Colloids and Surfaces A: Physicochem. Eng. Aspects 468 (2015) 103–113

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Physicochemical behaviors of kaolin slurries with and without cations—Contributions of alumina and silica sheets

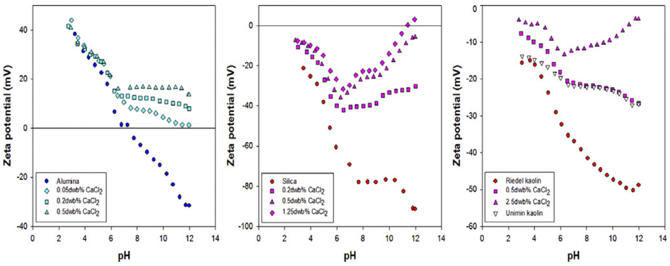
Lavanya Avadiar[a], Yee-Kwong Leong[a,*], Andy Fourie[b]

[a] School of Mechanical and Chemical Engineering (M050), The University of Western Australia (UWA), 35 Stirling Highway, Crawley, WA 6009, Australia
[b] School of Civil and Resource Engineering (M051), The University of Western Australia (UWA), 35 Stirling Highway, Crawley, WA 6009, Australia

HIGHLIGHTS

- Zeta potential-pH and yield stress-pH behaviors observed.
- Silica and kaolin behaviors were similar to each other with and without cations.
- However, alumina's behaviors were less similar to (silica's) and kaolin's.
- Silica sheets compared to alumina sheets control kaolin behaviors more.
- Silica and kaolin particle interactions with hydrolyzed products could be similar.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 October 2014
Received in revised form 4 December 2014
Accepted 9 December 2014
Available online 19 December 2014

Keywords:
Cationic hydrolysed products
Alumina slurries
Silica slurries
Kaolin slurries
Zeta potential-pH
Yield stress-pH

ABSTRACT

Numerous studies on the surface charge-pH and yield stress-pH behaviors of kaolin slurries with respect to the pH-dependency of alumina (Al) sheets, silica (Si) sheets and edges in kaolin particles have been carried out. There is, however, still a paucity of studies that explain if the alumina sheets or the silica sheets in kaolin particles contribute in greater extents to the surface charges of kaolin particles that will consequently affect the kaolin particle interactions and yield stresses. In this study, the contributions of the alumina and the silica sheets to the zeta potential-pH and yield stress-pH behaviors of Riedel kaolin particles, which display no isoelectric points (IEPs), are analyzed by comparing these behaviors of Riedel kaolin slurries to that of alumina and silica slurries with and without Mg^{2+} and Ca^{2+} cations. With and without cations, the behaviors of Riedel kaolin slurries were more similar to the behaviors of silica compared to alumina slurries. The principal reason for this similarity is due to the high concentrations of negative charges on both silica and Riedel kaolin particles at all pH compared to the lower concentrations of negative charges on alumina particles. This explains that the permanently negatively charged silica sheets contribute in greater extents to the surface charge-pH and yield stress-pH behaviors of Riedel kaolin slurries compared to the alumina sheets.

1. Introduction

Kaolin particles comprise of one octahedral alumina (Al) sheet and one tetrahedral silica (Si) sheet that fit together to form the basic repeating unit layer of the particle (Fig. 1) [1]. In the alumina and silica sheets, isomorphic substitution of Mg^{2+} for Al^{3+} and of Al^{3+} for Si^{4+} respectively occurs. This substitution results in silica sheets to be pH-independent and permanently negatively charged.

Abbreviations: CR, charge reversals; IEPs, isoelectric points; BET, Brunauer, Emmett, Teller; SEM, scanning electron microscopy; PSDs, particle size distributions; wt%, weight percentages; ESA, electrokinetic sonic amplitude; dwb%, dry weight percentages; HRTEM, high-resolution transmission electron microscopy.

* Corresponding author. Tel.: +61 8 6488 3602; fax: +61 8 6488 1024.
E-mail addresses: avadil01@student.uwa.edu.au (L. Avadiar), yeekwong.leong@uwa.edu.au (Y.-K. Leong), andy.fourie@uwa.edu.au (A. Fourie).

http://dx.doi.org/10.1016/j.colsurfa.2014.12.019
0927-7757/

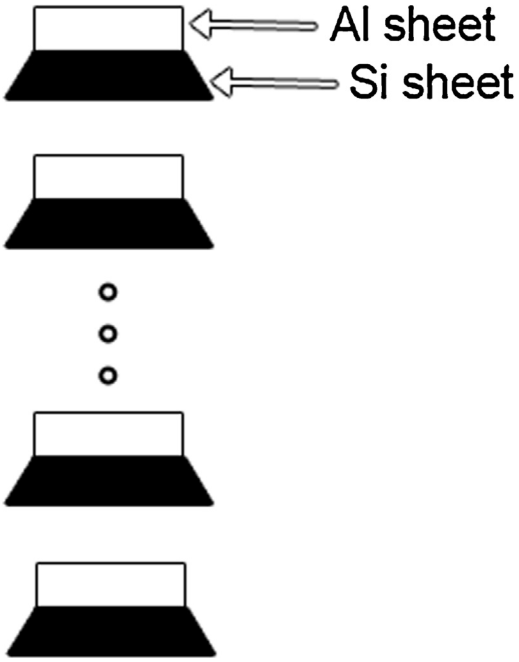


Fig. 1. A schematic diagram representing the kaolin crystal layer structure and the primary building blocks of the kaolin particle.
Adapted from Palomino and Santamarina [1].

On the other hand, despite the substitution, the presence of surface hydroxyls (—OH) on the alumina sheets causes these sheets to display patch-wise charge heterogeneity that is dependent on the pH and ionic strength of surrounding medium. This results in alumina sheets to display an isoelectric point (IEP) between pH 6.0–8.0 [2]. At the edges of the kaolin particles, bonds on these alumina and silica sheets are broken to comprise of aluminol (Al—OH) and silanol (Si—OH) groups respectively. These groups (i.e. broken bonds) cause the edges on kaolin particles to display charge heterogeneity and carry an IEP between pH 5.0 and 7.0 [3].

Numerous studies, including studies by Lagaly [4], Flegmann et al. [5] and Rand and Melton [6] have analyzed kaolin particle interactions and consequent kaolin rheological behaviors in relation to these surface charge-pH properties of alumina sheets, silica sheets and especially edges in kaolin particles. Teh et al. [7], via sequential zeta potential-pH and yield stress-pH measurements on the same kaolin suspensions, have shown that most (low CaO content) kaolin slurries obey the yield stress-DLVO force model (i.e. the yield stress decreases linearly with increasing square of zeta potential) to indicate that high kaolin yield stresses occurs at low kaolin particle zeta potential magnitudes. These studies have indicated that at low pH when alumina sheets and edges are positively charged (i.e. when *average* zeta potential magnitudes are low), particle interactions and thus high yield stresses occur within most kaolin slurries where at high pH when alumina sheets, silica sheets and edges are all negatively charged (i.e. when *average* zeta potential magnitudes are high), weak interactions or complete de-flocculation and thus low or negligible yield stresses are respectively recorded within most kaolin slurries. This explains the yield stress-zeta potential-pH behavior of pristine kaolin slurries without cations.

The zeta potential-pH and yield stress-pH behaviors of kaolin slurries with cations have also been analyzed in literature [8,9]. For example, Mpofu et al. [8] stated that the first hydrolysis product of Ca(II) ions forms at $\text{pH} > 10.5$ to increase dramatically in concentrations at pH 10.5–14 that caused the reductions in (negative) zeta potential magnitudes and induced a charge reversal (CR) from negative to positive charges at $\text{pH} > 10$ within kaolin slurries. They attributed the CR to the specific adsorption of Ca(OH)^+ and possibly the surface nucleation of Ca(OH)_2 [10]. Atesok et al. [11] also observed that Ca adsorption concentrations on Na-kaolinite particles increased with pH to display a sharp increase at $\text{pH} > 10$ where they attributed the dramatic reduction in negative zeta potentials at pH 11.3 to the adsorption of CaOH^+. Divalent Mg^{2+} and Ca^{2+} cations hydrolyze to form hydroxy complexes (Mg(OH)^+ and Ca(OH)^+) and hydroxide precipitates (Mg(OH)_2 and Ca(OH)_2) at high pH that adsorb to possibly alter and reverse kaolin particle surface charges from negative to positive at the specific (high) pH regions of product adsorptions [12]. In addition, these adsorptions could enhance or cause variations in kaolin particle interaction forces at the specific pH regions of hydrolyzed product adsorption to alter the kaolin slurry flow, i.e. rheological-pH behavior [5,8,13].

Particles could also (naturally) carry cations in sufficiently high concentrations to display varied physicochemical behaviors. An example is the Unimin kaolin particle, which is understood to carry sufficiently high Ca^{2+} concentrations. The presence of Ca(II) hydrolyzed products is observed to cause Unimin kaolin slurries to display high yield stresses at high pH while most kaolin slurries, such as Riedel, Sigma and Fluka, with negligibly high cationic concentrations commonly display high yield stresses only at low pH [7,9].

While knowledge on the yield stress-zeta potential-pH relation of (most) pristine kaolin slurries and literature on the effects of cations on the zeta potential and yield stress of these kaolin slurries are abundant, the knowledge on if it is the alumina or the silica sheets that contribute in greater extents to these zeta potential (i.e. surface charge) and yield stress (i.e. particle interactions and rheology) behaviors of kaolin slurries with and without cations is still scarce. Due to the varied surface charge-pH densities of alumina sheets vs. silica sheets in kaolin particles, it is possible that cationic hydrolyzed products could adsorb in greater extents on one of these interacting sites that would control the behaviors of kaolin particles. While the dominant interacting particle site that controls the behaviors of homogeneous particles such as silica and alumina are clearly evident, identifying the dominant interacting site of kaolin particles, which comprise of heterogeneous surface charge densities, is not as straightforward.

As a result, the aim of this study was to analyze the contributions of the alumina sheets and the silica sheets in the Riedel kaolin particles to the zeta potential-pH and yield stress-pH behaviors of these Riedel kaolin particle slurries. (This study did not include analysis on the edges of the Riedel kaolin particles.) Similar to most kaolin particles, Riedel kaolin particles (which are of low CaO content) display no IEP (or IEP at very low pH) [9] and obey the yield stress-DLVO force model [14] to display high yield stresses at low zeta potential magnitudes and vice versa. In order to analyze the contributions of the alumina and silica sheets to Riedel kaolin behaviors, the zeta potential-pH and the yield stress-pH behaviors of Riedel kaolin slurries were compared to the zeta potential-pH and the yield stress-pH behaviors of alumina and silica slurries with and without Mg^{2+} and Ca^{2+} cations. The yield stress-pH data comparisons is understood to confirm or alter possible inferences made from the zeta potential-pH data comparisons, which could involve discrepancies with regard to the kaolin particle zeta potentials measured (explained in Section 2.2). Alumina and silica slurries were chosen for comparison to the Riedel kaolin slurries as the constituent elements in kaolin particles are alumina and silica (Fig. 1). Similarities in the behaviors of the alumina and/or the silica slurries to the Riedel kaolin slurries indicated that the alumina and/or the silica sheet(s) contributed in greater extents to the Riedel kaolin surface charges and particle interactions.