Observation of gaseous films at solid–liquid interfaces: Removal by ultrasonic action

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ABSTRACT

The critical role of dissolved gas nano-bubbles at solid surfaces in particle association, aggregation, adsorption and flotation has been recognised in the recent literature. The principles of mineral processing, fine particle separation, and water recovery depend upon changing the surface properties at the solid–liquid interface. It has been assumed that the solid surfaces are either in direct contact with the liquid or may have nano-bubbles attached only at hydrophobic surfaces. This paper shows that gaseous layers 50–100 nm thick can be attached surrounding high proportions of solid clay mineral surfaces restricting reagent access, producing buoyancy and aggregation. Ultrasonic treatment before flocculant addition effectively removes these gaseous layers as well as dispersed micro-bubbles. Re-aggregation after brief ultrasonication produces denser (less buoyant) flocs, demonstrated with cryo-SEM statistical analysis, giving more complete access of the flocculant to the aggregate surfaces. In the subsequent flocculant addition, the settling rates of the denser flocs can be increased up to 40%. If ultrasonic action is continued, the bridged flocs are disturbed with some redispersion of smaller flocs and individual platelets and consequent slower settling rates.

1. Introduction

This paper shows for the first time that surfaces on fine clay mineral particles in aqueous suspension can have attached gaseous coatings likely to partially control particle aggregation and restrict reagent access to the solid–liquid interfaces. The implications of these findings are important in high-priority water recovery from fine particle slurries [1,2] by flocculant addition and in valuable mineral separation by froth flotation where adsorption of hydrophilic "depressant" molecules to the unwanted (gangue) mineral surfaces governs recovery and selectivity [3]. Separation of fine clay is of particular importance to water recovery from tailings in coal, heavy minerals and some base metal processing operations. Because clay particles are generally less than 200 nm in major dimension, natural solid–liquid separation by sedimentation, governed by Stoke's Law, is very slow. To achieve fast sedimentation, separate particles have to be bonded into larger, denser aggregates. This is usually achieved by bridging flocculant addition using long chain polymers but the aggregate structure and properties before flocculant addition are critical in this process because the flocculant locks together these initial aggregates and their contained water as we have shown [4].

Contemporary approaches to fine particle suspension control are based on the electrical double layer DLVO theory of colloid stability where electrostatic and van der Waal's forces determine whether a particular suspension will be stable or destabilised [1]. Opportunities for control have focussed on methods to collapse the electrical double layer and allow particles to be brought close enough for van der Waal's forces to bond particles into larger aggregates which significantly speed up the sedimentation rate [1]. However, in clay suspensions, particles are found already contacting each other to form quasi-gels [1,4,5] before flocculant addition often as a three-dimensional continuous network with high porosity and slow settling rate. This structure is associated with the presence of attractive forces holding the platelets together and trapping both inter- and intra-aggregate water [2,4].

The flocculation of fine colloidal clay with water soluble polyacrylamide (PAM) polymer in industrial thickeners generally experiences three regimes during the dewatering processing [1]:

- The free settling (unhindered) zone, where fine clay particles adsorb long chain polymers forming small flocs and some chain-like structures of limited extension.
- The hindered settling zone, where larger flocs and extended chains contact each other forming a network with some yield stress limiting settling and consolidation.
- The compression zone, where the self-weight of the sediment can overcome the yield stress to compact the network.

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The mechanism of kaolinite flocculation, the structure of aggregate formation and consolidation (dewatering) in these three regimes has been reported in our previous paper on this system [4]. Statistical cryo-SEM image analysis shows that the structure of aggregates formed before flocculant addition has a determinative effect on these outcomes. Without flocculant addition, three stages occur in the mechanism of primary dewatering of kaolinite at pH 8: initially, the dispersed structures already show edge–edge (EE) and edge–face (EF) inter-particle associations but these are open, loose and easily disrupted; in the hindered settling region, aggregates are in adherent, chain-like structures of EE and stair step face–face (FF) associations; this network structure slowly partially rearranges from EE chains to more compact face–face (FF) contacts densifying the aggregates with increased settling rates. During settling, the sponge-like network structure with EE and FF string-like aggregates, limits consolidation because the steric effects in the resulting partially gelled aggregate structures are dominant. With flocculant addition, the internal structure and networking of the pre-aggregates are largely preserved but they are rapidly and effectively bound together by the aggregate-bridging action of the flocculant.

Nano-bubble coalescence has been presented as an explanation for strong, long-range attractive forces measured between hydrophobic surfaces [6–10]. Zbik and Horn [11] have shown that nano-bubbles on the edges of clay crystals may cause clay particles to flocculate. A clay platelet attached to an oil drop by its edge and clay flocs were attached by a vertically placed Teflon strip but not by the hydrophilic mica basal plane. A much less dense, porous sediment occurred in CO_2-saturated water solution compared to vacuum degassed water. In the context of this paper, it is noted that degassing using ultrasonic agitation is a much more practical method (in reduction of treatment time, energy and increased throughput) of degassing than vacuum degassing of water or low-density dispersions. Zbik and Smart [12] have also shown that reducing voids in aggregates and end sites for bubble attachment in kaolinite and talc gives much improved dispersion. Some of these studies have imaged the form of the gaseous attachment, e.g. [8]. In particular, an AFM study by Attard et al. [13] has observed flattened nano-bubbles partly covering a designed hydrophobic surface using atomic force microscopy. In general, these imaged nano-bubbles associated with long-range attraction between surfaces are 10–20 nm in thickness. This distinction is important in relation to the >100 nm micro-bubbles reported here as will be discussed.

2. Materials and methods

2.1. Kaolinite

The materials used for this study were well-characterised kaolinites. Two different kaolinites were studied to assess the generality of changes due to ultrasonic action; a low-defect well crystallized K15GM and a high-defect poorly crystallized Q38 kaolinite both supplied by Unimin Australia Ltd. These two kaolinites have been extensively characterised and reported in previous papers [2,4,12,14–17]. In summary, K15GM is produced at Adelaide, South Australia from the Unimin Birdwood quarry: surface area 19.7 m²/g; Hinckley crystallinity index 1.3. A detailed comparison of the K15GM kaolinite with Georgia kaolinite using cryo-SEM has been given in [14,15]. The kaolinite is generally represented as pseudo-hexagonal or euhedral crystals with diameters down to ~50 nm. The crystals are typically thin and flexible plates. AFM investigations of this kaolinite [6] show that crystals are on average 160 nm in diameter and ~13 nm thick giving aspect ratio values ~12 [4,12]. The zeta potential of K15GM across the pH range

3–10, reported in [4], displays negative zeta potential values above pH 3 with a pH-dependent profile due to surface hydroxyl groups present at the platelet edges. It does not show evidence of any adsorbed species that may have influenced this profile. This kaolinite has a relatively high measured gel point in the range 10–12 wt%. The Q38 kaolinite from Granville, New South Wales with surface area 18.9 m²/g and 0.49 Hinckley index is a dry milled kaolinite with characteristics similar to Weipa kaolinite described by Zbik and Smart [16,17]. The particles are in a similar size range to the K15GM but their surfaces are generally highly stepped and irregular due to the lower crystallinity. The close similarity in behaviour of the two different kaolinites therefore suggests that the flocculation and aggregation mechanism described is general. For the initial studies, dry K15GM kaolinite was mixed with aqueous 0.01 M NaCl electrolyte at high solid content by shaking in a SPEX mill for 5 min. The slurries were then diluted to the required solid concentrations (4 wt%) and stirred for 2 h using a magnetic stirrer before sampling for cryo-SEM studies.

For the subsequent studies, dry kaolinite (either K15GM or Q38) was mixed with aqueous 0.01 M KCl electrolyte at 50 wt% for 0.5 h in a bucket with baffles by a Rushton turbine cell running at 100 rpm. Slurries were refrigerated for at least 12 h before use. The slurries were then diluted to the required solid concentrations (2 wt%) and stirred for 0.5 h in the bucket with baffles by a Rushton turbine cell at 220 rpm to keep the suspension homogenous and ensure that samples are representative. This 2 wt% suspension was used for cryo-SEM imaging and for settling tests.

2.2. Cryo-vitrification

For the microstructural studies of the suspensions, as in our previous studies [4], the cryo-transfer method of sample preparation was used to avoid structural rearrangement caused by surface tension during oven or freeze drying. In the cryo-vitrification SEM studies, the sample is taken by a large-aperture (>2 mm) pipette directly from the flocculating system immediately after dispersion and deposited into a 2 mm diameter double-ended rivet sealed by wax from one side. The sample is immediately plunged into the liquid nitrogen of the cryo-vitrification unit, which reduces the temperature at >800 °C/min freezing the water without allowing crystallization to ice structures, i.e. vitrifying [18]. Vitrified samples are placed onto the liquid nitrogen-cooled specimen stage of the field emission scanning electron microscope Philips XL30 FESEM with Oxford CT 1500HF Cryo stage. The sample is fractured under vacuum to expose a fresh internal surface and a small amount of vitrified H_2O sublimed off by raising the stage temperature to −95 °C for ~30 s (removing ~250 nm) then lowering back to ~−180 °C. This technique exposes the structure of the snap-frozen aggregates just above the surface of the vitrified water greatly improving imaging and quantitative image analysis. Finally, a 3 nm, high resolution platinum coating is sputtered on to the exposed surface to increase conductivity before SEM imaging. The sample was then examined in the SEM using a low cathode voltage (5 kV for secondary; 10 kV for backscattered electron imaging) to protect the sample during imaging. No changes in structure were observed in the normal time of image collection (2–5 min).

2.3. Cryo-SEM and STIMAN analysis

In the FESEM, micrographs from selected suitable areas of the cryo-vitrified samples were taken at magnifications of 500×, 1000×, 2000×, 4000×, and 8000×. Micrographs at higher magnifications than those listed were also taken and used for morphology description. The micrograph series of magnifications from 1000× to 8000× were statistically analysed using the STIMAN (STructural