Muscovite mica and koalin slurries: Yield stress–volume fraction and deflocculation point zeta potential comparison

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ABSTRACT

Mica slurries were found to be flocculated over the whole pH range of between 2 and 12. These slurries of different solid loading appeared to obey the yield stress–DLVO force model producing a single value for the deflocculation point zeta potential or the critical zeta potential (at point of flocculated-disperse state transition) of ~48 mV. Such a high value indicates the presence of an additional attractive force in addition to the van der Waals force. This force is attributed to edge-face unlike charge attraction. The use of pyrophosphate additive to minimize edge–face interactions via positive edge charge neutralization caused a large reduction in the critical zeta potential, to 22 mV. With this new value, the Hamaker constant of mica in water was determined to be ~13 zJ. This falls within the range of values reported for mica. Low Ca(II) kaolin suspension displayed a lower critical zeta potential of 41 mV and the use of pyrophosphate additive at 0.2 and 0.4 dwb% appeared not to decrease the magnitude of the critical zeta potential. This pyrophosphate-influence critical zeta potential is also independent of Ca(II) content in the kaolin. The established model of edge–face attraction for kaolin suspension at low pH may not be completely correct. A face–face interaction model may be more appropriate. A power law model relating the maximum yield stress with volume fraction showed a very high exponent value of 8 for mica slurries, only 3.1 for the low Ca(II) kaolin and 3.6–3.9 for the high Ca(II) kaolin suspensions. This exponent value may reflect the predominant particle–particle interaction configuration in the clay suspensions.

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1. Introduction

The surface chemistry of muscovite mica powders and sheets such as charge density and charging behavior, has been investigated quite extensively [1–4]. Mica, a 2:1 layered non-swelling clay, is found in significant quantities in some mineral slurries and tailings. Hence its rheological behavior under various surface chemistry conditions have also been closely examined by Nosrati et al. [5,6] with the objective of optimizing the processing of these slurries. Such a study on the surface chemistry–rheology relationship provides useful information that enables us to make the correct decision on the specific approach employed to treat, mix, thicken and pump these slurries. After the hydrometallurgical extraction process, the clay-rich tailings are often subjected to flocculation, thickening and compression processes in a thickener so as to increase the underflow solid content and to recover as much as possible of the water for reuse. All mining and mineral processing companies are forced by legislations in Australia to minimize their environmental footprint in tailing handling and disposal. Thus to meet these legislative requirements, all mining companies have added extra resources in terms of new technology, research and training, into tailing processing, handling and disposal. Thickening and compression are significantly

affected by the strength and nature of the interparticle forces and the type of particle interaction configuration; edge–face (EF), face–face (FF) and edge–edge (EE). These factors have a marked effect on the particle packing behavior and hence the underflow solid concentration. The surface chemistry condition such as pH and ionic strength, determines the nature and strength of the inter-particle force in the network structure and the type of particle interaction configuration. The approach that we pioneered has been to characterize the yield stress as a function of pH as this will provide us with an inter-particle or surface force spectrum of the suspension at various pH levels. Together with zeta potential and adsorbed additive information we can identify the dominant surface force operating in the suspension at any given pH [7–9]. However, the relationship between the strength of the inter-particle attractive force in the network structure and the type of particle interaction configuration is still unclear. A major objective of this investigation is to evaluate whether such a relationship exists at the state of maximum yield stress or the strongest inter-particle attractive force. Most yield stress–solid volume fraction data of suspensions obeyed a power law relationship. We will explore the use of the power exponent to identify the type of particle interaction configuration at the maximum inter-particle attractive force.

Like other clays such as bentonite (a similar 2:1 layered clay), the heterogeneous charge behavior of the mica particles leads to complex behavior in particle packing and rheology. Unlike bentonite, mica

slurries do not display time-dependent rheological behavior. Kaolin slurries are also not thixotropic [10].

Apart from being present in mineral wastes, there are actually several commercial applications for mica sheets and powders. The uses for the sheet are as electrical insulator, electronic components and detector window of Geiger counter, and for mica powder are as drilling fluid ingredient, paint pigments and joint compounds for wall filling. Muscovite mica sheet is molecularly smooth and relatively transparent and these properties make it an ideal material for colloidal force–distance study. Sheet mica is hence an integral component of the Surface Force Apparatus (SFA) developed by Tabor and Winterton to measure the interaction force between cross-cylinder mica sheets in air and vacuum as a function of nanometer or micrometer separation distance [1]. These data were used to validate the van der Waals interaction theory. The force–distance measurement capability of this apparatus was subsequently advanced to include interaction in liquid medium, in particular, water [2,11]. These advances allowed colloidal force theories such as DLVO interaction model to be tested. The testing required the surface properties of mica sheet in water to be accurately known, in particular, surface charge density or potential and its dependence upon pH and ionic strength. The force–distance data obtained for interaction between cross-cylinder mica sheets in electrolyte solutions validated the DLVO theory. Those data obtained at very high ionic strength were used to extract the mica Hamaker constant in water from the van der Waal force equation used to fit the data [2]. The double layer repulsive force was unimportant at high ionic strength and hence was ignored. A value of 22 zJ was obtained for the Hamaker constant [2]. The edge of the mica sheet did not play a role in these interaction force characterizations. The nature of the charge and the surface charge density of the edge are pH-dependent [12,13]. The point of zero charge (pzc) of the edge was deduced to have a value of pH 7.5 [13]. An objective of this study is to present a new approach for the determination of the Hamaker constant of mica in water. This uses the yield stress–DLVO force model method. The issue of interactions involving the particle edges of mica slurries must be addressed in this investigation. A long accepted model for kaolin at low pH is that the particles in suspension interact predominantly via the EF configuration [14]. Our comparisons of the surface chemistry and rheological results of mica and low Ca(II) suspensions must therefore be conducted at low pH where the particle interaction configuration of both is supposed to be EF in addition to the yield stress being close to maximum and the zeta potential being very low [19,20]. This comparison may review important information of the relative strength of the EF interactions, where appropriate results for high Ca(II) kaolin suspension will also be included.

Unlike the more common clay slurries such as kaolinite and bentonite, where rheological studies are numerous [14–20], this is not the case with muscovite mica slurries. Past studies have shown that the yield stress and zeta potential of mica slurries is pH-dependent [5,6]. The point of zero zeta potential obtained via high to low pH titration was reported to be located at pH 4.2. However this point was shifted to a higher pH when the direction of pH titration was reversed [5]. This was attributed to leached metal ions such as Si(IV), Al(III), Fe(III) and Cu(II), produced at low pH forming hydrolysis products at higher pH that adsorb readily on the mica surface altering its surface properties. These adsorbed metal hydrolysis products also affect the clay slurry rheological properties [5,6]. Leong [21] has reported that adsorbed Cu(II) and Al(III) ion hydrolysis products can bring about yield stress increase of silica suspensions by a few orders of magnitude. Thus in this study, the direction of pH change employed will always be from high to low pH.

An important objective of this study is to determine the zeta potential value of the mica slurries at the point of transition from flocculated to dispersed state or at deflocculation point in the absence of multivalent metal ion hydrolysis products. This critical zeta potential value is a strong indication of the maximum strength of attraction between mica particles [22]. It can be used to calculate the Hamaker constant of

the mica in water [22,23] or to gauge the presence of an additional attractive force. Thus, the second major objective of this study is to determine the Hamaker constant of mica in water from the yield stress and zeta potential data. The knowledge gained will lead to a better understanding of the relationship between the surface chemistry and the rheology of mica slurries. A good outcome of this study would be the identification of good surface chemistry control tools that can be used to manipulate with ease the slurry rheological or processing properties.

In summary, the objectives of this study are:

i) to use the power law relationship between maximum yield stress and solid volume fraction to evaluate the type of clay particle interaction configuration such edge–face, edge–edge,

ii) to determine the Hamaker constant in water of mica via the critical zeta potential parameter at the point of transition from flocculated to disperse state where the edge positive charge has been neutralized with an peptizer, and

iii) to acquire a good understanding of the relationship between surface chemistry parameters and suspension rheology for these clays.

2. Experimental methods

The mica powder was sourced from Export Linker (Calcutta, India), sodium pyrophosphate $Na_4P_2O_7$ and other chemicals were all supplied by Sigma Aldrich. For zeta potential and yield stress tests, nitric acid (HNO_3) and sodium hydroxide (NaOH) were used to vary the pH.

The particle size distribution of the mica powder characterized with a Malvern Mastersizer Microplus, was relatively narrow. It has a D_{10} of 1.67 μm, a D_{50} of 7.94 μm and a D_{90} of 18.83 μm. The volume average diameter, $D_{4,3}$, is 9.3 μm. This mica has a BET surface area of 7.9 m²/g measured with a Micromeretic Gemini instrument. The SEM image of the particles is shown in Fig. 1. The particles are clearly platelet in shape. It is also clear from this image that most of the surface area of the powder is contributed by the basal plane of the particles.

The composition of mica ($KAl_2(AlSi_3O_{10})(OH)_2$) evaluated via XRF comprised of 47.9% SiO_2, 32% Al_2O_3, 0.136% TiO_2, 3.77% Fe_2O_3, 0.107% CaO, 9.39% K_2O, 0.296% MgO, 1.28% Na_2O and <0.01% SO_3. Unlike bentonite [9], mica is characterized by a high potassium content. This mica has very similar content of SiO_2, Al_2O_3, Fe_2O_3 and K_2O to that was used by Nosrati et al. [5,6].

Muscovite mica slurries at alkaline pH were prepared by adding clay powder to distilled water to the required weight percent solids. The pH of the slurries was adjusted with NaOH to a value of ~12. Additive, if required, was first dissolved in the distilled water prior to clay powder
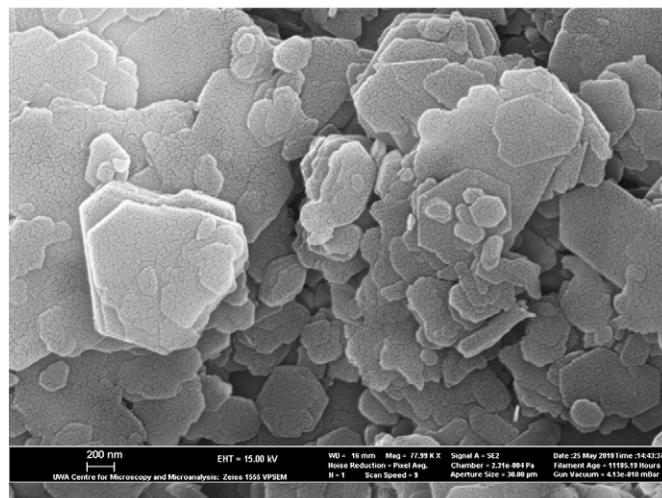

Fig. 1. The SEM image of mica particles.