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Application of Colloids and Its Relevance in Mineral Engineering

Abhyarthana Pattanaik and Rayasam Venugopal

Abstract

Mineral engineering is an interdisciplinary branch which includes many branches like physics, chemistry, math and sub branches like instrumentation, chemical engineering, mechanical engineering, geology etc. Amongst the various separation/beneficiation techniques of mineral processing, froth flotation is one of the most important fines beneficiation technique, which depends upon the surface and colloid chemical phenomena as the basis of selectivity. The method of separation relies on the surface state and colloidal chemistry of the ore particles and chemical reagents. Adsorption at the mineral solution interface is of major importance for the behaviour of mineral particles in the solution and for successful flotation performance. Adsorption of simple ions determine the change of the particle surface and electrochemical properties of the pulp/slurry phase and therefore affect the colloidal stability and the adsorption behaviour of reagent on the mineral surface. This chapter describes in detail about the role, importance and application of colloidal chemistry in mineral processing especially froth flotation. Froth flotation will remain a key unit operation for the treatment of low-grade ore fines for the decades to come with the overarching challenge as the need of the hour is to modify and improve existing process conditions so as to maintain an acceptable grade and recovery response for the feed whose liberation is more finer, more complex association of minerals and of lower grade.

Keywords: mineral processing, iron minerals, colloids chemistry, surface chemistry, adsorption, zeta potential, interfacial chemistry

1. Introduction

Mineral Engineering is a multidisciplinary and inter disciplinary branch, which includes many other branches and sub branches. Due to depletion of high-grade ores and liberation size being finer, particles are approaching colloidal size range, mineral processing is becoming more and more applied colloid chemistry. Colloid chemistry is inevitably involved in all aspects of mineral processing, ranging from rheological phenomena in grinding, in froth flotation in which selective adsorption of various chemical additives (flotation collectors, flocculants, dispersants, depressants etc.) onto mineral surfaces, dewatering, tailings management and analysing the forces which control the stability of dispersion as well as the wettability of mineral surfaces. Surface phenomena control both the dewatering of “fines” and area involved in dust suppression. So, to understand the colloidal science and colloidal chemistry in mineral engineering, a basic knowledge on surface science (surface physics, surface chemistry, surface mineralogy etc.) should be there. Colloidal solution is formed by dispersing one phase into another and the phase change can be easily described in terms of attractive and repulsive

interactions in the dispersed phase. Different mineral beneficiation processes along with the application of colloid chemistry are depicted in **Figure 1**.

Along with the application in Mineral industry, colloidal chemistry has the application in non-mineral industry also in deinking, waste water treatment etc. We can't just use the word colloid science, in this modern era, interdisciplinary is more accurate word for Mineral Engineers as it has been justified. Fine mineral particles (colloidal particles), when present in slurry exert an affect on the ionic environment surrounding the particle. To understand or to get an extensive knowledge about colloidal systems in mineral processing, a knowledge on basic surface science is required.

So, as flotation, flocculation are (physico-chemical surface based separation processes), involves the application of certain surfactants in the slurry phase, hence valuable understanding of intermolecular forces at the interfaces is mandated.

1.1 Colloidal chemistry in froth flotation

Amongst the various beneficiation/upgradation technologies of Mineral processing, froth flotation is the most innovative and ingenious process development for the treatment of low-grade ore fines, slimes and tailings [2–4]. The basis of separation in froth flotation process rely on the surface state and colloidal chemistry of the particles and chemical reagents [5, 6]. Adsorption of the surfactants/reagents at the mineral solution interface is of the major importance for the behaviour of mineral particles in the solution and for the successful execution of the froth flotation [7].

Grinding of ore for liberation inevitably results distribution of particle sizes. Colloidal chemistry also plays a role between grinding particle sizes and contact angle in the physio chemical processes [8].

Flotation process is not fully interpretable and remains a challenge, as it requires a good understanding of the interactions involved between the major phases (macro processes) and the number of inter related events (micro processes), as represented in **Figure 2**.

Adsorption of simple ions will determine the change of surface characteristics of the particles in the pulp/slurry phase and therefore affect the colloidal stability and the adsorption behaviour of reagents on the mineral surface. A comprehensive understanding of the flotation colloid chemistry is essential to enhance flotation performance and adapt them for treatment of more complex and low-grade ores.

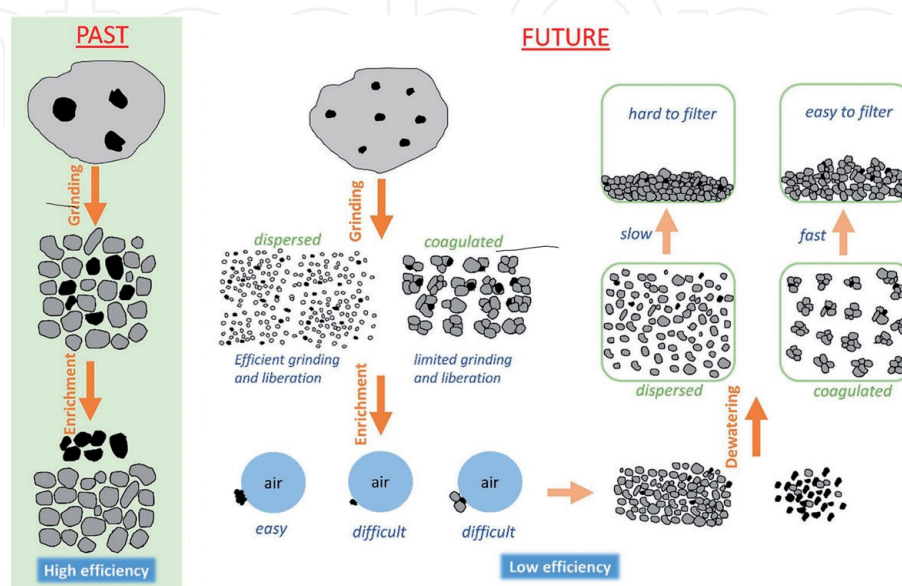


Figure 1. Important role of Colloid chemistry in mineral processing [1].

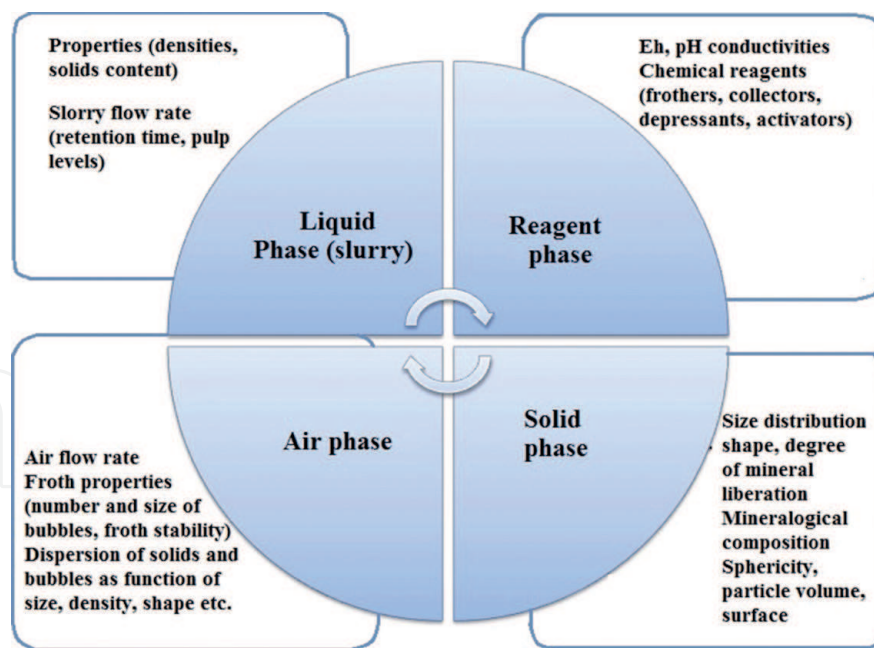


Figure 2.
Different colloidal phases and interfaces of froth flotation [7].

Colloidal chemistry plays an important role in flotation particularly surface and interfacial forces (Vander Waals, electrical double layer, hydrophobic, hydrodynamic, hydration, and adhesion forces) are of great importance in order to understand interparticle, interbubble and bubble-particle interaction mechanisms. However due to complexity of flotation system and difficulty in experimental verification and due to various particle size range, the physicochemical principles of flotation colloid interactions are still not fully understood.

2. Surface energy in Froth flotation

The concept of surface energy provides a satisfactory basis for explaining a wide range of “capillary phenomena”, many of which are pertinent to the flotation process.

1. The shapes of liquid drops, bubbles, or menisci at equilibrium, either with or without deformation by gravity.
2. The internal pressure difference across curved interfaces.
3. The vapour pressure over curved interfaces of droplets or small particles.
4. The growth of particles (or bubbles) at the expense of smaller ones, either through the vapour phase or via a solvent.
5. The creepage or retraction of a film of liquid over another liquid or solid.
6. The establishment of an equilibrium angle of contact of a liquid on a solid substrate — as governed by Young's equation
7. The accumulation of one or more components at an interface — adsorption.



Figure 3.
Surface and Interfacial tensions for the molecules in bulk liquid.

According to molecular theory, different crystal structures have different surface energy [9–11]. Interface is the boundary between two or more phases exist together. The properties of the molecules forming the interface are different from those in the bulk that these molecules are forming an interfacial phase. Several types of interface can exist depending on whether the two adjacent phases are in solid, liquid or gaseous state.

2.1 Interfacial tension

In the liquid state, the cohesive forces between adjacent molecules are well developed. There are various forces present between surface and interfaces molecules presented in **Figure 3**.

Cohesive forces are present with the other molecules which are situated below or adjacent to them. Adhesive forces are being developed with the molecules of other phases in the interface. Surface tension (γ) is the force per unit length that must be applied parallel to the surface so as to counter balance the net inward pull. Interfacial tension is the force per unit length existing at the interface between two different phases.

3. Methods for characterization of colloidal slurry phases

Potential determining ions [H^+ and OH^-] at the interface plays a very important role in determining electrical charge at the surface in the colloidal system [12–15]. There are many diagnostic methods such as particle size analysis and turbidity measurements, surface force measurement with atomic force microscope (AFM) and surface force apparatus (SFA) are direct approaches for studying colloidal interactions, which could provide insights into molecular mechanisms of operating colloidal forces with high resolution [1]. After invention of these advanced techniques, these have become the most important tools in colloid and interface science to directly measure the interactions between particles and liquid substrates, and even the single molecular force involved in the rupture of a single chemical bond and the stretching of polymer chains. These are not only limited to hard or non-deformable surfaces, are also used to measure the forces between one solid particle and an air bubble or an oil drop. Although progress has been made in studying bubble-particle interactions using AFM in recent years, the deformation of the bubble by both the hydrodynamic and surface forces remains a bottleneck in determining the absolute separation and the surface forces.

4. Parameters affecting colloidal stability in mineral processing

Mineral processing is influenced in many ways by colloidal and surface forces (**Figure 4**).

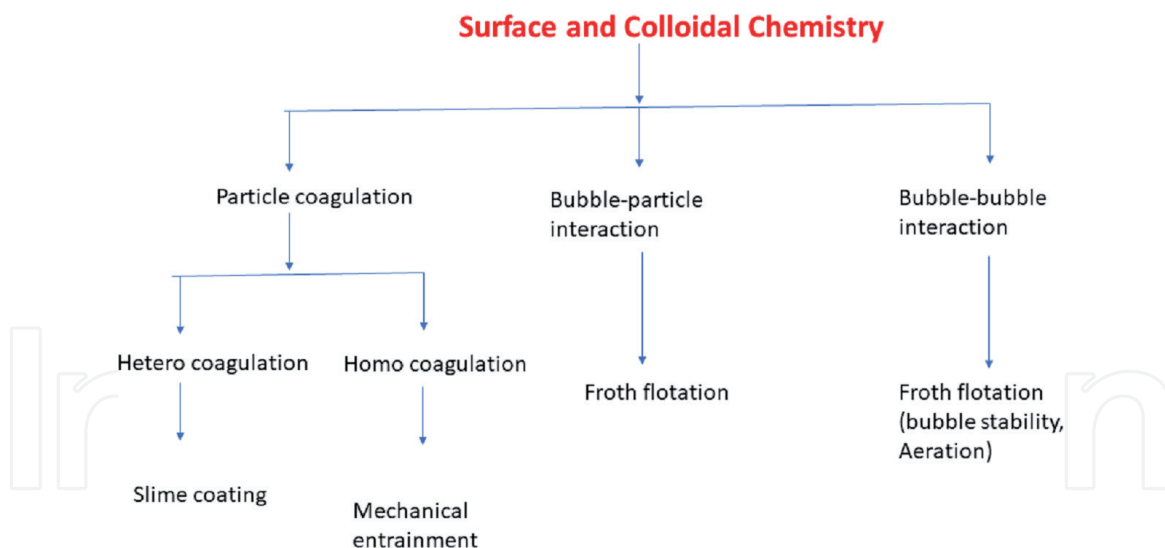


Figure 4.
Colloidal chemistry in Mineral Processing.

Rheology is dominated by particle coagulation and thus affects the effectiveness of grinding. Selective homocoagulation/flocculation is advantageous by decreasing mechanical entrainment or dewatering for fine particle flotation of valuables. Flotation of fine particles also depends on the interaction of bubble-bubble and bubble-particle interaction. However, for thickening/dewatering, hetero-coagulation/flocculation that is detrimental to selective flotation by slime coating is desirable.

4.1 Colloidal stability

The stability of colloidal system is mainly affected by interactions among the particles. The coagulation kinetics of multicomponent colloidal systems with regard to the different electrical double layers for each dispersed species will vary.

The reduction of diffuse layer potential by surfactant adsorption can result in coagulation. Another important factor affecting the coagulation of mineral particles is hydrophobicity and thus affecting the rheology of suspensions. This is particularly true when the particles are sufficiently hydrophobic, being able to counteract electrostatic repulsion through strong hydrophobic attractive forces.

Colloidal interactions of slimes particles ($<10\ \mu\text{m}$) requires careful attention, because it results in slime coating and hence diminishing the separation performance.

4.1.1 Methods to study colloidal stability

Many advancements have been made in the past several decades for accurate and direct measurements of forces acting between particles as a function of the surface separation. Although the findings were consistent with the colloidal forces double-layer hypothesis, deviation was found at very short distances, mainly due to hydration forces or surface roughness.

The presence of cations in the aqueous process, which makes it possible to adsorb hydrated cations on the solid surface, is responsible for the resulting hydration force between the two mineral surfaces and is a significant flotation factor.

On the other hand, for predicting hetero-coagulation such as slime coating, zeta potential calculation can be used.

No attraction, weak attraction, or strong attraction between different mineral fines can be distinguished from the zeta potential measurements for a slurry mixture system containing various mineral fines.

Zeta potential, electric double layer is first prescribed by Helmholtz [16]. The counter ions in an electrical double layer can exchange with ions of the same sign from the solution. In a similar way, the moment of counter ions occurs, with the application of electric field because of the concept of surface conductivity.

4.1.1.1 Atomic Force Microscopic (AFM) analysis

The bubble-particle attachment forces can be calculated by attaching a bubble to a stationary solid surface and a particle to an AFM cantilever. Strong long range attractive forces can be determined for a hydrophobic particle and an air bubble before any double-layer and van der Waals forces can be established, with the gas bubble acting like a hydrophobic surface.

The attractive hydrophobic attraction between the solid-water and the water-gas interfaces is assumed to be the main driving force for film rupture and the attachment of air bubbles to hydrophobic mineral particles, taking into account the repulsive existence of electrostatic repulsion and van der Waals forces between particles and air bubbles encountered in flotation. The development of a dimple due to a hydrodynamic pressure greater than the internal bubble pressure is highly dependent on the velocity of the air bubble's approach. Although the higher bubble approach velocity leads to a more pronounced dimple, in order to evaluate the film thickness of the first dimple and the form of the film for hydrophobic solid surface systems, the surface hydrophobicity needs to be taken into account. By changing the reaction conditions such as electrochemical potential and solution pH, it is possible to maximise the alteration of hydrophobicity with/without collector.

4.1.2 Effect of water chemistry

As water is a polar liquid and moderate conductor of electricity, potential difference will not be observed in the absence of electric current. The chemistry of water has a great influence on the interaction forces in aqueous solution between solid surfaces. The colloidal stability of various slurry phases is influenced by various ions (monovalent, divalent, trivalent, etc.) present in the water. Cations function as a binder to bridge various charged surfaces in certain instances. If present in process water, reagents/surfactants bind with cations to minimise the amount of free cations in the liquid, are able to mitigate the undesirable effect of cations and thus promote the release of mineral particles. The water chemistry of the aqueous system where the attachment occurs is strongly influenced by bubble-particle attachment. Electrolytes in water compress the electrical double layer for the already hydrophobic particles and thus lower the energy barrier created during the collision between hydrophobic particles and air bubbles, which is advantageous for the bubble particle attachment. Knowledge about the surface properties and zeta potential is very important for flotation. The literature may define the ideal situation for different ores, but due to the presence of different interfering ions, the actual situation of different ores with varied mineralogy differs. Therefore, for flotation process effectiveness, the particle size distribution proportions of coarse and fine size groups, surface features of bulk and size fractions of different mineral species and their interactions with the reagents need to be understood and closely monitored.

4.1.3 Effect of reagents

Flotation reagents play the most important role in flotation, as the hetero-coagulation that could contribute to the loss of liberated valuables in the tailings

due to slime coating will affect less than the optimum quantity, while the optimum quantity helps to selectively homo-coagulate fine valuable particles, increasing the kinetics of fine particle recovery.

4.1.3.1 Collector

Collectors are reagents which render minerals' surface hydrophobic by adsorption. The selection of an appropriate collector is critical for selective separation of valuable minerals from gangue minerals. Collectors can be classified into non-ionic, anionic and cationic depending on their ionic charge and active ion participation.

4.1.3.2 Frothers

Frothers are organic compounds that dissociate into ions at the air-water interface and decrease the surface tension, thus stabilising the froth consisting of a multitude of mineral-laden air bubbles and inducing the mineralized surface buoyancy effect.

4.1.3.3 Modifiers

These are chemical compounds applied to the pulps of flotation to strengthen the collector-mineral Adsorption, that is, selectivity enhancement. This may be achieved by either (a) creating an environment or revitalizing the floatability of the desired mineral, (b) by suppressing the flotation activity of the undesired mineral (at a particular stage of flotation operation), (c) by removing the deleterious elements which hinder effective flotation of desired minerals or (d) by providing proper hydrophobicity for the selective adsorption between the mineral and collector.

There are different types of modifiers.

I. Activators

II. Depressants

III. Dispersants

IV. pH regulators

Along with flotation, colloidal chemistry plays an important role in flocculation. Inorganic salts and synthetic high-molecular - weight polymers are commonly used in the treatment of mine waste and oil sands tailings to coagulate/flocculate the solid particles. Following its biomedical applications by settling experiments, the feasibility of using highly biocompatible glycopolymers in solid-liquid separation has been explored.

4.1.4 Effect of surface charge

Yield stress measurements are used in combination with electrophoretic and zero charge point measurements as a function of solution pH to detect the surface charge characteristics of particles that play a very important role in froth flotation. Although the coagulation peak, the isoelectric point and the zero charge point all converge at the same value for isotropic minerals, they spread across a wide range of anisotropic minerals, and with the addition of anionic polymer as a dispersant to

the mineral suspensions, this disparity between isotropic and anisotropic minerals is even accentuated.

5. Conclusions

In mineral processing, colloidal interactions play an important role.

Developments of different techniques allow us to research the phenomenon of colloidal interactions, including slime coating, homocoagulation, particle and bubble coalescence, and mineral attachment of air bubbles.

Hence, in the analysis of colloidal and surface force in mineral processing, it is important to use complementary techniques.

To control the state of colloidal dispersions by creating favourable conditions, it is of paramount importance to study the colloidal interactions in a relevant system, including such considerations as different electrolyte concentrations, the presence of divalent cations, the co-existence of various cation species and natural surfactants in industrial process water, different pH values, the presence of reagents such as collectors, dispersants, and activators, and the existence of other surfactants. It can be reiterated that lower solution pH, higher salinity, and higher ionic concentration affects the repulsive forces present in a colloidal solution, made the adhesion forces stronger, while both decreasing long-range repulsive forces and increasing adhesion forces are beneficial for mineral froth-flotation and flocculation process [17–20].

The factors affecting the surface colloidal chemistry of fines beneficiation process in Mineral Processing are

- I. Equilibrium of mineral particles in the pulp phase at a given pH
- II. Equilibrium of mineral surfactants in the solution at a given pH
- III. Adsorption of reagents on the particle surfaces
- IV. Hydrophobic interaction of hydrophobic particles
- V. Oil agglomeration of mineral particles
- VI. Attachment of air bubbles to hydrophobic particles.

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