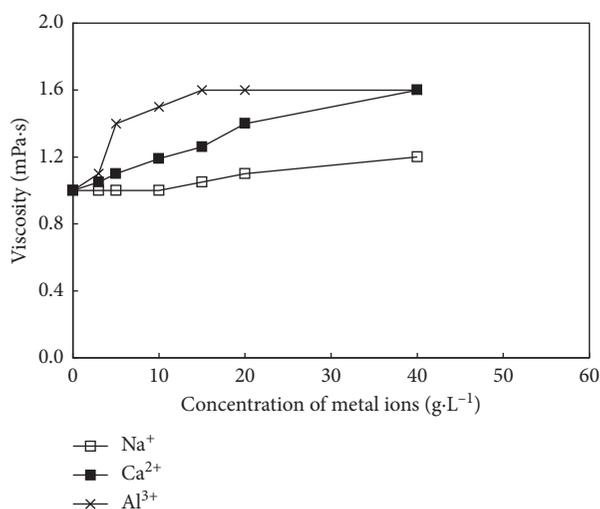


FIGURE 7: Effect of metal ions addition (Al^{3+} (x), Ca^{2+} (■), and Na^+ (□)) on the viscosity of a zinc ore slurry (after [48]).

associated with bubble deformation or frictions between bubbles. Thus, it is reasonable to use mineral slurry to represent the pulp in rheology measurements.

To measure pulp rheology, various setups including capillary viscometers, vibrating sphere viscometers, and rotational rheometers have been used, but the rotational rheometer prevails over the others since it can be operated at a specific shear rate in addition to the ease of completing

measurements and data analysis [51–53]. Rotational rheometers generally involve the relative rotation about a common axis of one of three geometries: concentric cylinder, cone and plate, or parallel plates (see Figure 8). The one with the concentric cylinder geometry (also known as the bob and cup style, Figure 8(a)) has been widely applied for pulp rheology measurements. This is because rheometer geometries including the cone and plate and the parallel plate have trouble in holding samples during measurements [15].

The rheology measurement for pulps made of good-quality ores has been a challenge. This type of pulps is generally of low viscosity, being Newtonian or very close to Newtonian. Wall slip often occurs as mineral particles do not always adhere perfectly to the smooth surface of the rheometer tools such as the cylinder in the Couette geometry during the measurement, causing an erroneously low viscosity and yield value [54, 55]. In the literature, modifications to the surface of bobs or using vane-style viscometers could be found to address this problem [56, 57]. More importantly, mineral particles in this type of pulps tend to experience fast settling during rheology measurement. This settlement of particles may also cause shear-induced particle migration along the rotation shaft of a rheometer [58, 59]. To avoid particle settlement, methods including slurry mixing and recirculation have been tried to keep the slurry in suspension for measurement, but these methods are generally limited by the interference of slurry flow created purposely for suspension such as Taylor vortices and

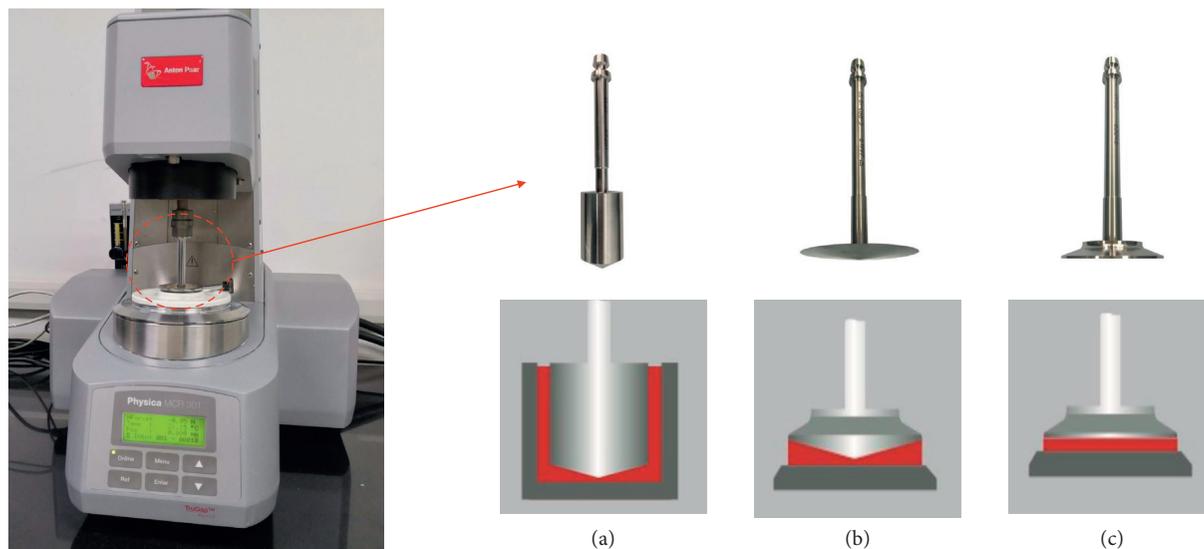


FIGURE 8: Basic geometries for the rotational rheometer: (a) concentric cylinder; (b) cone and plate; (c) parallel plate.

turbulent flow, leading to severe deviations in rheometer readings [9, 10, 51, 60]. Other approaches have also been provided such as using capillary viscometers or making use of zone settling properties of coarse particle suspensions for measurement [61, 62], but these methods also have disadvantages which have been detailed in the review by Cruz and Peng [10]. At the current stage, there has not been a promising technique for measuring the flotation pulp with fast settling solids.

It is worth noting that, however, in most flotation operations, pulps made of high-quality ores are not thought to cause detrimental rheological effects on flotation performance. In this sense, pulp rheology measurement becomes particularly critical when processing low-grade and complex ores which can produce a highly viscous pulp. Researchers have demonstrated that consistent measurement for this type of pulps can be obtained using the bob and cup style rheometer [10, 24, 43, 63, 64]. All concerns over rheology measurement of high-quality ore slurries can be minimal as to problematic ore slurries with high viscosity. The rheology measurement includes a preshear for 15 s at 1000 s^{-1} followed by 3 s of resting period before the measurement that lasts for 35 s. Besides, at the low shear rate, yield stress for the non-Newtonian flotation pulp may occur. Boger [9] has suggested using the rheometer with a vane head to detect yield stress. Air bearing with high sensitivity is also recommended to apply very low torques [15].

Also, Cruz and Peng [10] suggested performing viscoelastic measurements such as dynamic oscillatory rheology measurement in the linear viscoelasticity region as a supplement to analyse rheological properties of non-Newtonian flotation pulps. In practice, there are few studies on oscillatory rheology in mineral pulps, but these have shown to be a good strategy to understand more about particle interactions. Viscoelastic modules are known to have physical sense only when a flotation pulp presents a linear viscoelastic response [15, 65, 66]. In some flotation operations, however,

the deformation is large and rapid [67]. Thus, the oscillatory rheology must necessarily be analysed under large amplitude oscillatory shear (LAOS) deformation. In this sense, considering deformation only under small amplitude oscillatory shear (SAOS) flow will be insufficient to interpret inter-particle interactions in the pulp.

3.3. Impact of Pulp Rheology on Flotation Performance

3.3.1. True Flotation. The impact of pulp rheology on true flotation recovery is basically associated with bubble-particle interactions and the transport of formed bubble-particle aggregates [22, 37, 68, 69]. For example, Patra et al. [69] carried out flotation tests using a copper ore in the absence and presence of two fibers, namely, fibrous Ni ore (1–6 wt.% chrysotile fibers) and nylon fibers (1–2 wt.%), and found that a viscous pulp was the key underlying reason for the poor flotation recovery of valuable mineral. High viscosity of pulp was caused by the entanglement of fibers, which prevented air dispersion and bubble transport, resulting in decreased copper recovery. This clearly shows the detrimental rheological effect that fibrous minerals would potentially have on the flotation recovery. As in ultramafic Ni ore beneficiation processes, slime coating of serpentines on the Ni sulphide minerals to deteriorate the flotation has been widely acknowledged. The findings by Patra et al. [69] evidently suggest that pulp rheological behaviour plays a critical role in the effective separation of ore containing fibrous minerals.

In a copper-gold flotation in the presence of bentonite (a swelling clay) and kaolinite (Q38 and Snobrite, nonswelling clays), Zhang and Peng [37] also observed a strong correlation between pulp viscosity and flotation recovery (see Figure 9). Clay minerals of different mineral types in the flotation pulp exhibit different rheological behaviours, leading to different effects on the true flotation recovery. Bentonite exhibited a more profound influence than Q38

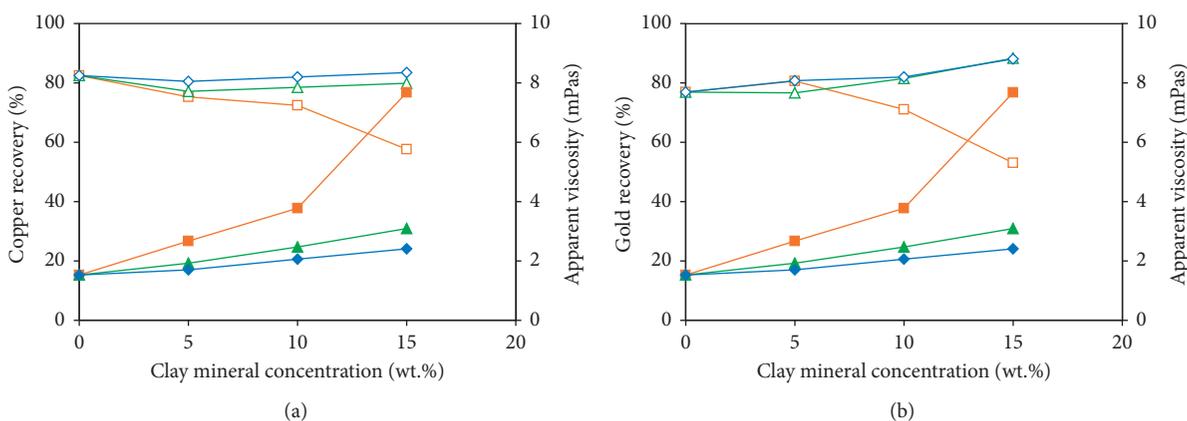


FIGURE 9: Effect of clay minerals on (a) copper recovery and (b) gold recovery (hollow points) and apparent viscosity (solid points) of flotation slurries: Snobrite (\diamond); Q38 (\triangle); and bentonite (\square) (after [37]).

and Snobrite in the pulp viscosity and flotation recovery when increasing the solid concentration. In general, a high pulp viscosity corresponded to low copper recovery (see Figure 9(a)), as these clay minerals would increase pulp viscosity that interferes with flotation hydrodynamics and prevented the probability of particle-bubble collision. Gold flotation showed some similarities to copper flotation in response to the addition of bentonite, as evidenced by that the addition of bentonite at greater than 5% concentration corresponding to higher apparent viscosity decreased gold recovery (see Figure 9(b)).

Not all the true flotation recovery decreases with an increase in pulp viscosity, as demonstrated by Zhang and Peng [37] that a slight increase in the pulp viscosity by Q38 (15 wt.% concentration) and bentonite (5 wt.% concentration) enhanced the gold recovery. This was attributed to a reduced detachment of gold particle from bubbles in the pulp as pulp viscosity increased. It is known that high bubble-particle detachment probability is the main reason for the poor recovery by true flotation in some flotation operations [70, 71]. Turbulent flow in the pulp is beneficial to bubble-particle collision and attachment, but the turbulent effect can also cause particles with high inertia to detach from bubbles, thus decreasing the flotation efficiency [70, 72, 73]. Thus, it can be seen that a proper pulp viscosity would stabilize bubble-particle aggregates that enhance the flotation of heavy metal minerals.

Similarly, a slightly viscous pulp is also beneficial to coarse particle flotation. Xu et al. [74] observed an increased recovery of coarse hydrophobic quartz particles when adding glycerol to increase the medium viscosity. In their study, a discernible change was found in the pulp viscosity, from 0.9 mPa·s in water to 7.6 mPa·s in a 50% glycerol/water mixture. When pulp viscosity increased, a more stable bubble-particle aggregate was formed as analysed by a novel electro-acoustic technique used for detachment experiments, leading to the increase in the quartz recovery. Therefore, using a proper viscous pulp is recommended for the flotation of either coarse particles or precious metals.

In addition, the pulp rheological effects on true flotation have also been extensively reported with respect to other

flotation variables such as particle size and flotation reagents including rheology modifiers, pH modifiers, and metal ions except for mineralogy and solid concentration [27, 44, 75, 76]. Fine/ultrafine particles are well known to decrease true flotation recovery by increasing the pulp viscosity and slime coating of fine gangue mineral particles onto the surface of the valuables [77]. In mineral flotation, various flotation reagents can be added to facilitate the separation. Farrokhpay et al. [27] have shown that different flotation pH modifiers and rheological modifiers have different effects on the pulp apparent viscosity and flotation performance. For example, in their study, the gold recovery and grade increased due to a low flotation pulp viscosity when the pH was adjusted by Na_2CO_3 , while NaOH was less influential. In general, due to the rheological complexities of low-grade and complex ores, different chemical additives would often result in different rheological effects on flotation by affecting the interactions between particles in the pulp. This basic understanding of pulp rheological effects offers essential insights into the methods used to mitigate the deleterious impact of pulp rheology on flotation, which will be presented in Section 5.

3.3.2. Entrainment. Apart from true flotation, gangue entrainment is also associated with pulp rheology. It is known that entrainment mechanism mainly accounts for the recovery of gangue mineral particles in flotation, and it is directly related to the ultimate water recovered to the concentrate and the entrainment factor for particles [7]. Since a large amount of fine/ultrafine particles such as colloidal particles and clays exist in pulps with low-grade and complex ores, pulp viscosity is very likely to change pulp flow patterns, which subsequently changes the water transferred to the froth from the pulp, and the degree of sedimentation of particles in the pulp (i.e., entrainment factor). Although there is no common agreement on how entrainment responds in the pulps with different degrees of pulp viscosity, the literature suggests a nonignorable impact of pulp rheology on entrainment in flotation [36, 39, 78, 79].

Kirjavainen [78] studied the entrainment of hydrophilic particles by performing flotation tests in a circulating system with granular quartz and flaky phlogopite at different slurry densities using only frother. Pulp viscosity was found to control particle entrainment, especially in the flotation of very fine materials. Chen et al. [39] also studied the correlation between pulp rheological property and gangue entrainment in flotation of a mixture of chalcopyrite (a particle size of P80 38 μm), quartz (a particle size of 38–75 μm), and amorphous silica (a particle size of 38–75 μm). It was observed that gangue recovery increased with a slight increase in pulp viscosity, but further increasing viscosity would reduce gangue entrainment. Note that the gangue particles with the size of 38–75 μm may have settled during the rheology measurement in their study, but using a preshear at 100 s^{-1} to avoid particle settlement would also be likely to make a turbulent flow which is not a valid measurement. In this sense, whether the observed trend can be transversal for all flotation systems is still unknown.

In a copper flotation reported by Farrokhpay et al. [36], a significant decrease in the copper grade was also found in the presence of muscovite. The copper recovery remained unchanged irrespective of the presence of muscovite. A maximum copper grade of 19% was observed without muscovite approximately, but it decreased to 2% in the presence of 30% muscovite. This decrease was a result of muscovite increasing the pulp viscosity that increased the gangue entrainment into the concentrate. Clearly, this observation also indicates the ignorable impact of pulp rheology on entrainment in flotation. In addition, it is worth mentioning that the rheograms obtained in their study may be unreliable, as extremely fast rheograms were made using a vane rheometer, i.e., measurement with an upward and downward ramp within the range 0–400 s^{-1} over a 60 s period. There may not be enough time for the pulps to stabilize at each shear rate, so the influence of the thixotropy cannot be appreciated, although the vane geometry is reported to result in less sample disturbance and thixotropic breakdown during rheology measurements [80–82].

In general, both the true flotation and gangue entrainment are closely associated with the pulp rheology. Table 1 summarizes some implications of correlation between flotation response and pulp rheological property mentioned above. As can be seen that no common agreement has been reached as to how flotation recovery and grade respond to pulp rheological property at different flotation conditions. These complex pulp rheological effects on flotation recovery and grade warrant further investigations in this topic.

4. Rheology of Flotation Froth

4.1. Variables Affecting Froth Rheology. Foam is an air-bubble dispersion in an aqueous solution with a packing fraction above 73% [49, 83]. In a foam, air volume fraction is normally high, and the packed bubbles are separated by thin watery films (lamellae) which form plateau borders and vertices [84, 85]. As indicated by Princen and Kiss [49], the rheological behaviour of a foam is affected by a number of variables including bulk liquid viscosity, foam quality, and

bubble size, and a model was developed to predict the apparent viscosity of foams that demonstrates how these variables affect foam rheology:

$$\eta = \frac{\tau_0}{\gamma} + 32.0(\varepsilon_f - 0.73) \left(\frac{R_{32}\gamma}{\eta_0\sigma} \right)^{-0.5} \quad (2)$$

where η is the apparent viscosity, γ is the shear rate, τ_0 is the yield stress, ε_f is the air volume fraction, η_0 is the viscosity of the Newtonian continuous phase, R_{32} is the Sauter mean bubble radius, and σ is the interfacial tension.

A flotation froth has a structure similar to a foam, but is a three-phase regime which has hydrophobic particles attached to liquid films of air bubbles, and both hydrophobic and hydrophilic particles in the plateau borders and vertices [85]. Although the literature suggests that flotation froths are non-Newtonian showing pseudoplastic characteristics which are similar to foams, the presence of solid particles makes froths' rheological behaviour more complicated [12, 13, 86–88].

Froth flow is also an irreversible process, which involves the rearrangement of bubbles and changes in bubble surface area [13]. In a series of flotation tests, in both pilot and industrial scale, conducted by [87–90]; the measured froths showed pseudoplastic behaviour. In their flotation tests, flotation variables including frother dosage, feed grade, air rate, froth depth, impeller speed, and valuable mineral particle size were investigated with respect to froth rheology [88, 89]. Table 2 shows the variables that significantly affected froth rheology [89]. Feed grade and froth height were positively correlated with froth apparent viscosity, whereas particle size and impeller speed were negatively correlated with froth apparent viscosity. Air rate was found to affect froth viscosity in a nonlinear way. Some of these variables were also observed to interact with each other to affect froth rheology, as shown in Figure 10. Frother dosage in a range of 10–15 ppm did not appear to result in any significant effect on froth rheology [88].

Furthermore, the mechanisms underpinning the effects of these significant variables reported in Table 2 were also explored, and it was found that froth characteristics including bubble size and bubble loading are primary determinants for froth rheology [87]. The variations in flotation variables could result in a change in these primary determinants, which significantly altered the froth rheology. In their studies, bubble size was found to negatively affect the froth viscosity while bubble loading had a reverse effect. In froths, viscous dissipation of energy is largely due to the relative motion of neighbouring bubbles and bubble deformation. As in their study a very low solids concentration was found in the plateau borders and vertices of the froth, solids volume fraction in the plateau borders and vertices determining froth rheology has not been identified.

In addition, a froth rheology model as a function of the primary determinants identified in their study was proposed (see equation (3)), by assuming that bulk viscosity remains unchanged due to a low solids concentration in the plateau borders and vertices of the froth as well as that the interfacial tension is associated with the fraction of the lamella covered

TABLE 1: Literature (part) related to pulp rheological effects on flotation recovery and grade.

Ore type	Froth rheological effect on recovery and grade	References
Copper flotation	Fibrous minerals increased pulp viscosity and decreased copper recovery	Patra et al. [69]
Quartz flotation	A slight increase in pulp viscosity by glycerol increased the recovery of coarse hydrophobic quartz particles	Xu et al. [74]
Gold flotation	Different pH modifiers and rheology modifiers had different effects on pulp viscosity, resulting in different gold recoveries and grades	Farrokhpay et al. [27]
Copper-gold flotation	Clay minerals increased pulp viscosity; copper recovery decreased as pulp viscosity increased; a slight increase in pulp viscosity increased gold recovery but further increasing the pulp viscosity reduced gold recovery	Zhang and Peng [37]
Copper flotation	Swelling clays increased pulp viscosity and reduced both copper recovery and grade, but nonswelling clays were less influential	Farrokhpay et al. [25]
Copper-gold flotation	Copper recovery and grade decreased with increasing pulp viscosity by bentonite; seawater (salt ions) reduced pulp viscosity in the presence of bentonite and improved copper and gold recoveries but further reduced copper and gold grade	Zhang et al. [27]
Copper flotation	Cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) reduced pulp viscosity and increased copper recovery	Wang et al. [44]
Copper flotation	Copper recovery remained unchanged first and then decreased with increasing pulp viscosity by amorphous silica, while copper grade decreased; gangue entrainment increased first and then decreased with increasing pulp viscosity	Chen et al. [39]
Gold flotation	Lignosulfonate-based biopolymer (DP-1777) increased gold recovery and grade through reducing pulp viscosity; gangue entrainment decreased with decreasing pulp viscosity	Liu et al. [76]
Copper flotation	Copper recovery remained unchanged with increasing pulp viscosity by muscovite, but copper grade decreased as pulp viscosity increased; gangue entrainment increased with increasing pulp viscosity	Farrokhpay et al. [36]

TABLE 2: Significance of flotation variables on froth apparent viscosity at different shear rates.

Flotation variables	Shear rate (s^{-1})			
	1	2	3	4
Froth height (FH)	98.9	99.2	98.9	98.4
Superficial gas velocity (J_g)	84.5	22.6	52.0	86.5
Impeller speed (IS)	100.0	100.0	100.0	100.0
Chalcopyrite size (CS)	100.0	100.0	100.0	100.0
Copper grade (CG)	99.8	100.0	100.0	100.0
J_g/J_g	99.9	99.9	99.9	99.9

by solids [87]. The model was found successful in predicting the rheological behaviours of froths generated in a copper flotation operated at different flotation conditions including frother dosage and feed grade [88]:

$$\eta = (\varepsilon_f - 0.73) \left(\frac{R_{32}\gamma}{k_0\alpha} \right)^{-0.5}, \quad (3)$$

where k_0 is the constant representing those parameters of the system that should not change between the experiments and α is the fraction of the lamella covered by solids.

Despite that concerns remain over the variables determining froth rheology. For example, for heavily entrained froths, a high solid content in plateau borders and vertices may distort the flow field and could presumably increase the energy dissipation during flow to increase froth viscosity [91]. Another example is that in a copper flotation performed by Li et al. [88], an increase in Dowfroth 250 dosage from 10 ppm to 15 ppm exhibited no effect on the froth viscosity. It is well known that frother could strongly affect bubble surface tension, air holdup, bubble size, and thus the fraction of the lamellae covered by solid particles [92–95],

which should have affected froth viscosity. In this respect, more work is still required to identify the variables determining the rheology of froths and to correlate flotation conditions including particle attributes such as clay minerals, operational variables, and flotation reagents with these primary determinants to elucidate the significant variables influencing froth rheology.

4.2. Froth Rheology Measurements. For decades, two-phase systems (air-liquid foam and solid-liquid emulsions) have been the subject of many studies on rheology and restricted information is available about the rheological behaviour of flotation froths, due mainly to the difficulty in the measurement of froth rheology [13, 86]. As stated previously, bob and cup style rheometers have been useful for pulp rheology measurement. However, the small clearance between the cup and the bob would result in a change in froth structure with no prevailing froth rheology properties obtained [13]. Due to the similarity between flotation froths and foams, rheometers and purpose-built setups, for example, parallel-plate rheometers and capillary viscometers, for determining foam rheological behaviour should have been useful in measuring froth rheology, but wall slip effect and froth degradation during froth sample transfer to the setups would cause deviations from genuine froth rheological properties.

To measure froth rheology, an initial attempt was made by Moudgil [96] who used a Brookfield viscometer in a laboratory flotation cell. The measurement was only taken at a constant rotational rate of 6 rpm, and no rheogram of the froth was generated due to the limitations of the viscometer. After that, Shi and Zheng [13] introduced an in situ measurement method that involves a direct immersion of a vane head into the flowing froth to perform measurement, with

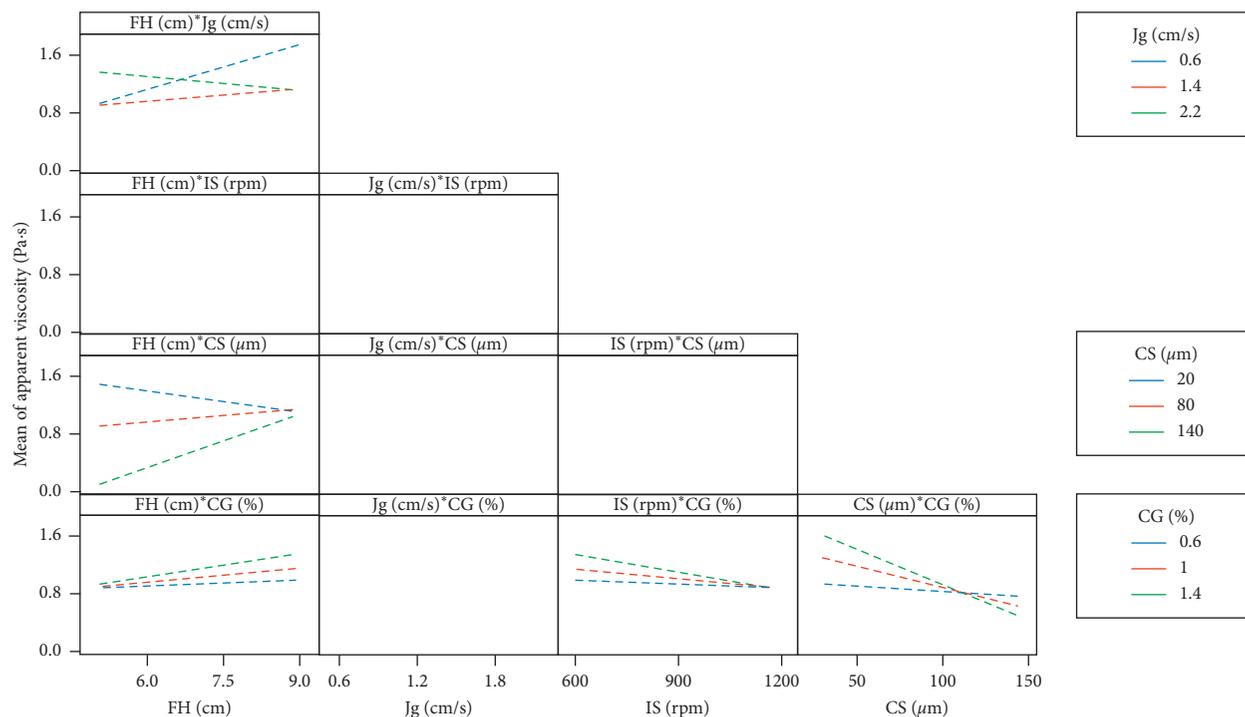


FIGURE 10: Interactions between flotation variables in determining froth rheology (after [89]).

the advantage of minimum disturbance caused by the vane and no apparent slip effect or filling influences [80, 97].

However, Li et al. [86] found that horizontal flow in the froth could significantly affect the torque readings and consequently influence rheology measurement results. Besides, the rheometer used by Shi and Zheng [13] was found to be suitable for measurement only in the shear rate range above 2.5 s^{-1} due to the mechanical bearing of the rheometer. Based on these concerns, Li et al. [86] modified the vane method for froth rheology measurement by encircling the vane using a tube with geometrically designed diameter in a vane rheometer with an air bearing, as shown in Figure 11. They evaluated the rheometer with a Newtonian silicone oil of known viscosity and claimed that it was capable of producing true flow curves. It should be noted that, as the vane is rotated in the horizontal direction during measurement, the effect of vertical froth velocity on the measurement has been assumed to be negligible in their study, which remains to be evaluated. Also, since the vane geometry is not a standard device to create rheograms, the acquired raw data (vane rotating speed and torque) are required to be converted to rheological parameters (shear rate and shear stress). The mathematical expressions used by Li et al. [86] to obtain the rheograms are based on the assumption that the deformation profile of the froth sample within the distance between tube and vane is linear. Whether this linearity could be preserved at different gaps is still unknown, which requires further investigation. Despite that the appliance has been applied to various flotation froths, showing that the shear rate of the flotation froth was less than 4 s^{-1} , much less than that in pulp phase of which the average has been believed to be around 100 or 160 s^{-1} ,

quantitatively confirming that flotation froth provides a much more tranquil environment (i.e., less turbulence) than the pulp phase for further product concentration.

Besides, Zhang et al. [98] have introduced a steady-state method for froth rheology measurement recently when investigating the effect of froth rheology on the dewatering of fine coals. Oscillatory rheology of froth was measured using a vane-in-cup system. Rather than measuring the froth rheology in situ, the measurement was conducted on the froth that was produced in the cup to avoid its degradation during transfer. The froth was generated by introducing air into a preconditioned coal slurry in the cup, and air injection was terminated when the coal froth was believed to be sufficiently high. The vane head was then placed into the froth to perform the measurement. Note that the froth regenerated in the cup is highly unlikely to reproduce the flowing froth in flotation, as bubbles in the froth tend to collapse or coalesce during froth transportation, leading to continuous changes in the froth structure and the content of air, liquid, and both hydrophobic and hydrophilic particles in the local froth. This may result in deviations from genuine froth rheological properties. Since oscillatory rheology measurement on flotation froths could provide complementary information about flotation rheological properties, delicate experiments should be designed for such measurements.

4.3. Impact of Froth Rheology on Flotation Performance

4.3.1. Flotation Recovery and Grade. The impact of froth rheology on flotation recovery and grade has long been recognised, and high viscosity can result in no froth

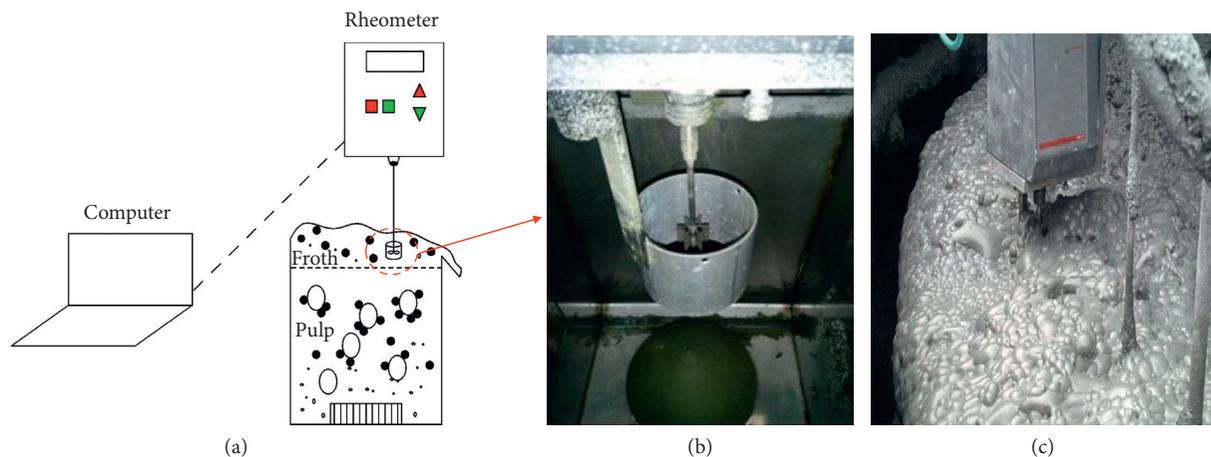


FIGURE 11: Froth rheology measurement device (the Anton Paar DSR 301 rheometer) by Li et al. [86]: (a) schematic diagram; (b) modified vane system; (c) setup of the rheometer in an industrial cell.

generated, and few valuable minerals loaded on the top of the froth [44]. To date, however, no consensus has been reached with respect to the correlations between froth rheology and flotation recovery or grade, as shown in Table 3. In the phosphate flotation reported by Moudgil [96], a higher solid loading of the froth led to a higher froth viscosity, which slowed the drainage of entrained particles in the froth. As a result, a decrease in the concentrate grade was observed as froth viscosity increased. In the copper flotation, however, Shi and Zheng [13] found that the grade of hydrophobic chalcopyrite was positively correlated with froth viscosity, while the grade of hydrophilic quartz was negatively correlated with froth viscosity. Interestingly, the recent study by Li et al. [90] showed that the entrainment recovery of hydrophilic quartz in a copper flotation was strongly correlated with froth rheology in a nonlinear way, as shown in Figure 12. An increase in froth viscosity (consistency index) would enhance quartz recovery at low froth viscosity, while at high froth viscosity, the recovery of quartz deteriorated when froth became more viscous.

4.3.2. Other Flotation Performance Indicators. Apart from flotation recovery and grade, froth rheology has also been correlated to other flotation performance measures including froth recovery, air recovery, and froth height. In a copper flotation, Li et al. [90] observed that froth height above the lip increased as froth viscosity increased, resulting in a prolonged froth residence time that determines froth drainage and froth recovery. Air recovery was also associated with froth rheology: at low froth viscosity, air recovery increased as froth viscosity increased, while at high froth viscosity, the opposite was found.

Farrokhpay [4] and Li et al. [90] have proposed that froth viscosity affects flotation performance through its effect on both froth mobility and froth stability. When froth is less viscous, froth stability dominates froth transportation. Increasing froth viscosity will result in a more stable froth where less bubble bursting and detachment of valuable minerals occur and considerably increases the flotation

recovery of valuables. When the froth becomes excessively viscous, froth transportation would be retarded due to poor froth mobility, and thus, flotation deteriorates. In general, a requirement for a froth is that the froth should not be too stable with low coalescence or of too low viscosity with high coalescence, which is targeted to achieve a balance between optimal recovery and minimal mechanical entrainment [99].

Note that froth mobility and froth stability are two aspects of froth characteristics that determine the flotation recoveries such as froth recovery and air recovery in mineral flotation. Froth rheological parameters such as yield stress and apparent viscosity are generally a measure of the degree of froth mobility. A positive correlation of froth rheology (froth mobility) and froth stability has been suggested from rheological investigations on the froth in a chalcopyrite flotation by Li et al. [90]. However, whether the observed trend can be transversal for all flotation systems is still unknown. Since the correlation between froth rheology and froth stability would be conducive to improving the current flotation recovery models for process prediction and optimization, more work is needed.

5. Mitigating Rheological Problems in Flotation

Rheology can be a useful tool for flotation optimization. Many approaches have been tried to mitigate the deleterious effects caused by rheology in flotation, but these methods mainly focus on the pulp zone [40, 77]. In mineral flotation, it is known that the nature of pulp and froth determines their rheological behaviour. When the nature is altered, either by the addition of chemical additives or by changing the proportion of each component material (i.e., liquid, air bubble, and particle), viscosity is also quite likely to change.

In flotation, the chemicals of many types have been tried to control the rheological properties of flotation pulps. The literature shows that rheology modifiers (dispersants) can be used to reduce the negative rheological impact of problematic ores with clay minerals in flotation [40, 76, 77]. For example, in studies by Seaman et al. [100] and Wei et al. [101] where biopolymers such as lignosulfonate-based polymers

TABLE 3: Literature related to froth rheological effects on flotation recovery and grade.

Ore type	Froth rheological effect on recovery and grade	References
Phosphate flotation	Concentrate grade decreased as froth viscosity increased	Moudgil [96]
Copper flotation	Concentrate copper grade increased as froth viscosity increased; concentrate quartz grade increased as froth viscosity decreased	Shi and Zheng [13]
Copper flotation	At low viscosity: air recovery and gangue recovery increased with froth viscosity increased; at high viscosity, air recovery and gangue recovery decreased as froth viscosity increased	Li et al. [90]

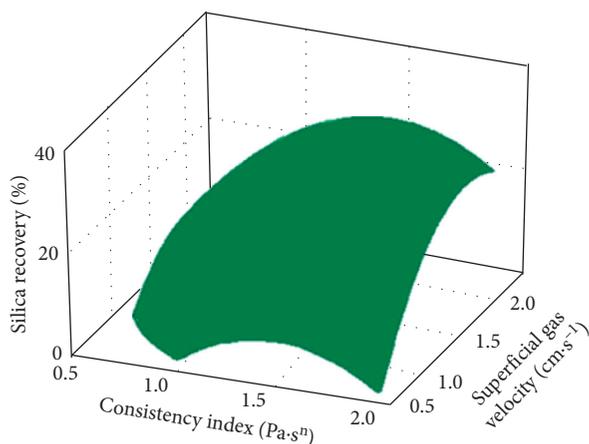


FIGURE 12: Surface plot of hydrophilic quartz recovery versus consistency index and superficial gas velocity (after [90]).

were used as effective clay dispersants to improve the flotation performance, the possible role of reduced pulp viscosity in the improved flotation was addressed by Chen and Peng [10] in addition to the effect of reduced slime coating of clays onto the valuables. In a different study where the effect of different commercial rheology modifiers on flotation performance of a gold ore with high clay contents from Carlin Trend was investigated, Cyquest 40E (a modified polymer) decreased the pulp apparent viscosity significantly and increased the gold recovery by about ten percent at a rheology-modifier dosage of 600 g/t and a pulp density of 32% [27]. As pulp rheology can strongly affect the dispersion of particles and air bubbles as well as the bubble-particle collision, this improvement in the gold recovery is highly likely to be related with the reduced pulp viscosity. In their study, BorreFlo D-919 (a lignosulfonate-based polymer) also decreased the pulp viscosity, but a reverse effect was observed on both the gold recovery and grade. This implies the difficulty in selecting the rheology modifiers to improve the flotation of various low-grade and complex ores.

The literature also suggests using salt ions to manipulate pulp viscosity to improve flotation recovery [44, 75, 77]. For example, Zhang et al. [75] found that the deleterious effect of bentonite could be mitigated in seawater containing the salt ions of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , and SO_4^{2-} . The salt ions reduced the swelling capacity of bentonite, modified the network structures of bentonite in flotation pulp, reduced the pulp viscosity, and improved both the copper and gold recoveries. In a different study, Wang et al. [44] examined the effect of different cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) on

pulp viscosity and copper flotation behaviour and found that these cations could effectively decrease the pulp viscosity, which contributed to an improved copper flotation recovery. These studies have experimentally confirmed the beneficial effect of some salt ions in reducing the pulp viscosity and improving flotation performance.

It should be stated that lack of froth rheological investigations in mineral flotation has led to no conclusion on whether froth rheology also changes with changing pulp rheology when using the abovementioned approaches. In addition to the incomplete understanding of the effect that froth rheology has on flotation recovery and grade, few techniques are developed targeting at manipulating the froth rheology to improve the flotation performance at the current stage. However, as can be seen in most industrial flotation columns, washing water is added at the top of the columns to facilitate the drainage of gangue particles in the plateau borders and vertices out of the froth zone. This added washing water is expected to result in a wetter froth of which the viscosity should be lower. Therefore, introducing washing water into the froth zone may be a feasible way for plant operators to mitigate the deleterious froth rheological effect on flotation.

It should also be stated that pulp rheology and froth rheology act as a whole to influence the flotation performance, and thus, to comprehend the correlation between pulp and froth rheology becomes particularly necessary in respect of adjusting flotation variables to achieve a better flotation result. To date, however, no studies on this correlation have been conducted yet due to its complexity. For example, the presence of different types of clays in flotation may result in different impacts on pulp and froth rheology. Increasing the content of clays in pulp would increase pulp viscosity regardless of clay type, while it may not be the case for froth rheology. The hydrophobicity and the swelling characteristics of clays could affect froth viscosity in addition to the contents [25, 87].

As a matter of fact, adjusting flotation operational variables can be a possible alternative, but caution must still be taken even if the correlation between pulp rheology and froth rheology is established. This is because operational variables themselves may also impose an undesired effect on flotation performance. For example, one of the most common ways to treat problematic ores in flotation plants is to process them at a lower solids concentration. Low solids concentrations can reduce both the pulp and froth viscosity [39, 87, 102], but this method would also inevitably lead to a reduced the flotation productivity [40]. As Wang et al. [44] argued, at present, no reliable and effective ways are available

in the case of manipulating rheology to improve the flotation efficiency of problematic ores.

6. Conclusions and Future Work

This paper reviews the pulp and froth rheology in mineral flotation. It reveals the rheological complexities encountered when processing problematic ores by the flotation technique, and analysis of pulp and froth rheology still has a long way to go before becoming a dependable tool for process control that would consistently produce an efficient performance in flotation plants. Although a few rheological investigations show some significant correlations between flotation recovery and grade and the rheological behaviours of flotation pulps and froths, no general agreement has been reached due to the complex nature of various flotation feeds. The essential flotation variables that affect pulp and froth rheology show similarities as well as differences, which indicates that these variables are interrelated to some extent to affect flotation rheology and flotation response. However, concerns remain over the principle variables affecting flotation rheology especially in the froth zone, and also no work has been done towards the intercorrelation between pulp rheology and froth rheology. This results in the difficulty in the mitigation of deleterious rheological effects on flotation by manipulating the influencing variables in both the pulp and froth zones. At the current stage, only some polymeric dispersants and metal ions are found effective with respect to reducing pulp viscosity and improving flotation in some applications. For rheology measurements, it is revealed that progress has been advanced in measuring the rheological behaviour of both flotation pulps and froths with a focus on rheological parameters yield stress and apparent viscosity and other techniques such as oscillatory rheology measurements are being introduced to the field to properly interpret interparticle interactions in mineral flotation. But caution must be taken when analysing the rheological data reported by rheology measurement devices, as a rheometer always reports data which are not always associated with rheology.

To better understand the rheological effects in mineral flotation, the following topics are recommended to investigate in future:

- (i) To develop sound techniques (measuring device and methodology) to characterise the complex flotation rheological behaviours based on the recognition of flow types and shear rate of flotation pulps and froths and to adapt froth rheology measuring technique by Li et al. [86] to various mineral flotation systems through experimental validation and mechanical modification.
- (ii) To classify the main gangue mineral components into groups to facilitate the rheological investigations based on the mineralogical understanding of various low-grade and complex ores.
- (iii) To identify the essential flotation variables that influence the rheological behaviours of flotation pulps and froths, to elucidate the effects of these variables on pulp and froth rheology and overall flotation performance, and to propose approaches combined properly to mitigate the deleterious rheological effects in flotation of different groups of mineral systems.
- (iv) To clarify the correlation between pulp rheology and froth rheology and the correlation between froth rheology and froth stability so as to allow flotation rheology to be a useful tool for process prediction and optimization.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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