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Review

A Brief Review on Micro-particle Slurry Rheology in Grinding and Flotation for Enhancing Fine Mineral Processing Efficiency

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Abstract: These years have witnessed growing research on applying rheology in grinding and flotation treatment of finely disseminated ores. The slurry rheology has long been identified as the comprehensive effect of inter-particle interactions, including their aggregation (coagulation and flocculation) 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 phenomenon 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 concluded and revealed thoroughly, without which the underpinning mechanism for enhancing the processing efficiency has been difficult to discover. This paper reviews the current application and importance of rheology in the fine mineral processing, and the potential research direction in the field is proposed.

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

1. Introduction

1.1. The characteristic of mineral slurry

Recent years have witnessed a quite fast development of minerals engineering due to the rapidly increasing need for various metal resources from modern industries. Mineral processing aims to recover or extract the valuable minerals from various ore deposits by crushing, grinding, beneficiation (gravity concentration, magnetic separation, electric separation, froth flotation and other methods). Due to its adaptability and effectiveness, froth flotation become the most widely used approach to treating complex low grade refractory ores. Flotation pulp is consisted of micro-particles with a certain grinding fineness, which is generally expressed as the mass ratio (%) of less than 0.074 mm to the total grinding product (Grinding fineness depends on the target mineral liberation degree) [1]. In minerals processing operations, the mineral slurry is usually treated by grinding, agitation, flotation, transportation, under which conditions the micro-particle slurry is often mixed with chemical reagent (mill and agitation tank), air bubbles and was always separated under certain shearing fields in water-used equipment, such as spiral separator, flotation cell or leaching tank [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 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, macromolecule, colloids of mining reagents, suspending particles and settling aggregation or grains [3]. For metallic minerals and coal particles in handling plant, the particle size in slurry locates in the average range of 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]. Generally, the average diameter

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size of solid particles in minerals processing is around 75 μm, usually represented by the percentage of particle content smaller than that value. As for the particle shape, most of the mineral crystals after crushing and grinding are in globule-like morphology. For the nesosilicate minerals and coal, the particles in the processing operation are usually in 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 fibrous shape or silkiness morphology [8,9]. In a real 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 is 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 effect. It has been widely acknowledged that these interactions are closely correlated to the particle size and morphology in the water system. For slurry with relatively coarse mineral particles, 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, the surface force that originated from solid surface phase change by chemical reactions or reagent adsorptions determines the particle interactions. It could lead to particle aggregation, flocculation or in stable dispersion. 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, and 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]. But for the mineral particles in platelike shape, aggregation with specific orientation occupying the particle interactions and the intertwining effect takes up the interactions among the fibrous or silkiness-like minerals [8,9].

During the mineral processing 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 attributed to the 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, viscous modulus vs. elasticity modulus curves measured by 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 by non-newtonian rheology, displaying 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 study on mineral slurry rheology started from noticing the effects of the high viscous fluid formed by very fine mineral particles on the grinding rate and efficiency [24]. At first, it was found out that there existed remarkable viscosity effect in 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]. Afterward, in other pro-

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cesses including dense medium separation, bevel flow separation, magnetofluid separation, and froth flotation, the slurry rheology not only provided information about the very complicated inter-particle interactions in processes related to the flow of mineral slurry, but also exhibited certain influences on the subtle processes of these operations [20].

In recent years, the scopes of mineral slurry rheology significantly expanded in the aspects of 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 systematically reviewed the current research development in mineral processing, including new rheological measurement methods and tools, the rheological property of micro-mineral slurry, and the influence of slurry rheology on processing efficiency which some potential developments in the area were predicated for more scientific discussions and technical investigations.

2. Micro-mineral particle slurry rheometry

The rheological measurement instruments in mineral processing have been developing and promoting the development of slurry rheology. In early times, the slurry rheology was mainly evaluated or measured by naked-eye observation or manual qualitative testing, such as spatula test, touching test and 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 in designed shearing field or shearing intensity. In this case, 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. Rheology 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 rotational viscometer and capillary (tube) viscometer [30,31]. For industrial slurry, the rotational viscometer has been proved to suits better 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, rotation rate to shear stress, shear rate, respectively based on the 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 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 value) could be obtained. However, the available shear rate selections of rotational viscometer do not always reflect the actual shear rate distributions in the shear fields of minerals processing operations. They may deviate quite when the micro-mineral slurry presents shear thickening, shear thinning and other specific rheological performances.

2.2. Rheology 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 viscometer, the rotational rheometer has a continuous control system that could measure the shear stress at any designed shear rate, making it more convenient for simulating the real 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 offer the viscous and elastic property of the aggregated or dispersed micro mineral slurry and reflect 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 quite many measuring tools used for rheology measurements, such as coaxial cylinders, cone plates, parallel plates, vane 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, vane and impeller 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 towards the measurement processes.

2.3. Developments in rheology measurement: dynamic oscillatory techniques

There also has been a recent rise on the measurement of viscoelasticity of mineral slurry, mainly realized by dynamic oscillatory techniques, 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 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 form into net-work structures or other super-specific structures, the new aggregates could obtain solid-like elasticity, which could not be effectively detected and quantified by viscosity or yield stress measurement [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 for giving the online and simultaneous characterization of the internal particle interactions, including both the viscous resistance and viscous attractions during the minerals processing operations.

3. Correlations between rheology and mineral processing operations

Since mineral slurry rheology has such close connections with the particle interactions, it has long been utilized to build relationships with processing operations. To some extent, it has been used as indications of the regulating variables.

3.1. Rheology in ore grinding

The rheology effect in grinding operations was the first to draw researchers' attention to the correlation between rheology and minerals processing operations. It was found in 1985 that there existed a critical pulp viscosity above which the grinding media tend to centrifuge because the balls cannot be detached from the mill wall during rotation. The polymeric additives were demonstrated to exhibit increasing [40] or decreasing viscosity effect, and the alteration on pulp rheology could make the balls no longer centrifuge, and the mill draw full power and higher grinding efficiency [25]. Later research confirmed that the shear rates inside a ball mill lie between approximately 13 and 730 s^{-1}.[31] As the rheological nature of the micro-mineral slurry changes, the grinding index could be quite different, and hence the solving strategies for increasing the grinding efficiency were also different. For pseudoplastic slurry with a relatively high solids content and a low proportion of fines, such as primary or secondary mill products, the method to increase the grinding efficiency was raising the viscosity by increasing the proportion of fines perhaps by suitable adjustment of the classifier. For dilatant slurry with a relatively low solids content and a high proportion of fines, such as tertiary or regrind mill products, the way to 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 particle size. For mineral processing grinding operations aiming to obtain the fully dissociated mineral particles in average of 50 μm, apparent viscosity was the main rheological parameter influencing the grinding efficiency [26]. However, for ultrafine grinding of industrial materials such as ceramic materials, pigments, chemical products, microorganisms, pharmaceutics and paper-making aiming at obtaining powders less than 1 μm, it has been proved and comprehensively reviewed that the yield stress is the dominant rheological parameter that strongly affects the power draw, particle breakage rate, net production of fines and the product size distribution [41].

Apart from the physical factors above-mentioned, chemical factors could also help adjust the slurry rheology and improve the grinding efficiency. It has been widely proved that chemical additives in mill, named grinding aids, can have some advantages such as enhancing grinding efficiency, reducing water usage, improving material flowability, and narrowing the particle size distribution of the grinding products [42,43]. The function mechanisms of the grinding aids in changing the slurry rheology and the subsequent product fineness, size distribution, energy expended and physicochemical environment, has been fully reviewed [44].

3.2. Rheology in froth flotation

3.2.1. Rheological properties of froth flotation slurry

Solid concentration had been widely demonstrated to be the fundamental parameter that determined the rheology of flotation slurry, which has been reviewed previously [23]. Unlike mineral slurry in the mill, a significant feature of the flotation slurry is that it contains large amounts of bubbles, which could exert remarkable influence on its rheological properties. In the flotation slurry, the internal structures are the comprehensive characters of the adsorption, collision, adhesion, bubbles merging, aggregation, dispersion and motion behaviors among all of the mineral particles, dissolved reagents, formed bubbles and filled air flow and 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, the flotation slurry could display typical rheological phenomenon such as shear thickening, shear thinning, dilatancy or pseudo-plasticity in agitation operations or separation processes [45]. Moreover, when one of the above characters is changed, the overall rheological behaviors will also meet 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 slurry rheology has the potential to act as a control variable for the flotation operations.

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In the flotation rheology field, the viscous effect of the micro-particle fluid is usually tested by 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 studying the shear stress vs. shear strain curves [12,46]. The former effect is often characterized by measuring the shear stress that exerted on the flotation slurry when the slurry is in shear conditions (for agitation tank commonly larger than 200 s^{-1}, for flotation cell usually in the range of 40 s^{-1}~150 s^{-1}), based on which the interactions between all of the fluid components in the dynamic conditions could be read [19]. The latter effect is usually presented by measuring the shear strain of the stabilized slurry when a gradually increasing shear stress is applied on in static shear conditions, based on which 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 could be evaluated [34].

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

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

Ore type	Rheology parameter	Relation to slurry properties and flotation performance	References
Fine galena ore	apparent viscosity, yield value	Apparent viscosity was reported and discussed in the context of the level of particle interaction; the yield value was used to evaluate the fine particle aggregation.	[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.	[49]
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, 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.	[50–58]
Chalcopyrite type copper ore	flow coefficient; flow index; yield stress; apparent	Flow coefficient and flow index were used to link the particle interactions between chalcopyrite and clays with flotation kinetics; yield stress was	[59–63]

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	viscosity	utilized to evaluate 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 ions concentration on the particle interactions, and could be correlated to the froth properties.	
Chalcocite type copper ore	Yield stress	Yield stress was found to be in a linear relationship against the square of the particle zeta potential. It could be used to judge the degree of sericite–chalcocite hetero-aggregation under certain flotation conditions.	[64]
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.	[65–71]
Nickel laterite	Bingham viscosity; yield stress	Viscosity value was found to play a key role in minerals slurry transportation; yield stress was reported to be closely linked to particle shape, roughness and porosity.	[72–78]
Fluorite	Yield stress	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.	[46]
Scheelite	Herschel Buckley flow index and yield stress	Flotation rate constant for slow-floating scheelite was demonstrated to decrease as Herschel Buckley flow index deviated from 1.	[12]
Coal	Shear viscosity; shear rate-shear stress curves	Viscosity corresponded to the entrainment of fine particles and the over the stability of 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.	[79–83]

In short, as a special industrial suspension, the rheology of flotation slurry in the separation process is determined by the variables including 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 the slurry rheology 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. And here, we classify these effects into three main parts: flotation kinetics, froth rheology and froth property.

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3.2.2. Effects of slurry rheology 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 is 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 the successful adhesion.

Slurry rheology 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 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 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 practice of a copper sulfide ore with magnesium aluminum silicate as gangue minerals, the tests on the relationship between the rheological property of the flotation pulp and the flotation kinetic have manifested that, when the viscosity coefficient of the flotation pulp increased from 0.002Pa·s to 0.02Pa·s (at the same time the yield stress of flotation slurry increased from 0.07Pa to 0.28Pa), the flotation rate constant of the copper sulfides decreased from $0.55min^{-1}$ to $0.11min^{-1}$ remarkably [59], and the multilayer flow of the flotation slurry was rather obvious, coupled with 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 rheology changes.

Slurry rheology 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 remarkably increased resistance towards 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, 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. Specially, in the flotation of finely disseminated ores, the fine particle effectiveness, such as high specific area, small mass, and small momentum, would 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 involve [8,9,60]. It has been suggested that increasing the energy input in the conditioning operation, adding agitation medium and using suitable slurry rheological reagents could adjust the complicated slurry rheology [93–95], and achieve the optimization of the kinetic environment and subsequent improvement in flotation rate.

In froth flotation, the slurry rheology not only reflects the overall comprehensive interactions of all the components in slurry, but also exhibit certain effects on the subtle processes of the 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 froth rheology

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, could act dural function of both collector and frother and exert a certain influence on froth rheology [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 networks 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 increased [79,99]. When MIBC is used as a frother, the bubbles are easily merged in the slurry phase, coupled with relatively low apparent viscosity of the slurry [100].

In oxidized ore and salt-type ore flotation, fatty acids and their derivatives are commonly used as a dual function of collector and frother, 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 collosols in the flotation solutions. The bubbles, minerals, ions and the collosols mixtures may lead to complicated rheology of the overall flotation pulp. Specially, if cationic surfactants, such as amines, are used, the flotation bubbles are hard to emerge and are always overstable [101,102].

In the slurry circulation inside the flotation cell, the flotation slurry usually exhibits certain flow stress and viscous effect and in deteriorated dispersion state in the flotation cell. When there are quite many fine particles or clays ores in the flotation slurry, the fine particle effectiveness will always remarkably change the rheology of the froth zone by forming relatively stable superstructures in slurry manifested as high viscosity and yield stress. Typical structures are net-work structure, aggregates structure, chain structure, and other superstructures [103,104].

3.2.4. Effects of froth rheology on mineral flotation froth properties

Apparent viscosity affects the "secondary enrichment" of flotation froth. It has been acknowledged that the property of the flotation froth will remarkably change if the apparent viscosity of slurry changes [105]. When the slurry apparent viscosity increases, the surface strength of the liquid film of the bubble increases, and the drainage time also increase, which will finally lead to the decrease of the "secondary enrichment" of flotation foam in the froth zone of the flotation cell [106]. For water solutions with bubbles, as its viscosity increases, the diffusion relaxation time of gas and the half-life period of the foam in the aqueous phase will all meet a significant rise. This rise will make it quite difficult for the bubbles to contact and merge in the flotation tank [107]. As the viscosity of flotation slurry rises, the mean size of bubbles in the slurry phase will decline and the shape of bubbles will become uniform, and the yield stress of the froth in the flotation cell will increase, coupled with the increased overall stability of the flotation system [92,108]. This is because the velocity of the yielding, deforming, merging and breaking of the foam is in direct proportion to the product of solubility and diffusion coefficient of the gas in the liquid phase, and the solubility and diffusion coefficient decreases as the viscosity of the solution rise [95,109].

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Slurry rheology 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 [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 of the equilibrium of three factors: gravity sinking, rising with liquid column, and solid diffusion. For a specific mineral particle, its flotation by entrainment mainly depends on the two actions of geometric diffusion and Plateau boundary diffusion [111,112]. As the stability of 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 get enlarged and the total flotation selectivity will be weakened.

The influence of the slurry rheology on the froth flotation practice of real ores is attracting more and more researchers, especially in relation to the froth behaviors. In the flotation separation of nickel sulfides minerals from fine chrysotile or serpentine, it was found that when the chrysotile content in flotation feed increased, both the overall apparent viscosity and the yield stress rapidly rose [52,55]; when the pulp yield stress exceeded the range of 1.5-2.0Pa, the flotation froth zone obviously thinned, and the concentrate grade quickly declined [57]. It was deduced that the fine chrysotile formed very stable network structures in the flotation pulp, which could hardly get sheared and 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 flotation medium, the apparent viscosity of the flotation slurry increased [78,113]. And the fine coal particles were promoted to form flocs with high yield stress and further increased the stability of the foam zone [7,82,114], and finally increased the flotation recovery of the fine coals. In the flotation of a copper-gold ore, it was found that when content of fine calcite and dolomite increased, the pulp rheology became complicated with shear thickening behaviors and a certain degree of 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 by the clays in the slurry, which could interfere with the effective dispersion of the bubbles in the circulation process and disturb the merging process of the bubbles carrying mineral particles [69–71]. As a result, the "secondary enrichment" of flotation froth behaviors was severely weakened as well as the normal flotation process.

As a whole, the slurry rheology could directly influence the stability, merging property of the flotation foam, and the corresponding changes will further exhibit acting effect on the entrainment of gangue minerals, the enrichment of valuable minerals and other flotation subtle processes. Therefore, it is of great potential value to clarify how the pulp rheology affects the flotation froth when searching methods to improve the foam property and then lift 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 the flotation rheology to eliminate this negative effect through regulating the process variables, mainly including reagent, external field, and rheological medium.

Some flotation reagents were found to have dual-functions, acting as surface modifier and rheological regulator. The pH modifiers such as lime and soda ash were observed to exhibit different effects on the flotation pulp rheology. The lime increased apparent viscosities more than soda ash in copper-gold ore mixed with kaolinite, for the Ca^{2+} released from lime could lead to the formation of stronger kaolinite aggregates that were

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more easily entrained during flotation. Therefore, more dilution of the flotation concentrate grade occurred when adjusting pH with lime [67].

Except lime, using cations, or even sea water, were also proved to effectively adjust the pulp rheology and enhance the flotation efficiency. For pyrite ore 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 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 therefore copper flotation than monovalent cation, Na^+, 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 flotation pulp. The results resulted in 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 minerals flotation. In copper and gold ore flotation pulp with non-Newtonian behavior with a high apparent viscosity, lignosulfonate-based bio polymer (DP-1777) was applied to improve both 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, was also put forward to attack and dissolve the inter-fiber networks made up of micro serpentine floccs that spread across the pulp volume, and by creating the acidic flotation conditions, the impact of pulp rheological behavior on Ni ore beneficiation was strongly alleviated [58].

External field reinforced pulp conditioning could also adjust the pulp rheology. It has been proved that the 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 rheological trouble- high viscosity and yield stress on the comminution and flotation operations [57]. Further, the microwave energy was found to closely linked to its ability to change the iron ore-water slurry rheology. It was tested that the microwave-treated ore have better rheological properties as compared to untreated ore. With larger microwave energy, the iron ore-water slurry tended to be shear thinning and easy to transport as it exhibited pseudo-plastic behavior. The action mechanism might lay on the decreased viscosity and density of the slurry with increased microwave energy [117]. As more novel pulp conditioning device or energy field are being developed for the fine particle flotation, the method for adjusting the challenging slurry rheology may also be put forward correspondingly.

Recent years have witnessed a growing attention on using coarse particles as medium to adjust the slurry rheology 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 the Fig.1 [118]. Interestingly, by adding garnet or glass beads as agitation medium, the network structures could be destroyed and resulted to changes in the flow index of the flotation slurry. It was calculated that as the spiked agitation medium became coarser, the flotation slurry became nearer to the Newtonian fluid with less particle interactions and improved flotation kinetics [12].

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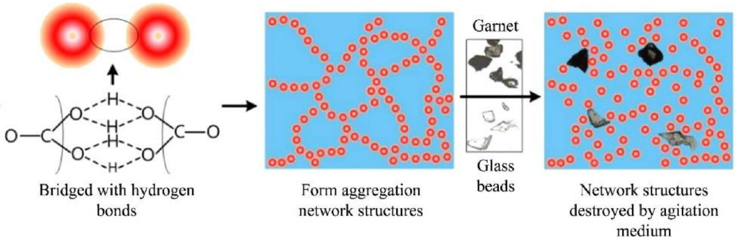

Figure 1. The interactions between fine calcite particles (-20 μm) in flotation slurry spiked with agitation medium.

Coincidentally, this method also worked in controlling the flotation rheology 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 remarkably decrease the pulp yield stress and limit the hetero-coagulation. In the meantime, the applied garnet could also decrease the pulp viscosity and the synthetic actions improved Cu-Ni sulfide flotation with increased Ni recovery [59].

4. Conclusions and potential future development

The micro-mineral slurry is a typical micro-particle fluid with a complicated mineral distribution, reagent dissolution and various shearing fields. Measuring the rheological parameters accurately and timely is the key to study the effect of the slurry rheology on fine particle processing efficiency. In conclusion, to obtain better grinding and flotation efficiency, investigating the following areas are proposed:

(1) Designing new measuring systems that could perform absolute shear rate vs. shear stress/strain measurement and avoid the coarse particle settling in the meantime, and developing rheological measuring schemes including preshear, stabilization and precise measurement for grinding and flotation systems;

(2) Monitoring the grinding process by device equipped with a rheometer and regulating the grinding process by adding effective rheology control reagents; correlating the grinding efficiency with apparent viscosity or yield stress and making them operating parameters;

(3) Optimizing the flotation kinetic processes including bubble-particle collision, adhesion, transportation and floating by adjusting the apparent viscosity or yield stress; linking the flotation index with these slurry rheology parameters and making it a new way to improve the fine particle separation efficiency;

(4) Improving the froth performance including bubble merging, foaming stability and the secondary enrichment processes by using froth rheology control reagents, connecting the froth rheology to flotation sub-processes and enhancing the enrichment ratio in the froth zones.

(5) Manipulating fine particle flotation rheology through various perspectives such as designing new rheology regulator or preparing new rheology adjusting medium. Since the "fine particle-effect" has been the key factor that limited the fine particle flotation efficiency, how to eliminate the effect by alerting or changing the slurry rheology might be the research focus in this area.

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