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Characterisation of kaolinite colloidal and flow behaviour via crystallinity measurements

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ABSTRACT

This study evaluates the possibility of predicting colloidal and flow behaviour of kaolinite suspensions by measuring kaolinite crystallinity. The Hinckley index of different samples was calculated from XRD spectra as an indicator of the crystallinity. Kaolinite samples with a high Hinckley index showed a defined platy morphology with smooth surfaces of low surface area, whilst progressively roughened basal planes with prevalent broken edges were observed in kaolinite samples of lower Hinckley indices. Despite similarity in the elemental composition, the kaolinite samples present different surface charge properties, likely due to variations in exposed pH dependent edge sites. Poorly crystallised kaolinite samples were characterised by higher yield stresses and viscosities. This study highlights the importance of crystallinity characterisation towards predicting colloidal behaviour and flow characteristics of kaolinite suspensions.

1. Introduction

The ideal structure of kaolinite ($Al_4(Si_4O_{10})(OH)_8$) is composed of an octahedral sheet of gibbsite ($Al(OH)_3$) linked to a tetrahedral sheet of silica. Upon breakage, two different surfaces are formed. The basal plane-face results from the cleavage of one layer from another, whilst the edges arise due to the rupture of the ionic or covalent bonds within the layers. Therefore, kaolinite pseudo-hexagonal platelets are composed of two distinctly different planes, each with different charge properties. The edges are believed to carry a pH dependent charge determined by the protonation and deprotonation of exposed aluminol and silanol amphoteric groups [1,2]. The charge on the edge sites characteristically changes from positive to negative with increasing pH. At the edge, point of zero charge (p.z.c), the charge on the edge site changes from positive to negative. The charge on the faces, however, is assumed to be largely due to the isomorphous substitution of higher valence ions with ions of a lower valence (e.g. Si^{4+} substitution by Al^{3+}), resulting in a permanent negative charge [3]. However, a charge dependency of this site has also been proposed, not inconsistent with the hydrolysis of silicon in the surface plane [4].

There have been extensive studies on the physico-chemical properties of kaolinite including the effect of factors such as pH, electrolyte type and ionic concentration [5–7]. The importance of physical properties such as particle shape, aspect ratio and surface area towards suspension colloidal behaviour has also been demonstrated [4,8–10]. However, little consideration has been made to variations in kaolinite crystallinity and its importance in predicting kaolinite suspension rheology and colloidal behaviour.

The non-homogeneity of kaolinite in deposits from the same geographic locations has been acknowledged by many researchers. However, most variations have often been attributed to macroscopic deviations, principally in texture, hardness, mineral and chemical impurities. The differences in the sharpness and resolution of kaolinite X-ray peaks highlighted that kaolinite minerals can also present variations in crystallinity. A number of empirical relationships have since been developed for the estimation of the degree of crystallinity. The most widely used relation for kaolin minerals is that proposed by Hinckley [11] which uses peaks within a shorter angular range to facilitate optimal peak resolution and intensity for more accurate index calculation. This calculation yields a dimensionless number which normally varies between 0.2 and 1.5, where a higher index value is indicative of well crystallised kaolinite particles with a smooth surface structure and defined edges and basal planes [12]. However, this ordered morphology is altered in poorly crystallised particles with low Hinckley indices which then comprise a rough surface structure with ragged, broken edges across the basal surface.

The aggregation of kaolinite particles can occur in three main modes of association, namely face-face (FF), edge-face (EF) and edge-edge (EE). FF association leads to the formation of lamellar structured aggregates of low apparent volume per plate. This type of particle association is characterised by low suspension yield stresses. EF and EE associations,

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on the other hand, lead to three dimensional "house of cards" structures where the volume occupied or swept out by an individual particle is maximised, and the apparent volume fraction of the suspension is also a maximum. This results in more rheologically complex suspensions than would occur with FF association [2,13]. The realignment from one form of particle association to another has traditionally been attributed to electrostatic attractive and repulsive forces between the edges and faces. It is generally believed that at pH values below the edge p.z.c, EF structures will exist due to the attraction between positively charged edges and negatively charged faces. This type of aggregation is enhanced in kaolinite particles, which inherently have thicker edges than other phyllosilicates such as muscovite or smectite. This renders the edge charge more significant. The changes in particle alignment as a function of pH are discussed in more detail by several researchers [1,2,7].

Although these are the forms of aggregation that have traditionally been assumed for kaolinite particles, recent study [12] demonstrated that particle aggregation may be more complicated depending on the crystallinity. It was demonstrated that for poorly crystallised kaolinite samples, self-aggregation may occur due to the hydrogen bonding between exposed silanol and aluminol broken edges on the basal surfaces of adjacent particles. This then results in additional randomised EE and EF structures, which were seen to have higher settling rates and bed densities than well crystallised kaolinite samples [12]. The flow properties (rheology) of kaolinite suspensions are already complicated due to the formation of heterocoagulated structures. Therefore, additional self-aggregation will likely result in even more complex suspension rheology. Such aggregation is also likely enhanced by a high frequency of broken edges as expected in poorly crystallised kaolinite particles. This means that, keeping all things constant, structural formation may differ for kaolinite samples with different crystallinity resulting in variable rheological characteristics. Moreover, differences in surface morphology from smooth to ragged surfaces may result in different surfaces being exposed and kaolinite samples of different crystallinity are likely to present dissimilar surface charge characteristics.

This study investigates whether there is a relationship between kaolinite crystallinity and its suspension colloidal behaviour, defined as surface charge and rheological characteristics in this case. The findings could be beneficial towards ongoing studies to more accurately characterise clay minerals or the characterisation of clay minerals.

2. Material and experimental methods

2.1. Materials

Three kaolinite samples (Snobrite, Q38 and KGa2) were chosen for this study, based on their differences in crystallinity as reported previously [12]; although they may be also different in composition or size distribution which will be discussed. These kaolinite samples were supplied in powder form. Snobrite and Q38 were provided by Unimin Australia Limited and KGa2 was from a mine site in Warren County, Georgia (USA) and supplied by the Clay Mineral Society (USA).

The mineralogy was determined using X-ray diffraction (XRD). Samples were micronised in ethanol and dried overnight at 40 °C prior to measurement. XRD spectra were obtained using a PANalytical X'Pert Pro MPD powder diffractometer (manufactured by PANalytical, Netherlands), equipped with an XCelerator detector. Samples were run with fixed divergence and anti-scatter slits, using Co-Kα radiation. PANalytical's HighScore Plus Software (v3.0d) was used for phase identification and quantification using the Rietveld refinement method. XRD quantification determined the abundances of each kaolinite sample with purities of 89%, 85% and 99% for Snobrite, Q38 and KGa2, respectively (Table 1). The impurities comprised mainly of quartz and illite. It has previously been shown that these minerals do not affect the suspension rheology [14,15]. Whilst the colloidal behaviour can still be assumed to be largely due to the bulk mineralogy i.e. kaolinite, the synergistic or antagonistic effects of these impurities on the colloidal properties is worth investigating in future analyses.

2.2. Sample characterisation

2.2.1. Crystallinity measurements

The crystallinity of each kaolinite sample was estimated using the Hinckley index calculation [16]. This is ratio of the sum of the net peak intensities of the $1\bar{1}0$ and $1\bar{1}1$ reflections measured from the inter-peak background to the total net peak intensity of the $1\bar{1}0$ peak measured from the background of the whole X-ray diffraction record. The <2 μm fraction of each kaolinite sample was also extracted to minimise the quartz material for Hinckley index calculation. Un-oriented samples were then analysed with the XRD spectra scanned over a 2 range of 20–32° 2 , covering the spectra for relevant Hinckley peaks.

2.2.2. Particle morphology

A field emission, environmental FEI Quanta 400 (FEI, USA) scanning electron microscope (ESEM) was used to investigate the surface morphology of each kaolinite. Representative samples were suspended in isopropanol and sonicated for 5 min. A drop of each suspension was then placed on a polished carbon block and allowed to evaporate prior to examination.

2.2.3. Particle size and surface area

The particle size distribution of each kaolinite was estimated using wet size light scattering technology using a Malvern Mastersizer (Malvern, UK). In each case, 0.5 g samples were dispersed in water, and the pH was adjusted to pH 10. At these conditions, kaolinite particles have high enough surface charge for repulsion which enhances dispersion. Sodium hexametaphosphate (Calgon) was also used as a dispersant at a concentration of 1 wt.%. The sample was sonicated for 60 s at 50% ultrasonic power for 60 s before the measurement. Pump and stirring speeds of 330 rpm and 350 rpm respectively were used during the measurement. For each kaolinite, tests were carried out in triplicate for reproducibility. The size distribution shown for each mineral is representative of the average size distribution of three individual measurements.

Table 1
XRD characterisation of Snobrite, Q38 and KGa2, bulk sample and <2 μm fraction.

Bulk sample (wt.%)								
	Kaolinite	Quartz	Calcite	Dolomite	Anatase	Rutile	Illite–mica	Smectite
Snobrite	89	5	2	2	<1			2
KGa2	99	<1			1			
Q38	85	5			1	<1	9	
< 2 μm size fraction (wt.%)								
Snobrite	96	<1			<1			4
KGa2	99	<1			<1			
Q38	91	2			1		5	1