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Review

A Brief Review of Micro-Particle Slurry Rheological Behavior in Grinding and Flotation for Enhancing Fine Mineral Processing Efficiency

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Abstract: Recent years have witnessed growing research interest in applying rheology in grinding and flotation treatment of finely disseminated ores. Slurry rheology has long been identified as the comprehensive effect of inter-particle interactions, including their aggregation and dispersion states in slurry, which are more impactive under the fine-particle effect. In this regard, rheology has the potential to play a significant role in interpreting the flowing and deforming phenomena of inter-particle aggregates, particle-bubble aggregates, and flotation froth. Though much attention has been paid to the rheological effect in industrial suspension, this has not been the case for mineral grinding and flotation for fine particles. The influential mechanism of rheology on the sub-processes of mineral processing has not been systemically determined nor revealed thoroughly, thus the underpinning mechanism for enhancing the processing efficiency has been difficult to discover. This paper reviews the current application and importance of rheology in fine mineral processing, and the potential research direction in the field is proposed.

Keywords: slurry rheology; froth rheology; grinding; flotation; fine particle

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1. Introduction

1.1. The Characteristic of Mineral Slurry

Froth flotation has been the most widely used approach for treating complex low-grade and finely disseminated ores. Flotation pulp consists of micro-particles with a certain grinding fineness, which is generally expressed as the mass ratio (%) of less than 0.074 mm/the total grinding product (the grinding fineness depends on the target mineral liberation degree) [1]. In mineral flotation operations, the mineral slurry is usually treated via grinding, agitation, flotation, and transportation, and the micro-particle slurry is often mixed with chemical reagent (mill and agitation tank) under such conditions, with air bubbles being separated under certain shearing fields in water-used equipment, such as a flotation cell or column [2].

One characteristic of the micro-mineral slurry is polydispersity, including size and shape. The particle size distribution of the micro-mineral slurry usually covers a quite large range, from less than 1 nm to larger than 1 mm, for there exists a series of dispersed components including organic/inorganic molecules, ions, macromolecules, colloids of mining reagents, suspending particles, and settling aggregation or grains [3]. For metallic minerals and coal particles in handling plants, the particle size in slurry is on average approximately 100 μm [4]; for some clay minerals, the particle size in handling operations is mostly less than 10 μm [5]; but for clay mineral-based materials, the particle size could decrease to less than 0.1 μm [6]. As for the particle shape, most of the mineral crystals after crushing and grinding have a globule-like morphology. For the nesosilicate minerals and coal, the particles in the processing operation are usually of an irregular angularity [7]. For the phyllosilicate minerals such as talc, graphite, and mica, particles in slurry are often in lamellar or platy, while the chain silicate minerals, such as chrysotile and serpentine, are often in a fibrous shape or have a silky morphology [8,9]. In a micro-mineral slurry, various kinds of minerals of different sizes and shapes always exist. Therefore, the complexity of the micro-mineral particle slurry makes it quite difficult to describe the size and shape using one or two of the single mineral characteristics.

Another typical characteristic of the micro-mineral slurry is the complex interactions among the different components, including solid-solid interactions, reagent-solid interactions, and dynamic bubble-liquid-solid effects. It has been widely acknowledged that these interactions are closely correlated to the solid content. For slurry with relatively coarse mineral particles and a small solid-to-liquid ratio, the particle interactions mainly manifest as simple mechanical actions, such as mutual friction, collision, and compression [10–12]. For slurry with relatively fine mineral particles and a high solid content, the surface force that originates from solid surface phase change via chemical reactions or reagent adsorptions determines the particle interactions. For slurry with agglomerated fine particles or flocs, the complex interactions should also include the parcel effect between the new-born flocs and primary fine slimes as well as the scrubbing effect between the new-born flocs and primary coarse grains [13–15]. For the particles with different shapes in slurry, it was thought that simple forces such as attractive or repulsive actions constitute the main particle interactions between the globule-like particles and irregular angular particles [16,17]. The solid content plays an important role in deciding the particle interactions, and it was widely thought that a high solid-to-liquid ratio could lead to more complicated slurry properties, especially for the fine mineral flotation process.

During the flotation operations, the particles in the slurry are not totally dispersed or isolated, and the slurry is not a homogeneous water system with stable flowability. The complex interactions among these particles depend on particle collision, aggregation, dispersion, floating, sinking, and transportation, which mainly determine the flow and deformation behaviors during the processing operations and have been understood using slurry rheology.

1.2. Rheology in Mineral Processing

Rheology is the science of studying the flow and deformation behaviors of fluid materials. The rheological parameters, such as viscosity, yield stress, viscoelasticity, have been demonstrated to indicate the particle interactions and the particle structures in a certain flowing field [2,17]. These common parameters are calculated by analyzing the shear rate vs. shear stress curves, shear stress vs. shear strain curves, and viscous modulus vs. elasticity modulus curves measured using a rheometer [18,19]. As a typical solid-gas-liquid suspension with polydispersity and complex interactions inside, the flow and deformation performance of micro-mineral processing slurry is usually determined using non-Newtonian rheology, since it displays common rheological behaviors including shear thickening, shear thinning, shearing yield, and compressing yield [20,21]. Therefore, slurry rheology has long been used as an effective parameter to understand the particle interactions and optimize processing efficiency, especially for fine mineral treatment [22,23].

Generally, the studying of mineral slurry rheology started when the effects of high viscous fluids formed by very fine mineral particles on the grinding rate and efficiency were first noticed [24]. At first, it was found that there existed a remarkable viscosity effect on the grinding process when the dilatant fluid, pseudoplastic fluid, or Bingham fluid were formed on a large scale inside the ball mill or rod mill [25,26]. Afterwards, in other processes, including dense medium separation, bevel flow separation, magnetofluid separation, and froth flotation, slurry rheology not only provided information about the very complicated inter-particle interactions in processes related to the flow of mineral slurry, but also explained the certain influences on the subtle processes of these operations [20].

In recent years, the scope of mineral slurry rheology has significantly expanded in regard to rheological methods [27]; rheological measurement tools [28]; and new rheological conceptions related to particle interactions, particle-bubble interactions, and bubble-bubble interactions under certain mineral processing operating conditions [29]. Therefore, this paper reviewed the published literature on the regulation and effect of applying pulp rheology to the grinding and flotation process, with the aim of establishing a quantitative relationship between the grinding-flotation efficiency and rheological parameters and to seek strategies that could accurately regulate rheological parameters. In addition, some discussions, as well as a potential research field for the application of rheology in the mineral processing industry, were also put forward.

2. Micro-Mineral Particle Slurry Rheometry

The rheological measurement instruments in mineral processing have been developing and promote the development of slurry rheology. In early times, slurry rheology was mainly developed via naked-eye observations or manual qualitative testing, such with the spatula test, touching test, or flow cup test. These measurement results were useful and effective for directly judging the viscosity and elasticity of tested materials. However, these qualitative testing results could not provide the dynamic rheological information for measuring the shearing field or shearing intensity. For this, the viscometer and rheometer, which could quantitatively measure the shear rate and stress, were developed successively. So far, most of the rheological measurements have been completed using the two kinds of rheology equipment.

2.1. Rheological Measurement Using Viscometers

Around the 1990s, various kinds of viscosimeters that could provide the flowing and deformation performance of slurry under several fixed shear rates were widely used, such as the rotational viscometer and capillary (tube) viscometer [30,31]. For industrial slurry, the rotational viscometer has been proven to better suit than the capillary viscometer for its measurement principle [18,32]. The rotational viscometer calculates the viscosity by measuring the torque that resists the deformation and flow of slurry and recording the rotation rate of the measurement fixture dipped into the suspensions [19,27,33]. The viscosity value is determined by transferring the torque and rotation rate to the shear stress and shear rate, respectively, based on device parameters such as shape, surface flatness, volume, dip angle of the measurement fixture, and sample holder [34,35].

Though the rotation mode of the viscosimeter could reflect the actual shear conditions in the mineral processing operations, such as agitation in the tank and flotation cell, it could only conduct single-point measurement services. Only the viscosity value under several limited and several fixed shear rate values (usually 4 to 6 fixed shear rate values) could be obtained. However, the available shear rate selections for the rotational viscometer do not always reflect the actual shear rate distributions in the shear fields of mineral processing operations. They may deviate significantly when the micro-mineral slurry presents shear thickening, shear thinning, and other specific rheological performances.

2.2. Rheological Measurement Using Rheometers

In the late 1990s and the 21st century, corresponding rheometers fixedly assembled with computers appeared and made it possible for the continuously variable measurement to overcome the drawbacks of the viscometer. Similar to the rotational viscometer, the rotational rheometers also measure the torque applied on the measurement tools and its rotational speed and utilize the torque and rotation rate values to calculate the rheological parameters [31,36]. However, different from the viscometer, the rotational rheometer has a continuous control system that can measure the shear stress at any designed shear rate, making it more convenient for simulating the exact shear conditions under any constant or variable moving or agitating speed [28,34,37]. What is more, the rheometers can measure the shear strains of the slurry under certain shear conditions, which provide the viscous and elastic property of the aggregated or dispersed micro-mineral slurry as well as the information on the very subtle dynamic changes in the internal particle structures of the slurry under a gradually applied yield stress [38,39].

There have been many measuring tools used for rheology measurements, such as coaxial cylinders, cone plates, parallel plates, vanes, and impellers. For homogeneous or uniformly dispersed solution systems, coaxial cylinders, cone plates, and parallel plates could accurately measure the rheological properties. For typical heterogeneous systems such as mineral slurry, vanes and impellers have been demonstrated to be more applicable because these tools could effectively mix the dispersed micro-mineral particles before rheology measurement and avoid the settling problems of particles or aggregations when it comes to the measurement processes.

2.3. Developments in Rheological Measurement: Dynamic Oscillatory Techniques

There has also been a recent rise in the measurement of viscoelasticity of mineral slurry, mainly realized using dynamic oscillatory techniques and which could help distinguish cross-linked network structures from isolated clay aggregates [37]. Unlike the viscosity measurement or yield stress calculation, the dynamic oscillatory techniques aim to characterize the particle network or specific superstructures by measuring the viscous modulus and elastic modulus of the slurry in the linear elastic region. Strain sweep and frequency sweep were suggested to be two main measurement methods used to clearly see the degree of dispersion and the strength of the inter-particle association in the slurry [38].

The fundamental theory of using the viscous modulus and elastic modulus to describe the multi-particle structures and dispersed particles is the viscoelasticity of network structures or super spatial structures formed by micro-mineral particles. When the micro-particles transform into network structures or other super-specific structures, the new aggregates can obtain a solid-like elasticity, which cannot be effectively detected and quantified via viscosity or yield stress measurements [39]. Therefore, the elastic modulus parameter was proposed to represent the elasticity property. The viscous modulus was used to characterize the viscous attraction among the particles in the multi-particle structures under relative static hydrodynamic conditions. One of the advantages of the dynamic oscillatory rheology test is that the micro-mineral slurry is not shear-destroyed. Only deformation and linear disturbance of the micro-mineral slurry happens using this measuring mode, and it is possible to determine its variation continuously. Another advantage of the oscillatory rheology test is that the testing results are independent of the shear rate, making it more objective when making a comparison [38,39].

In short, the development of micro-mineral particle slurry rheometry is heading toward the online and simultaneous characterization of inter-particle interactions, including both the viscous resistance and viscous attractions during the mineral processing operations.

3. Quantitative Correlations between Rheological Parameters and Processing Efficiency

Since mineral slurry rheology can shed light on particle interactions, it has long been utilized to build relationships with processing operations. To some extent, it has been used as an indication of the regulating variables.

3.1. Rheology in Ore Grinding

The rheology effect in grinding operations was the first to draw the attention of researchers to the correlation between rheology and mineral processing operations. It was found in 1985 that the grinding medium tended to be centrifugal when the slurry viscosity exceeded a specific value (named the critical value), which resulted in the balls sticking to the mill wall during rotation. The polymeric additives were demonstrated to exhibit increasing [40] or decreasing viscosity effect, and an alteration in the rheological behavior of the pulp could prevent the balls from centrifuging, with the mill subsequently drawing full power and achieving higher grinding efficiency [25]. Later research confirmed that the measured shear rates inside a ball mill were approximately located in the range of 13 to 730 s^{-1} [31] As the rheological nature of the micro-mineral slurry changes, the grinding index can become quite different, and hence the solving strategies for increasing the grinding efficiency can also be different. For pseudoplastic slurry containing a higher solid content and a lower proportion of fine particles, such as primary or secondary mill products, the approach to increasing the grinding efficiency was to enhance the viscosity by increasing the fine particles mass ratio and observing appropriate regulation of the classifier. For dilatant slurry with a relatively low solids content and a high proportion of fine particles, such as tertiary or regrind mill products, the way to achieve a high grinding efficiency was found to raise the slurry density by reducing water addition, except in cases where the slurry already has a high yield stress [24].

The rheology effect on grinding efficiency also differs from the effect of the particle size. For mineral processing grinding operations aiming to obtain the fully dissociated mineral particles that are within an average of 50 µm, apparent viscosity was the main rheological parameter influencing the grinding efficiency [26]. However, for the ultrafine grinding of industrial materials such as ceramic materials, pigments, chemical products, microorganisms, pharmaceutics, and paper that aims to obtain powders less than 1 µm, it has been proven and comprehensively reviewed that the yield stress is the dominant rheological parameter and exhibits a high correlation with the power draw, particle breakage rate, net production of fine particles, and the product size distribution, and their relationships are displayed in Figure 1 [26,41].

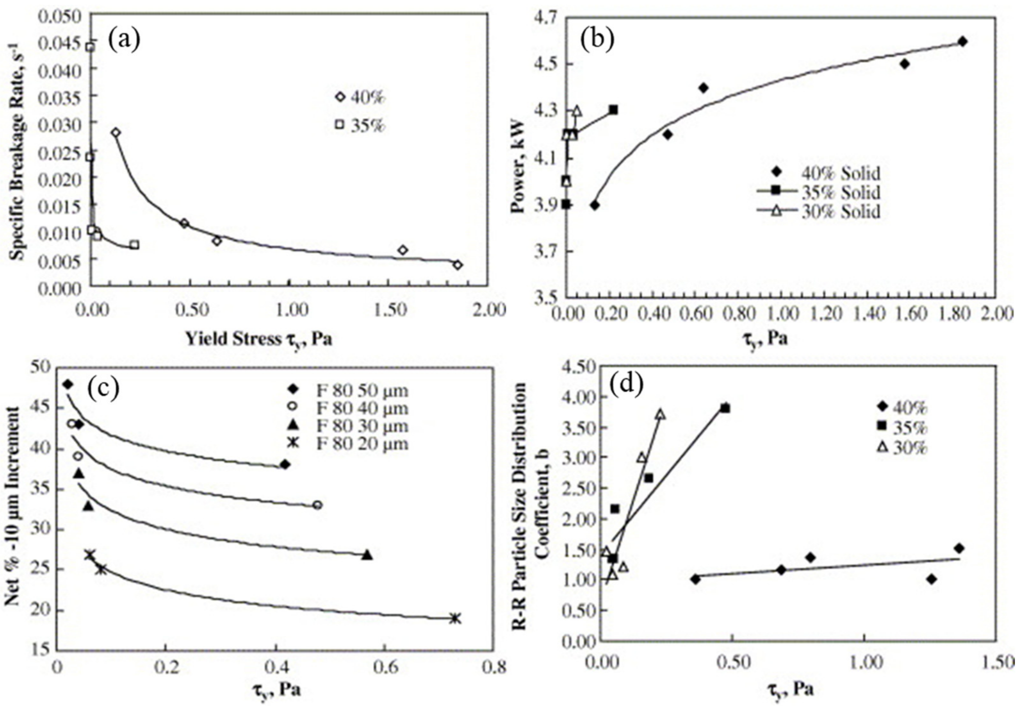


Figure 1. Specific breakage rate (**a**), agitator power (**b**), net production of −10 µm (**c**) and Rosin-Rammler particle size distribution coefficient (**d**) vs. pulp yield stress [26].

Apart from the physical factors mentioned above, chemical factors could also help adjust the slurry rheological behavior and improve the grinding efficiency. It has been widely proved that chemical additives in mills, named grinding aids, have the benefits of promoting grinding efficiency, decreasing water consumption, optimizing material mobility, and reducing the size distribution range of grinding products [42,43]. The function mechanisms of the grinding aid in changing the slurry rheological behavior and the subsequent product fineness, size distribution, energy expended, and physicochemical environment, and have been fully reviewed [44].

3.2. Rheology in Froth Flotation

3.2.1. Rheological Properties of Froth Flotation Slurry

Solid concentration has been widely demonstrated to be the fundamental parameter that determines the rheological behavior of flotation slurry and has been reviewed previously [23]. Unlike mineral slurry in mills, a significant feature of flotation slurry is that it contains large amounts of bubbles, which could exert remarkable influence on its rheological properties. With flotation slurry, the internal structures are dependent on the adsorption, collision, adhesion, bubbles merging, aggregation, dispersion, and motion behaviors among all of the mineral particles, dissolved reagents, formed bubbles, and filled air flows, as well as other components. They are mainly determined by the attractive forces and repulsive forces due to all kinds of electrical interactions, adsorption layer interactions, and Van der Waals interactions [13,22]. As a result, flotation slurry can display typical rheological phenomena such as shear thickening, shear thinning, dilatancy or pseudo-plasticity in agitation operations, or separation processes [45]. Moreover, when one of the above aspects is changed, the overall rheological behaviors will also undergo non-negligible changes and further influence the subtle processes of flotation operations, such as conditioning and mineralization particle-bubble transportation and enrichment of froth. Based on this, the utilization of slurry rheology has the potential to act as a control variable for flotation operations.

In the field of flotation rheology, the viscous effect of the micro-particle fluid is usually tested using the shear rate vs. shear stress curves in the dynamic conditioning and flotation processes. The aggregation effect of the internal structures in the slurry is often studied by observing the shear stress vs. shear strain curves [12,46]. The former effect is often characterized by measuring the shear stress that is exerted on flotation slurry when slurry is in shear conditions (for agitation tanks is it commonly larger than 200 s^{-1}, and for flotation cells it is usually in the range of 40 s^{-1}~150 s^{-1}), which allows the interactions between all of the fluid components in the dynamic conditions to be determined [19]. The latter effect is usually presented by measuring the shear strain of the stabilized slurry when gradually increasing shear stress is applied in static shear conditions, which allows for the information about the shear resistance strength of internal structures that reflect the electrostatic force, Van der Waals force, hydrophobic force, and steric hindrance between the dispersed or aggregated particles to evaluated [34].

At the present time, the research on slurry rheology in flotation fields has been widely extended to sulfide ores, oxide ores, salt-type ores, and clay ores, as shown in Table 1.

Table 1. A collection of published papers related to the rheology parameters and flotation performance.

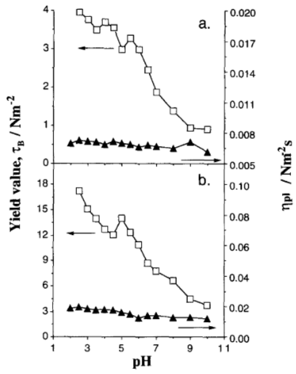
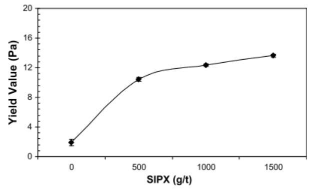
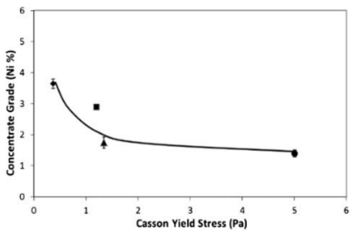
Ore Type	Rheology Parameters	Relation to Slurry Properties and Flotation Performance	Key Figures	References
Fine galena ore	Apparent viscosity; yield value	Apparent viscosity was reported and discussed in the context of particle interaction; the yield value was used to evaluate the fine particle aggregation.	 Extrapolated yield values and plastic viscosities for galena particle slurries as a function of pH: particle solid volume fractions were 0.0625 (**a**) and 0.1 (**b**).	[47,48]
Ultrafine sphalerite ore	Yield value	Yield value was used as a measure of particle interaction; the yield stress of flotation slurry significantly increased from 2.0 MPa to approximately 14.0 MPa with the addition of 1800 g/t of copper sulphate and 1500 g/t of iso-propyl xanthate, reflecting the reagent effect on particle interactions.	 Yield value as a function of xanthate concentration for the mixed system (60% wt sphalerite + 0.5% wt silica) in 10^{-3} M NaCl at pH 9. Samples were previously conditioned with 1800 g/t of copper sulphate prior to xanthate addition.	[49,50]
Sulfide nickel-copper ore	Apparent viscosity; shear rate-shear stress curves; yield stress	Apparent viscosity was used to represent the coagulation of ground serpentines and reflect the mineralogical properties of serpentines; the shear rate-shear stress curves were used to report the shear viscosity behavior of different mineral slurry such as serpentine and nickel sulfide. The concentrate grades consistently decrease when Casson yield stress exceeds 1.5–2.0 Pa; other kinds of yield stress were found to decrease the flotation selectivity as it rose, which could be used as a regulation variable in flotation study.	 Effect of Casson yield stress on grade of flotation concentrates: 5% solid (◆), 10% solid (■), 15% solid (▲), and 20% solid (●).	[51–59]

Table 1. *Cont.*

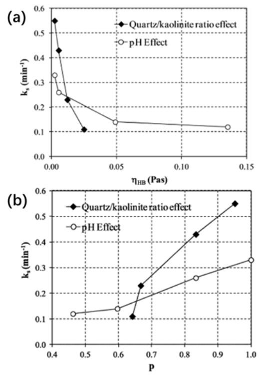
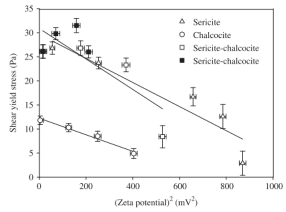
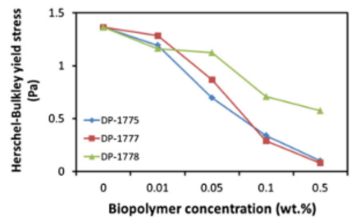
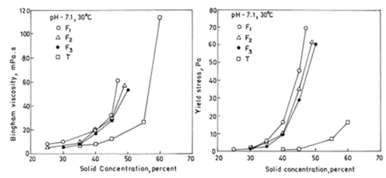
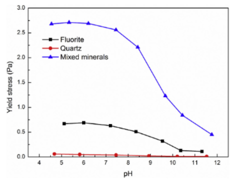
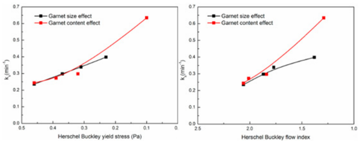
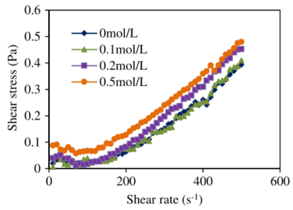
Ore Type	Rheology Parameters	Relation to Slurry Properties and Flotation Performance	Key Figures	References
Chalcopyrite type copper ore	flow coefficient; flow index; yield stress; apparent viscosity	Flow coefficient and flow index were used to link the particle interactions between chalcopyrite and clays with flotation kinetics; yield stress was utilized to evaluate the effect of the clay type on the shear behaviors of mineral slurry and quantified the reagent effect on the surface modification of clays; apparent viscosity could reflect the effect of ion concentration on the particle interactions and could be correlated to the froth properties.	 Flotation rate coefficient for slow floating material as a function of the Herschel-Bulkley (**a**) flow coefficient (η_{HB}) and (**b**) index (p).	[60–64]
Chalcocite type copper ore	Yield stress	Yield stress was found to be in a linear relationship with the square of the particle zeta potential. It could be used to judge the degree of sericite-chalcocite hetero-aggregation under certain flotation conditions.	 A linear relationship arising from the plot of the shear yield stress against the square of the particle zeta potential for individual sericite and chalcocite and their mixed-phase pulps.	[65]
Copper-gold ore	Shear rate-shear stress curves; shear stress-apparent viscosity curves	Shear rate–shear stress curves were used to illustrate the mineral slurry with different content of clays and state the viscous effect of calcium-containing gangue minerals in flotation processes; shear stress-apparent viscosity curves were used to link the entrainment with flotation variables such as depressant type and dosage.	 Herschel-Bulkley yield stress in the absence and presence of DP-1775, DP-1777, and DP-1778.	[66–72]
Nickel laterite	Bingham viscosity; yield stress	Viscosity value was found to play a key role in mineral slurry transportation; yield stress was reported to be closely linked to particle shape, roughness, and porosity.	 Variation in Bingham viscosity (**left**) and yield stress (**right**) with the solid concentrations for lateritic ores of four particle sizes (T is tailing; F_1, F_2, and F_3 are three different fine fractions).	[73–78]

Table 1. *Cont.*

<table>
<tr><th>Ore Type</th><th>Rheology Parameters</th><th>Relation to Slurry Properties and Flotation Performance</th><th>Key Figures</th><th>References</th></tr>
<tr><td>Fluorite</td><td>Yield stress</td><td>Yield stress was used as a degree of evaluating the hetero-coagulation between fluorite and quartz and found to be able to decrease the flotation rate constant.</td><td>

The yield stress of fluorite, quartz, and mixed-minerals slurry as a function of the pH (the total solid concentration at 15 vol%).</td><td>[46]</td></tr>
<tr><td>Scheelite</td><td>Herschel-Bulkley flow index and yield stress</td><td>Flotation rate constant for slow-floating scheelite was demonstrated to decrease as the Herschel-Bulkley flow index deviated from 1.</td><td>

Flotation rate constant for slow-floating scheelite as a function of Herschel-Bulkley yield stress (τ_{HB}, **left**) and flow index (p, **right**).</td><td>[12]</td></tr>
<tr><td>Coal</td><td>Shear viscosity; shear rate-shear stress curves</td><td>Viscosity corresponded to the entrainment of fine particles and the over-stability of the flotation froth; shear rate-shear stress was found to correlate to the micro-structure of slurry, reflecting the formed net-work structures in flotation conditions.</td><td>

Shear stress as a function of the shear rate in the pulp with different NaCl concentrations.</td><td>[79–83]</td></tr>
</table>

In short, as a special industrial suspension, the rheological behavior of the flotation slurry in the separation process is determined by variables such as the solid concentration, particle size distribution, surface charge, surface wettability, foam size, dissolved ions, and shearing fields. Therefore, it is of great importance to clarify how slurry rheological behavior affects the flotation subtle processes, such as collision, adhesion, aggregation, dispersion between particles, bubbles, and other components in dynamic flotation conditions to improve the flotation efficiency and selectivity. Additionally, here, we classify these effects into three main parts: flotation kinetics, froth rheology, and froth properties.

3.2.2. Effects of Slurry Rheological Behavior on Mineral Flotation Kinetics

Generally, the mineral froth flotation contains four kinetic processes between mineral particles and bubbles: collision, adhesion, transportation, and separation. If the flotation time keeps constant, a successful froth flotation process depends on the probability and rate of the above four kinetic processes. In the collision process between the mineral particle and the bubble, the particle could possibly adhere to the bubble only when the kinetic energy of the mineral particle could break through the hydration film and when the induction time was shorter than the contact time [84,85]. Therefore, the kinetic energy of the mineral particles and the induction time of the thinning/breakage of the bubbles is key to successful adhesion.

The rheological behavior of slurry affects the efficient collision process between the mineral particles and bubbles. Quantitative research on the correlation between the apparent viscosity of flotation slurry and the decaying rate of the kinetic energy of the mineral particle has demonstrated that, if the apparent viscosity of the flotation slurry increased by 5%, the decaying rate of the kinetic energy of the mineral particle would double, and the probability of the efficient collision and adhesion between the mineral particle and flotation bubble would decrease by 12% [51]. In the flotation process, when the apparent viscosity is relatively high, the motion and transportation of the mineral slurry will flow into different layers in the horizontal direction where the shear rate is similar [86]. Inside each layer, the motion velocity and path of the mineral particles, bubbles, and flotation medium are nearly the same; between different layers, these values exhibit noticeable differences [87]. In this situation, mineral particles and flotation bubbles almost have little chance to collide and adhere. The transportation and the flotation of the bubbles carried with mineral particles almost totally depend on the circulation of the flotation medium in the cell, which will inevitably decrease the flotation rate of the desired minerals in the flotation operations [88]. In the flotation of a copper sulfide ore with magnesium aluminum silicate used as gangue minerals, tests on the relationship between the rheological property of the flotation pulp and the flotation kinetics have found that, when the viscosity coefficient of the flotation pulp increased from 0.002 Pa·s to 0.02 Pa·s (at the same time the yield stress of flotation slurry increased from 0.07 Pa to 0.28 Pa), the flotation rate constant of the copper sulfides decreased from 0.55 min^{-1} to 0.11 min^{-1} [59], and the multilayer flow of the flotation slurry was rather obvious, coupled with demonstrating quite low collision efficiency [54,89]. In this case, the flotation could hardly proceed, and the separation efficiency was greatly influenced due to the flotation slurry's rheological behavior changes.

The rheological behavior of slurry affects the efficient dispersion process of the mineral particles. When the rheological property of the flotation slurry is changed, the intensity of the particle interactions and the shear fields will occur a certain degree of variation. For example, when the apparent viscosity of the flotation pulp rises, the turbulent flow intensity of the flotation pulp in the shear cyclic process will decrease significantly, which will bring about markedly increased resistance toward the motion of the bubbles and mineral particles [52,55,90]. In this case, a general intensity of mechanical agitation could hardly realize the uniform distribution of the slurry density or reagent concentration, and will further result in the decrease in the dispersion of the mineral particles and bubbles in the flotation cell [91,92]. The series of changes in the cell will inhibit the effective interactions between mineral particles and flotation bubbles and influence the transportation of the bubbles attached with mineral particles. As a result, the foundation of flotation will be destroyed. Especially in the flotation of finely disseminated ores, the fine particle effectiveness, such as high specific area, small mass, and small momentum, will enhance the formation of super structures in slurry. The super structures will induce a high degree of particle aggregation in certain agitation areas where the agitation distributions could not be involved [8,9,60]. It has been suggested that increasing the energy input in the conditioning operation, adding an agitation medium, and using suitable slurry rheological reagents could adjust the complicated slurry rheology [93–95], thus achieving optimization of the kinetic environment and subsequent improvements in the flotation rate.

In froth flotation, slurry rheology not only reflects the overall comprehensive interactions of all the components in slurry, but also helps explain certain effects on the subtle processes of flotation kinetics. Therefore, it is of great significance to consider it when studying the flotation rate and improving the flotation kinetic environment and the flotation efficiency.

3.2.3. Effects of Frother Type on the Rheological Behavior of the Froth

Pine oil and MIBC (methyl isobutyl carbinol) are two main kinds of frother widely used in froth flotation operations and were reported to induce quite different rheological effects on froth characteristics. In addition, fatty acids and their derivatives, and even amines, can act as both collectors and frothers and exert a certain influence on the rheological behavior of froth [96,97].

When pine oil is used as the flotation frother, especially in sulfide ore flotation, the attraction performance between the bubbles is high. Therefore, the bubbles carried with hydrophobic mineral particles can easily form structured network slurry [98]. In the transportation and motion process of the networks from the slurry phase to the froth zones, the networks with high yield stress can stably exist in the high shear fields, and the overall apparent viscosity of the flotation slurry is therefore increased [79,99]. When MIBC is used as a frother, the bubbles are easily merged in the slurry phase, relatively low apparent viscosity of the slurry is achieved [100].

In oxidized ore and salt-type ore flotation, fatty acids and their derivatives are commonly used as both collectors and frothers, and they always form very stable froth due to their own foamability and their interactions with the ions dissolved by the minerals, which may result in a large number of colloids in the flotation solutions. The bubbles, minerals, ions, and the colloid mixtures may lead to complicated rheological behavior when it comes to the overall flotation pulp. Specially, if cationic surfactants such as amines are used, the flotation bubbles are hard to generate and are always over-stable [101,102].

In the slurry circulation inside the flotation cell, the flotation slurry usually exhibits a certain flow stress and viscous effect, resulting in a deteriorated dispersion state in the flotation cell. When there are many fine particles or clay ores in the flotation slurry, the fine particle effectiveness will always markedly change the rheological behavior of the froth zone by forming relatively stable superstructures in slurry, as seen with high viscosity and yield stress. Typical structures are network structures, aggregate structures, chain structures, and other superstructures [103,104].

3.2.4. Effects of the Rheological Behavior of Froth on Mineral Flotation Froth Properties

Apparent viscosity affects the "secondary enrichment" of flotation froth. Some studies indicate that the flotation froth properties will markedly vary with the slurry's apparent viscosity [105]. The increase in the slurry's apparent viscosity results in an enhancement of the surface strength of the bubble liquid film and drainage time, which will finally weaken the "secondary enrichment" of the flotation froth in the slurry froth zone [106]. When the bubble is dissolved in the aqueous solution with increasing viscosity, the diffusion relaxation time of the gas and the half-life of the aqueous froth will be obviously extended, which will prevent the bubbles in the slurry from contacting and merging [107]. Additionally, with the strengthening of the slurry viscosity, the average size of the bubbles in the slurry will decrease, the bubbles tend to be uniform in shape, and the resulting increase in froth yield stress will improve the overall stability of the froth [92,108]. This is due to the fact that the velocity of the yielding, deforming, merging, and breaking of the froth is proportional to the product of the solubility and diffusion coefficient of the gas in the liquid phase, and it is worth noting that the latter two gas parameters decrease with the rise in solution viscosity [95,109].

The rheological behavior of froth affects the entrainment behavior of the flotation froth. As the viscosity and yield stress of the flotation slurry increase, the froth stability will increase, which will lead to the rise in the mechanical entrapment of the fine gangue minerals and decrease the flotation selectivity (see Figure 2) [59,110]. When the apparent viscosity of the flotation slurry increases, the amount of the fine gangues entering the foam zone from the fluid column within the Plateau boundary will increase and the entrainment will rise [61]. Inside the Plateau boundary, the motion state of the entrained mineral particle is dependent on the equilibrium of three factors: gravity sinking, rising with liquid column, and solid diffusion. For a specific mineral particle, its flotation via entrainment mainly depends on two actions: geometric diffusion and Plateau boundary diffusion [111,112]. As the stability of the froth rises, the resistance of the two diffusion actions will also increase, and therefore, the probability of the flotation of the gangue minerals due to entrainment will also increase and the total flotation selectivity will be weakened.

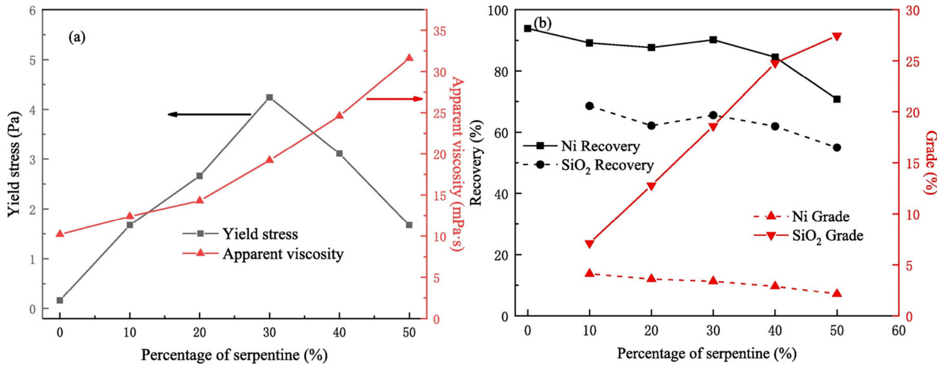


Figure 2. Effect of the percentage of serpentine on (**a**) rheological behaviors and (**b**) flotation performance of mixed minerals in the presence of PBX with a total pulp concentration of 40 wt% (pH = 9.5~10, PBX: 1.5×10^{-3} mol/L, MIBC: 100 mg/L) [59].

Based on the above-mentioned understanding of the relationship between pulp apparent viscosity and froth stability, the influence of the rheological behavior of slurry on the froth behaviors in the froth flotation of various practical ores is attracting more and more researchers. In the separation of fine chrysotile or serpentine and nickel sulfide minerals, it was observed that when the mass proportion of chrysotile in mixture minerals increased, both the overall apparent viscosity and the yield stress rapidly rose [52,55]; when the pulp yield stress was higher than the 1.5–2.0 Pa range, the thickness of the flotation froth zone was obviously reduced, along with the rapid decline in the concentrate grade [57]. It was noted that the fine chrysotile existed in the pulp as a network of intertwined fibers, which were hardly sheared or damaged. Further, it prevented the nickel sulfides from being adhered to and carried by the bubbles, and finally resulted in decreased flotation efficiency [54]. In the flotation of fine coal, when sea water rich in Na^+, Ca^{2+}, Mg^{2+} and other ions was used as a flotation medium, the apparent viscosity of the flotation slurry increased [78,113]. Additionally, the fine coal particles were promoted to form flocs with high yield stress and further increased the stability of the froth zone [7,82,114], thus improving the flotation recovery of the fine coals. In the flotation test for a gold-bearing copper ore, the results proved that the higher the fine calcite and dolomite content, the more complex the pulp rheology, which was accompanied with shear-thickening behaviors and stability influence; the merging property of the flotation foam and the corresponding changes will further exhibit an effect on the entrainment of the gangue minerals, the enrichment of valuable minerals, and other flotation subtle processes. Therefore, the result can be determined as aggregation [53,66–68] coupled with deteriorated copper ore flotation. The rheological measurement and the froth property test verified that the dissolution of the calcium-containing minerals could induce the formation of network structures using the clays in the slurry, which would generate an adverse influence on the sufficient dispersion of the bubbles in the circulation process and the merging of bubbles carrying mineral particles [69–71]. As a result, the "secondary enrichment" of flotation froth behaviors was severely weakened, as was the normal flotation process.

On the whole, slurry rheology demonstrates great potential when it comes to clarifying how pulp rheology affects the flotation froth when searching for methods to improve the foam property as well as increase the separation efficiency.

3.2.5. Manipulating Flotation Rheology

Based on the pulp rheological effect on the froth flotation performance, many researchers have tried to manipulate flotation rheology to eliminate this negative effect through regulating the process variables, mainly including a reagent, external field, and rheological medium.

Some flotation reagents were found to have dual functions, acting as surface modifiers and rheological regulators. The pH modifiers, such as lime and soda ash, were observed to exhibit different effects on rheological behavior of flotation pulps. The lime increased apparent viscosities more than soda ash in copper-gold ores mixed with kaolinite, for the Ca^{2+} released from lime could lead to the formation of stronger kaolinite aggregates that were more easily entrained during flotation. Therefore, more dilution of the flotation concentrate grade occurred when adjusting the pH with lime [67].

Except lime, using cations or even sea water also proved to effectively adjust the rheological behavior of the pulp and enhance the flotation efficiency. For pyrite ores with bentonite, the addition of $CaCl_2$ was found to modify the rheological characteristics by suppressing the swelling properties of bentonite and altering the surface charge properties of bentonite clay particles. Further, the rheological effect of the bentonite, i.e., the decreased movement of bubbles and particles within the flotation pulp, was reduced [115]. Other cations, such as Na^+, K^+, Mg^{2+}, and Ca^{2+}, were also demonstrated to interact with bentonite and reduce the apparent viscosity of the copper ore. What is more, the divalent cations, Mg^{2+} and Ca^{2+}, had a more significant effect on pulp viscosity and copper flotation than monovalent cations Na^+ and K^+ [64]. Based on these findings, the sea water was introduced as the flotation medium to reduce the swelling capacity of bentonite and modify the association modes of bentonite platelets in the flotation pulp. The results showed the breakup of links between the structures with relatively large pores, and finally contributed to the improvement of copper and gold flotation [69].

Dispersant was found to be able to mitigate the negatively rheological effects of clay mineral flotation. In the copper and gold ore flotation pulp with non-Newtonian behavior and a high apparent viscosity, a lignosulfonate-based bio polymer (DP-1777) was applied to improve both the gold grade and gold recovery significantly through the reduction of mechanical entrainment and pulp viscosity, respectively [71]. The lignosulfonate dispersant could also eliminate the negative effect of clay minerals on copper and gold flotation when the amount of iron oxidation products originated from the grinding media was minimized [116]. Other reagents, such as H_2SO_4, were also used to attack and dissolve the inter-fiber networks made up of micro serpentine flocs that were spread across the pulp volume, and by creating acidic flotation conditions, the impact of the pulp's rheological behavior on Ni ore beneficiation was strongly alleviated [58].

External field-reinforced pulp conditioning could also adjust the rheological behavior of pulp. It has been proven that microwave pre-treatment could greatly reduce the shear viscosity (average 80% reduction at 200 s^{-1}) and direct yield stress (peak yield stress reduced by 92%–93%) of ultramafic nickel ore slurries. The underlying mechanism for this rheological change was ascribed to the conversion of serpentine to olivine, which effectively avoids the serpentine's troubling rheological effects in the form of high viscosity and yield stress on the comminution and flotation operations [57]. Further, the energy of the microwave was found to be closely linked to the change in the iron ore-water slurry rheological behavior. We tested to see whether the microwave-treated ore had better rheological properties compared to the untreated ore. With more microwave energy, the iron ore-water slurry tended to undergo shear thinning and was easy to transport as it exhibited pseudo-plastic behavior. The action mechanism might be dependent on the decreased viscosity and density of the slurry with the increase in the microwave energy [117]. As more novel pulp conditioning devices or energy fields are being developed for fine particle flotation, the method for adjusting the challenging slurry rheological behavior may also be put forward correspondingly.

Recent years have witnessed a growing attention on using coarse particles as medium to adjust the rheological behavior of slurry and improve the flotation efficiency of fine particle flotation. In fine skarn-type scheelite ore flotation, fine calcite was found to dominate the high viscosity and yield stress due to the bridging effect of the hydrogen bonding between the fine calcite surfaces that formed the network structures, as shown in Figure 3 [118]. Interestingly, by adding garnet or glass beads as an agitation medium, the network structures could be destroyed, resulting in changes in the flow index of the flotation slurry. It was calculated that as the spiked agitation medium became coarser, the flotation slurry was found to be more similar to the Newtonian fluid with less particle interactions and improved flotation kinetics [12].

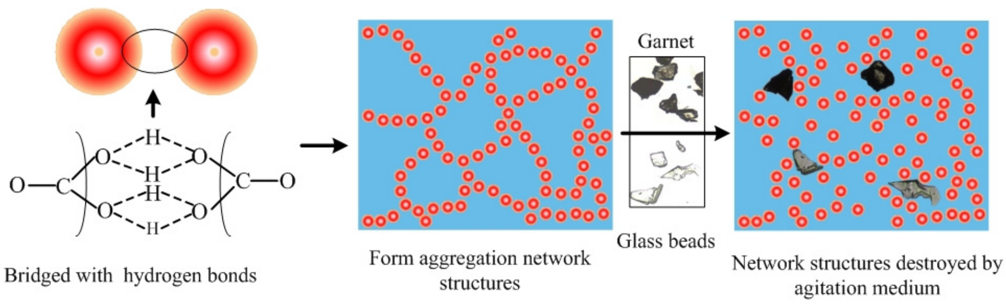


Figure 3. The interactions between fine calcite particles (−20 μm) in flotation slurry spiked with an agitation medium [118].

Coincidentally, this method also worked for controlling the flotation rheological behavior of the Cu-Ni sulfide ore containing large amounts of fine serpentine. It was found that the hetero-coagulation was not the only factor affecting the flotation of Cu-Ni sulfide-containing serpentine, the high pulp viscosity could also worsen that. The addition of coarse garnet particles (−104~+44 μm) could markedly decrease the pulp yield stress and limit the hetero-coagulation. Meanwhile, it was observed that the applied garnet could also decrease the pulp viscosity and that the synthetic actions improved Cu-Ni sulfide flotation, showing increased Ni recovery [59].

4. Conclusions and Potential Future Development

This paper reviewed the progress of rheological measurement technology and the influence of rheological behavior in grinding and flotation. It revealed that apparent pulp viscosity and yield stress were two important rheological parameters guiding grinding and flotation operations and that the measurement technology measuring them had achieved satisfactory progress. At the grinding stage, pulp rheology was highly correlated with power draw, particle breakage rate, net production of fines, and product size distribution, and it was observed that the energy consumption for crushing and grinding occupied the largest proportion in the total energy consumption of the beneficiation process, up to 40%–60%. Therefore, adjusting the rheological behavior of the pulp shows high application value in grinding energy saving and efficiency. In froth flotation, the rheological behavior of the pulp not only reflected the comprehensive interaction among mineral particles, bubbles, and flotation media, including collision, adhesion, transportation, and separation, but also had a significant impact on flotation kinetics. In addition, increasing the flotation froth stability would lead to the weakening of the flotation froth's secondary enrichment and the enhancement of mechanical entraining, thus worsening the mineral processing index, which could be eliminated by adjusting the pulp apparent viscosity. Based on the importance of rheology in mineral processing operations, more and more researchers are paying attention to improving grinding and flotation efficiency by controlling the rheological parameters of pulp and froth through the adjustment of process variables. However, it was worth noting that the real-time monitoring and controlling of the rheological parameters of pulp and froth was the key to achieving the successful application of rheological properties in the fine mineral processing industry.

In conclusion, to obtain better grinding and flotation efficiency, investigating the following areas is recommended:

(1) Monitoring the pulp and froth's rheological parameters in real-time using rheological equipment and establishing correlations with mineral processing industry indexes and process variables, so that rheological control becomes an effective approach for increasing the grinding and flotation efficiency.

(2) Based on the obvious significance of fine particles (−10 μm) on slurry and froth properties, rheological research on the enhanced collection and inhibition of over-grinding mineral particles could be investigated so as to improve the fine particle flotation efficiency.
(3) Identifying the crucial flotation variables such as pH, solid concentration, dispersants and particle size, etc., affecting the sulfide minerals floatability, then exploring the influence of these variables on the pulp and froth's rheological properties in an attempt to reveal the internal mechanism of serpentine inhibition from the perspective of particle interactions and flotation kinetics.
(4) The rheological behavior of froth potentially acts as a correlation index to predict the recovery and grade of flotation concentrate, helping us to respond quickly to variations in the complex flotation pulp system, which is of great significance to stabilize the production indexes.

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