Significance of Particle Aggregation in the Reverse Flotation
of Kaolinite from Bauxite Ore

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Abstract

Significant interest has been demonstrated for the removal of kaolinite from bauxite ore by flotation. The reverse flotation of kaolinite from bauxite ore at low pH with dodecylamine hydrochloride collector has been reported. However, resolving the mechanism of the reverse flotation process is largely limited by the misunderstanding of the anisotropic surface properties of kaolinite particles. Based on recent fundamental study of the surface properties of kaolinite particles and their interaction, the significance of particle aggregation in the reverse flotation of kaolinite from bauxite ore has been revealed. The wetting characteristics of the basal plane surfaces of kaolinite with dodecylamine hydrochloride collector have been estimated by contact angle measurements at model surfaces. The improved hydrophobicity of the kaolinite nanoparticles is not enough to account for the significant increase in the flotation recovery at low pH when compared to the flotation performance at high pH. Instead, particle aggregation is expected to be the major factor which contributes to the improved flotation response at low pH. Both simulation results and X-ray CT results have demonstrated aggregation and formation of kaolinite clusters at low pH. It appears that these kaolinite clusters have sufficient mass and hydrophobicity to account for the successful reverse flotation of kaolinite from bauxite ore at low pH.

Keywords: Model surfaces; Pyrophyllite; Gibbsite; Dodecylamine; Contact angle

Introduction

Froth flotation has been considered as one of the most widely applied and efficient particle separation processes for the recovery of mineral resources. Kaolinite exists as a common

gangue mineral in many valuable ore deposits, including bauxite, potash ore, iron ore, sulfide ores, oil sands, phosphate and rare earth ores. In some cases it is desired to depress kaolinite during flotation while in other cases the kaolinite is removed by reverse flotation. Of particular interest is the development of flotation for the removal of kaolinite from low grade bauxite ores. An important result of recent bauxite flotation research was the opening in 2002 of the first bauxite mineral processing plant in China (and in the world) which uses direct flotation to prepare a bauxite concentrate for the Bayer process (Zhao et al. 2010). One million tons/yr of bauxite ore can be treated at this plant. Now more than 80% of the two billion tons of low grade diasporic bauxite in China can be used instead of being discarded, extending the usable amount of bauxite resources for the China aluminum industry from only about 10 years to more than 50 years. Another significant bauxite reserve (~10%) is located in Brazil (Bray 2014). Although extensive research has been done to study the flotation of Brazilian bauxite, the flotation practice is still new and not yet practiced in the Brazilian bauxite industry (Bittencourt et al. 1990; Massola et al. 2007). To understand and develop future industrial practices for bauxite flotation, the surface/colloid chemistry associated with the reverse flotation of kaolinite needs to be considered.

In spite of the difficulty in the development of technology for the flotation of fine particles, such as kaolinite, some success has been achieved. Both direct flotation and reverse flotation processes have been developed for bauxite flotation (Marino 2012). For direct flotation of low grade bauxite ore, gibbsite or diasporite can be floated with hydroxamate collector at high pH (pH 9–10), in the meantime, the silicate minerals (such as kaolinite) are depressed by sodium silicate and iron oxide minerals are depressed by starch. On the other hand, in the case of the reverse flotation process for low grade bauxite ore, the silicate minerals (such as kaolinite) are floated with amine and the bauxite minerals, gibbsite and/or diasporite, are depressed with starch at low pH (pH 4–5). Recent studies have suggested that reverse flotation is economically favored over the direct flotation process (Xu et al. 2004; Zhao et al. 2010), due to the fact that 1) clays (kaolinite) are more readily liberated than gibbsite/diasporite at a coarse size, thus significant

energy for the grinding process is expected to be saved in reverse flotation and 2) hydroxamate collectors used for direct flotation are much more expensive than the amine collector used for reverse flotation. In addition, the hydroxamate collector consumption in direct flotation is greater due to the greater amount of gibbsite/diaspore in the bauxite ore when compared to the clay minerals.

Extensive research has been conducted to improve the flotation of kaolinite from bauxite, including the development of new collectors, adjustment of pH and ionic strength, and design of the flocculation-flotation process (Bittencourt et al. 1990; Hu et al. 2004; Hu et al. 2005; Zhong et al. 2008; Ma et al. 2009; Marino 2012). Yuehua Hu has led his team and made significant contribution to the study of the reverse flotation of low grade bauxite, efforts which include the development of new collectors as well as fundamental studies on the reverse flotation of kaolinite (Hu et al. 2001; Hu et al. 2003a, b; Hu et al. 2004; Hu et al. 2005; Zhong et al. 2008; Liu et al. 2009). Recently, many researchers have been dedicated to developing new cationic collectors which can improve the flotation behavior of kaolinite from bauxite, and a large variety of the collector types have been investigated, such as the primary amine (dodecylamine), tertiary amines (N,N-diethyl-dodecyl amine (DEN), N,N-dimethyl-dodecyl amine (DPN), and N,N-dibenzyl-bodecyl amine (DBN)), quaternary amines (cetyl trimethyl ammonium bromide (CTAB), dodecyl trimethyl ammonium chloride (DTAC), cetyl trimethyl ammonium chloride (CTAC)), n-(2-aminoethyl)-dodecanamide, n-(3-aminoprpyl)-dodecanamide, and N,N-dipropyl-dodecyl amine (PN) (Hu et al. 2003a,b; Zhao et al. 2003a,b;; Liu et al. 2009; Xia et al. 2009; Jiang et al. 2011; Liu et al. 2011). Primary amines are some of the most common collectors used in reverse flotation, and the recovery of kaolinite from bauxite is ~70%. Newly developed collectors mentioned earlier can improve the recovery to as high as 80–90%. Additionally, it has been demonstrated that the flotation recovery of kaolinite is significantly increased by decreasing the pH of the flotation slurry (Bittencourt et al. 1990; Hu et al. 2003a,b; Hu et al. 2005).

However, the nature of kaolinite flotation using cationic collectors (alkyl amines) is not well understood. The mystery lies in the fact that half of the kaolinite surface is exactly the same as the surface of gibbsite, including crystal structure and composition. Nevertheless, kaolinite particles are able to be separated from gibbsite particles by amine flotation at low pH ($\text{pH} < 5$). Simulation results have suggested that dodecylamine prefers adsorption at the silica face surface of kaolinite over the alumina face surface (Hu et al. 2005). However, a detailed explanation for the better flotation recovery of kaolinite in acidic solution has not been reported in the literature. Only recently has the fundamental surface chemistry of kaolinite particles been established (Gupta and Miller 2010; Liu et al. 2014). The alumina face surfaces of kaolinite particles are reported to be positively charged, the silica face surface and the edge surface are negatively charged even in acidic solution. In addition, the kaolinite particle interaction has recently been studied (Johnson et al. 1998; Johnson et al. 2000; Gupta et al. 2011; Liu 2014; Liu et al. 2015). These surface chemistry studies of kaolinite particles provide fundamental knowledge for the analysis of the flotation behavior of kaolinite particles with dodecylamine collector.

In order to reveal the nature of the reverse flotation of kaolinite from bauxite ore, the interaction between two basal plane surfaces of kaolinite particles and dodecylamine was investigated in this current research. Due to the difficulty in the study of fine kaolinite particles (~ 500 nm), model surfaces with similar properties to the two face surfaces of kaolinite have been used to describe the behavior of kaolinite. The basal plane surface of pyrophyllite, a trilayer phyllosilicate, was selected to represent the silica face surface of kaolinite; gibbsite, an aluminum hydroxide mineral with octahedral structure, was used to represent of the alumina face surface of kaolinite particles. The pyrophyllite basal plane surface and the gibbsite octahedral surface are good candidates as model surfaces for the silica surface and alumina surface of kaolinite because of their structures. In addition, the surface charge and wettability of the pyrophyllite basal plane surface and gibbsite surface compare favorably to the properties of the silica face surface and the alumina face surface for kaolinite as summarized in Table 1. It is evident that good agreement is

found between the model surfaces and kaolinite face surfaces. On this basis, the pyrophyllite basal plane surface and the gibbsite surface were selected to be the model surfaces for the silica face surface and alumina face surface of kaolinite.

Table 1. Surface charge and wettability of pyrophyllite and gibbsite as model surfaces to represent the silica face surface and alumina face surface of kaolinite.

Surfaces	Point of Zero Charge	Cation Exchange Capacity (meq/100g)	Wetting Characteristics
Pyrophyllite Basal Plane Surface	<pH 3 (Hu et al. 2003a)	1.24-1.56 (Prasad and Saxena 2008; Desai et al. 2010)	Surface, 40-50° (Hu et al. 2003a) Powder, 79.2° (Giese et al. 1991)
Silica Face of Kaolinite	<pH 4 (Gupta and Miller 2010)	3-15* (Carroll, D. 1959; Bhattacharyya et al. 2008)	Modestly hydrophobic (Yin et al. 2012)
Gibbsite Surface	pH 7.5-11.3 (Jodin et al. 2005; Kosmulski 2009; Adekola et al. 2011)	N/A	Hydrophilic (Liu 2014)
Alumina Face of Kaolinite	pH 6-8 (Gupta and Miller 2010)	N/A	Hydrophilic (Yin et al. 2012)

*Note this value indicates the cation exchange capacity for kaolinite surfaces in general.

Dodecylamine, one of the most common amines used for the flotation of kaolinite from bauxite, has been chosen as collector for this flotation study. The interactions between the model surfaces and dodecylamine collector were studied and based on these results the nature of the interaction of dodecylamine with kaolinite surfaces is suggested. In addition, the flotation mechanism of kaolinite from bauxite was analyzed and clarified based on the kaolinite surface properties, particle interaction, and the interaction between kaolinite surfaces and dodecylamine. These results provide further fundamental information for the future development of new flotation technology, including flotation conditions, control, and evolving new chemicals for the reverse flotation of kaolinite from low grade bauxite ores.

2. Materials and Methods

2.1. Materials

A pure and white gibbsite specimen was purchased from Ward's science. The sample was polished to a very smooth surface, with polishing paper, followed by polishing with 0.3 μm and 0.05 μm gamma alumina powders on a polishing cloth. The gibbsite sample was cleaned with ethanol alcohol and high purity Milli-Q water (Millipore Inc.), followed by plasma cleaning for 20 minutes.

The pyrophyllite sample was obtained from a collection in the Department of Geology, University of Utah. The basal plane of pyrophyllite was polished to a flat surface and then, a fresh surface was acquired by peeling off several layers of pyrophyllite using adhesive tape.

The collector, dodecylamine hydrochloride, with a purity of 99.5%, was purchased from Sigma Aldrich. The following concentrations of the dodecylamine collector were prepared for contact angle measurements, 1×10^{-5} M, 5×10^{-5} M, 1×10^{-4} M and 2×10^{-4} M. The pH was varied from pH 3 to pH 10. The fresh surface of gibbsite or pyrophyllite was conditioned in the collector solution at the desired concentration for 30 minutes before contact angle measurements were made.

2.2. X-Ray Diffraction (XRD)

The mineralogy of the gibbsite and pyrophyllite samples was verified by X-ray diffraction (XRD). A piece of the gibbsite sample was used for XRD analysis of the mineral surface. For the case of pyrophyllite, the sample was treated as follows. A small amount of pyrophyllite powder was acquired by grinding the sample with an agate mortar and a pestle. Two XRD experiments were used for analysis of the pyrophyllite sample. First, XRD was conducted with the pyrophyllite powder which was smeared on a glass slide with ethyl alcohol. Second, a portion of the pyrophyllite sample was exposed to ethylene glycol at 60 °C for 24 hours and then analyzed by XRD. The purpose of the second treatment was to determine if any swelling clay was in the pyrophyllite sample.

2.3. Zeta Potential Measurements

The zeta potential of the gibbsite sample was measured by electrophoresis (ZetaPALS, Brookhaven Instrument Corp.). The particle suspension was prepared at the desired solution concentration (0.05% by weight) with a background electrolyte of 10mM KCl, and placed in the ZetaPALS chamber. The particle mobility was measured when the electric field was applied and converted to zeta-potential (ξ) using Smoluchowski's equation as follows:

$$U = \frac{\varepsilon \xi}{4\pi\eta} E_{\infty} \quad (1)$$

Where E_{∞} is the applied electric field, and U is the particle velocity in a fluid with dielectric constant ε and viscosity η .

2.4. Contact Angle Measurements

The equilibrium contact angles for gibbsite and pyrophyllite surfaces were measured as a function of pH and dodecylamine collector concentration using the captive bubble method. The contact angle was recorded after the bubble initially contacted each surface for 30 seconds. A contact angle goniometer was used and the results of at least 5 individual bubbles were recorded for each measurement. The average of multiple measurements was calculated and found to have a variation of ± 5 degrees.

It is usually expected that the captive bubble method achieves better approximation for the surface hydrophobicity of mineral surfaces in flotation compared to the sessile drop method. Note, the equilibrium contact angle is a definition in comparison to the advancing and receding contact angles, where an external force is usually applied for their measurements. In addition, the equilibrium contact angles, which are measured to describe the hydrophobicity of model surfaces, are expected to be between the corresponding advancing and receding contact angles.

2.5. Image Analysis (SEM and X-ray Tomography)

2.5.1. SEM Imaging with WETSEM Capsule

A concentrated kaolinite suspension (~50% wt) was prepared at the desired pH for SEM imaging. A WETSEM capsule (QX-102, QuantomiX Ltd., Israel) allows the SEM imaging of a fully hydrated kaolinite suspension at high vacuum (Barshack et al. 2004). A schematic drawing of the WETSEM system is shown in Figure 1. The procedure involved injection of 15 μl of the suspension into a well-sealed WETSEM capsule, which was separated from the interior of the electron microscope by a thin, electron-transparent partition membrane. This membrane is strong enough to sustain a 1 atm pressure difference and, in this way, the sample inside the capsule can be maintained at atmospheric pressure while the SEM chamber reaches high vacuum. The electrons penetrate a few microns into the wet cluster and a SEM image of the cluster structure can be obtained.

Figure 1. Schematic drawing of SEM imaging with a WETSEM capsule.

2.5.2. X-ray Tomography

The 3D structure, size, and shape of kaolinite clusters was established using X-ray nano computerized tomography (nano CT), to provide for further characterization. Following the procedure reported in the literature, the kaolinite particles were sized to a narrow size range (~300–500nm) in order to facilitate imaging (Liu et al. 2014). The kaolinite suspension at pH 4 was prepared and consolidated overnight. The wet sediment was packed and sealed in a 226 μm kapton tube for nano CT scanning. The X-ray radiation is transmitted through the sample, located on a rotational stage. A projection, formed by a set of line-integrals of the attenuation coefficients of the material along a given direction followed by the ray, is acquired with a 2D detector. The X-ray attenuation coefficient at each voxel depends on the material properties, including the mineral density, effective atomic number, and the X-ray energy (McCullough 1975). A set of transform functions and algorithms are applied to reconstruct the three dimensional images of the sample from the projection data, a procedure which has been described in the literature (Lin and Miller 2002; Videla et al. 2006).

3. Results and Discussion

3.1 Characterization of Gibbsite and Pyrophyllite Samples

XRD analysis confirmed that high quality gibbsite and pyrophyllite samples had been selected. The main intensity peaks of the gibbsite sample were an excellent match with the intensity peaks acquired from the database. Silver powder was introduced during preparation of the gibbsite sample in order to isolate surface areas of interest. It was found that the gibbsite sample was of uniform structure.

For the case of pyrophyllite, consistent XRD results were observed between the ethanol alcohol smeared sample and the ethylene glycol smeared sample. These results indicate that there was no swelling clay in the pyrophyllite sample. The intensity peak at 2θ of 9.6° with a c-spacing of $9.2 \text{ \AA}$ is indicative of the 001 basal plane of pyrophyllite. Other minerals present in small amounts may include kaolinite and quartz.

The zeta potential of gibbsite was measured by electrophoresis and the point of zero charge (PZC) of the gibbsite sample was found to be pH 9.5 as shown in Figure 2. The PZC of the gibbsite sample in this study falls in the range of pH 7.5–11.3 as reported in the literature (Kosmulski 2009; Adekola et al. 2011).

In summary, the surface properties of the selected model surfaces (gibbsite and pyrophyllite) were quite similar to those of the alumina surface and silica surface of kaolinite particles. In this case, the interaction of kaolinite surfaces with dodecylamine collector can be anticipated from the interaction of the model surfaces (gibbsite and pyrophyllite) with dodecylamine collector.

Figure 2. Zeta potential results of gibbsite particles from this current study and the literature as a function of pH in a solution of 10mM ionic strength.(Huittinen et al. 2009)

3.2. Contact Angle of Kaolinite Model Surfaces

3.2.1. Effect of pH

The contact angle results for the gibbsite surface with/without dodecylamine hydrochloride collector are summarized in Table 2. Without the collector, the water film between

the bubble and gibbsite surface doesn't rupture which indicates the gibbsite surface is very hydrophilic in nature. With the addition of collector, the gibbsite surface remains hydrophilic in acidic solution, suggesting no adsorption of the collector. In fact, the adsorption of the collector at the gibbsite surface is not expected to happen since both the gibbsite surface and the amine are positively charged in acidic solution resulting in repulsion due to electrostatic interaction.

At high pH (pH 8–10), the contact angle of the gibbsite surface increases and the gibbsite surface becomes somewhat hydrophobic. The change in the wettability of the gibbsite surface suggests the adsorption of dodecylamine hydrochloride. At pH 10, the gibbsite surface is negatively charged and the amine collector is positively charged. In this way, the amine molecules could adsorb at the gibbsite surface by electrostatic attraction, stabilized by hydrophobic interaction of the hydrocarbon chains of adsorbed amine. The interaction between the alumina face surface of kaolinite particles and dodecylamine collector is anticipated to be similar to that observed between the gibbsite surface and the amine collector. In this regard, the alumina face surface of kaolinite particles is expected to remain hydrophilic at low pH, but to adsorb amine collector at high pH and become somewhat hydrophobic with a contact angle of about 20–40° at pH 10 as shown in Table 2.

Table 2. Contact angle results for the gibbsite surface in dodecylamine hydrochloride solution using the captive bubble method.

Collector Concentration	Contact Angle*				
	pH 3	pH 4	pH 6	pH 8	pH 10
None	NA	NA	NA	NA	NA
1×10^{-5} M	NA	NA	NA	NA	20.1
5×10^{-5} M	NA	NA	NA	17.0	25.0
1×10^{-4} M	NA	NA	NA	16.6	30.3
2×10^{-4} M	NA	NA	NA	16.3	39.0

*NA stands for no attachment.

The contact angle measurements at the pyrophyllite basal plane surface with and without dodecylamine hydrochloride are revealed in Table 3. The results illustrate that the pyrophyllite basal plane surface is naturally hydrophobic, with a contact angle of 45–50°. The point of zero

charge of pyrophyllite is believed to be below pH 3. With the addition of amine collector, the pyrophyllite surface becomes more hydrophobic due to the attractive electrostatic interaction between the negatively charged pyrophyllite basal plane surface and the positively charged amine collector. However, like other phyllosilicate minerals, the pyrophyllite basal plane surface (silica surface) carries a permanent negative charge due to isomorphous substitution in the crystal and is not so dependent on pH (Yin et al. 2012). From pH 8 to pH 10, the increase in the water contact angle of the pyrophyllite surface at collector concentrations of 1×10^{-5} M and 5×10^{-5} M is expected to be related to the solution chemistry of dodecylamine as described in equations (2) and (3). At pH 10, the dodecylamine molecule ($RNH_{2(aq)}$) and dodecylamine colloid ($RNH_{2(s)}$) are favored compared to the system at pH 8. Slight precipitation of dodecylamine may account for the increase of the contact angles. Note the sudden decrease of the contact angles at pH 10 and collector concentration greater than 1×10^{-4} M which is discussed in section 3.2.2. Similarly, the silica face surface of kaolinite particles is anticipated to be slightly more hydrophobic with the addition of collector as well as with increasing pH.

Hydrolysis of dodecylamine:

In a saturated system,

Table 3. Contact angle results for the pyrophyllite basal plane surface in dodecylamine hydrochloride solution using the captive bubble method.

Collector Concentration	Contact Angle				
	pH 3	pH 4	pH 6	pH 8	pH 10
None	46.8	49.9	48.4	50.9	36.7
1×10^{-5} M	52.2	49.7	55.4	55.7	70.0
5×10^{-5} M	56.5	57.6	64.0	57.8	81.5
1×10^{-4} M	60.4	57.3	62.4	63.8	58.1
2×10^{-4} M	56.8	60.8	56.9	54.8	48.0

3.2.2. Effect of Dodecylamine Concentration

The impact of dodecylamine concentration on the wettability of kaolinite model surfaces, namely the gibbsite surface and the pyrophyllite basal plane surface is presented in Table 2 and Table 3 along with the effect of pH. At pH 4, the hydrophobicity of the pyrophyllite surface increases with increasing concentration of amine collector, suggesting that the coverage of the amine molecules on the pyrophyllite surface is below monolayer; in contrast, the wettability of the gibbsite surface doesn't change much with the addition of collector, as shown in Figure 3. It is believed that the electrostatic repulsion accounts for the lack of amine adsorption at the gibbsite surface in acidic solution, whereas electrostatic attraction accounts for adsorption of the amine collector at the pyrophyllite surface.

Figure 3. The comparison of the contact angle results for gibbsite and pyrophyllite surfaces after the adsorption of dodecylamine hydrochloride (DDAH) at pH 4.

At high pH (pH 8–10), the hydrophobicity of the gibbsite surface increases slightly with increasing collector concentration due to the electrostatic attraction between gibbsite and the amine. See Table 2. Although the surface charge of the gibbsite surface is reversed to being slightly negative at pH 10 (see Figure 2), the low surface charge density leads to limited

adsorption for the collector dodecylamine on the gibbsite surface. In contrast, the impact of the collector addition on the hydrophobicity of the pyrophyllite surface is significant especially at pH 10, where the contact angle of the pyrophyllite surface increases from $\sim 40^\circ$ to $70\text{--}80^\circ$. The hydrophobicity of pyrophyllite increases slightly with increasing collector concentration but decreases with collector concentrations greater than 1×10^{-4} M at pH 10 as shown in Table 3.

According to the phase equilibrium diagram for dodecylamine solution (Laskowski 1989), the solubility limit of the dodecylamine solution is reached with a concentration of 1×10^{-4} M at pH 10. During the experiment, precipitation of the dodecylamine collector was observed for an amine concentration of 1×10^{-4} M and 2×10^{-4} M at pH 10. For the case of significant amine precipitation, interesting phenomena occur, and the contact angle of the pyrophyllite surface is found to change with time. The contact angle is large ($\sim 90^\circ$) when the bubble first attaches at the pyrophyllite surface, but immediately the contact angle decreases reaching $\sim 50^\circ$ within several seconds. Note that the results presented in Table 2 and Table 3 are recorded after 30s, when the bubble is relatively stable on the pyrophyllite surface. Similar phenomena of a dynamic contact angle for dodecylamine solution have been reported in the literature (Smith 1963; Finch and Smith 1979; Smith and Scott 1990). It is reported that the contact angle for a quartz surface in dodecylamine solution can vanish from an initial value of $80\text{--}86^\circ$ to nil at equilibrium. In our experiments, the contact angle doesn't totally vanish, instead it is stabilized at $\sim 40\text{--}45^\circ$ after several minutes, even hours. Of course, the final equilibrium contact angle is expected to rely on the features of the mineral surface. It is known that quartz is hydrophilic without the collector, while the pyrophyllite surface is naturally hydrophobic, which may account for the observed equilibrium contact angle to some extent. It appears that the dynamic contact angle is related to the precipitation of dodecylamine at the mineral surface, which may result in multilayer coverage. Unfortunately, a complete understanding of the dynamic contact angle phenomenon has not yet been achieved.

3.3. Kaolinite Particle Aggregation

3.3.1. WETSEM Analysis

Kaolinite particle aggregation is known to occur in acid solution and the structure of kaolinite clusters has been simulated in a recent paper (Liu et al. 2015). The kaolinite layer to layer interaction (alumina face surface to silica face surface) and the edge surface to alumina face surface interaction were observed at low pH (pH 5), however, the kaolinite suspension is well dispersed at high pH (pH 8). In this regard, SEM images of a kaolinite suspension contained in a WETSEM capsule were acquired at low pH and high pH as shown in Figure 4 (A) and Figure 4 (B). As expected from the simulation results, kaolinite clusters are formed at low pH (pH 4–5) and kaolinite particles are well dispersed at high pH (pH 8).

3.3.2. Nano Tomography

A three dimensional image of particle aggregation from a kaolinite suspension (pH 4) was prepared after sedimentation using nano tomography, as shown in Figure 5. Images suggest that the kaolinite clusters at pH 4 have a thickness of 300–500nm, which corresponds to the primary size of kaolinite particles. It seems that the individual clusters with a size of 1–3 μ m are able to connect with surrounding clusters and form a more complex network structure as shown in both Figure 4 (A) and Figure 5. The network structure can grow to considerable size depending on the conditions. In Figure 4 (A), the network structure is found to be as large as 5–30 μ m. It is believed that weak interaction of the elementary clusters account for the network structures. In some cases, the network structures take on interesting shapes, the characteristics of which are currently being studied. The formation of elementary cluster structures and network structures are important phenomena associated with kaolinite suspensions at pH 4. The significance of the formation of these structures in the flotation of kaolinite from bauxite ore is discussed in Section 3.4.

3.3.3. Summary

Experimental results from SEM and tomographic image analysis show the structural features of kaolinite clusters similar to the structural features revealed from coarse grain simulations of kaolinite particle aggregation reported in the literature (Liu et al. 2015).

Figure 4. SEM images of kaolinite suspensions in WETSEM cells at pH 4.3 (A) and pH 8.1 (B) (Liu et al. 2015).

Figure 5. Thin section (130nm) of sedimented kaolinite clusters (white structure) at pH 4 as revealed from a 3D X-ray nano tomography image. A typical area (white rectangular region) in image (A) is selected and zoomed in as shown in image (B).

3.4. Discussion of Reverse Flotation

The reverse flotation of kaolinite from bauxite using amine is achieved at pH 4–5 as shown in Figure 6 (Hu et al. 2005; Marino 2012). Unfortunately, the nature of the reverse flotation of kaolinite is not well understood. Only recently have details of the kaolinite surface been established (Gupta and Miller 2010; Liu et al. 2015). It is known that kaolinite has three different surfaces, the silica face surface, the alumina face surface and the edge surface. The silica face surface and edge surface are negatively charged above pH 4; however, the alumina face surface is positively charged below pH 6 and negatively charged above pH 8. Based on our results of the interactions between kaolinite basal plane surfaces and the amine collector, it is suggested that the collector adsorption at kaolinite surfaces is not the only factor which accounts for improved flotation efficiency of kaolinite at low pH. In addition, the significance of kaolinite particle aggregation for the flotation of kaolinite should be recognized. At low pH (~pH 4), the layer to layer interaction between the alumina face surface and the silica face surface is significant, as well as the interaction between the alumina face surface and the edge surface. In this case, the cluster structures, and even more complex network structures, are formed by kaolinite particle aggregation. At high pH (pH 8–10), the kaolinite suspension is well dispersed, with minimal aggregation of primary kaolinite particles.

Figure 6. The flotation recovery of kaolinite with 2×10^{-4} M dodecylamine (Hu et al. 2005).

Based on our previous simulation of kaolinite particle interaction, about 10% more of the silica face surfaces are exposed in kaolinite clusters when compared to the alumina face surfaces at low pH (pH 4–5) (Liu et al. 2015). The silica surfaces are negatively charged and have modest natural hydrophobicity. The charge of dodecylamine is positive below pH 11, and the resulting clusters promote dodecylamine collector adsorption at the silica surfaces, giving rise to clusters with a hydrophobic character ready for flotation. A typical kaolinite cluster was selected from the simulation results (Liu et al. 2015) and a simple drawing in Figure 7 illustrates the adsorption of dodecylamine collector by the kaolinite cluster at low pH ($\sim$ pH 4), forming a hydrophobic structure. In addition, the cluster size of kaolinite is significantly increased, the cluster having a size of 5–30 μm , much larger than the size of the primary kaolinite particle ($\sim$ 500nm). It is reported that the collision efficiency (defined as the probability of collision) between the particles and bubbles is positively correlated with the particle size when the particle size is much smaller than the bubble size (Gaudin 1957; Jameson et al. 2007). The cluster formation with larger size significantly increases the possibility for bubble attachment at cluster surfaces, thus resulting in

greater flotation recovery. In contrast, the gibbsite particle surfaces and the alumina face surfaces of kaolinite particles do not appear to adsorb dodecylamine collector and such surfaces remain hydrophilic. In this way, kaolinite clusters are floated with dodecylamine and separated from gibbsite.

At high pH (pH 8–10), all the surfaces of kaolinite particles as well as gibbsite are able to adsorb dodecylamine by electrostatic attraction. In this case, good separation efficiency cannot be achieved. It is expected that cluster formation will reduce collector consumption because of the reduction in surface available for adsorption.

Figure 7. Kaolinite cluster adsorption of dodecylamine collector at low pH (~pH 4). Pink surfaces represent the silica face surfaces of kaolinite particles, and blue surfaces represent the alumina face surfaces of the primary kaolinite particles.

4. Summary and Conclusions

Gibbsite and pyrophyllite basal plane surfaces have been used as model surfaces to simulate the two face surfaces of kaolinite and their adsorption of dodecylamine collector. The effect of pH and the collector concentration on the hydrophobicity of the model surfaces have been investigated based on contact angle measurements. With the addition of dodecylamine, the gibbsite surface (or alumina face surface of kaolinite) remains hydrophilic at low pH (pH 3–6), but becomes somewhat hydrophobic at high pH (pH 8–10), indicating that amine adsorption only occurs at high pH.

In contrast, the pyrophyllite basal plane surface (or silica face surface of kaolinite) becomes more hydrophobic with the addition of dodecylamine for the whole pH range studied, indicating the adsorption of collector occurs in both acidic solution and alkaline solution. Interesting phenomena have been observed beyond the solubility limit of dodecylamine (a concentration of 1×10^{-4} M at pH 10), in that the initial high contact angle ($\sim 90^\circ$) of the pyrophyllite surface decreases rapidly after bubble attachment, reaching an equilibrium contact angle of $\sim 50^\circ$ after several seconds.

The mechanism of kaolinite flotation from gibbsite is discussed based on the surface properties of kaolinite particles, cluster structure, and collector adsorption. A reasonable explanation for the kaolinite flotation process is now available. The efficient flotation of kaolinite at low pH is caused by the fact that large clusters of primary kaolinite particles are formed. The increased size of the clusters and collector adsorption at the exposed silica face surfaces account for the effective reverse flotation of kaolinite from bauxite ores.

In this case, the significance of particle aggregation in the reverse flotation of kaolinite from bauxite ore should be recognized. In addition to the traditional concept that collector adsorption defines flotation efficiency, it is clear that, in some cases, the particle interaction can be significant and impact flotation behavior. Finally it should be mentioned that particle aggregation of kaolinite determines the sedimentation/consolidation of suspensions so that

interaction of flocculants with aggregated particle clusters is an important issue to be considered in future research.

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