Applied Clay Science 148 (2017) 11–16

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Determination of kaolinite floc size and structure using interface settling velocity

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ARTICLE INFO

Keywords:
Stokes diameter of floc
Kaolinite
Settling of floc
Settling velocity
Visualization of floc

ABSTRACT

Although interface settling methods are generally simple, they are not used to determine physical properties such as size of flocs because the relationship between the physical properties of a floc during the settling process and its settling velocity is poorly understood. In this study, the interface settling method was extended to soft matter such as kaolinite floc, and a technique was developed to measure the size and diameter of the floc during the settling process using an interface settling method. An equation proposed by Michaels and Bolger, based on the relationship between interface settling velocity and the solid volume concentration of interfering hard spheres as originally developed by Richardson and Zaki, can be applied to soft matter such as clay floc. The present study demonstrated that the effective volume of floc, as well as the diameters of individual floc particles, can be measured by the interface settling method. This was achieved by incorporating the equation for the settling of spheres in a viscous fluid into Michaels and Bolger's settling velocity equation. To investigate the validity of the effective volume and diameter of floc, the diameter and settling velocity were also measured visually. The experimental work in this study involved constructing a device in which soft floc material could settle without interruption, recording the settling with a video camera attached to an optical microscope, and measuring the diameters of individual flocs and their settling velocities from the recorded images. The interface settling method and the optical visualization method provide similar results for the effective volume and the diameter of the floc particles when they are compared at the same pH and the same ionic concentrations. This work demonstrates that the interface settling method is an efficient way to measure the size and diameter of soft matter such as kaolinite floc.

1. Introduction

The formation of coagulated structures in a kaolinite suspension is believed to occur when large numbers of aggregates (called flocs) gather and come into contact each other (Sekiguchi et al., 2004; Ooi et al., 2007). Flocs are the basic unit of aggregates; their sizes and structures have been studied frequently, using research methods that can be categorized into two principal approaches. The first approach is to determine the size and porosity of the kaolinite flocs by measuring the interface settling velocity of an aggregated suspension. This method, developed by Michaels and Bolger (1962), can be applied to the settling velocity of soft aggregates (floc) by extending the empirical formula of interface settling velocity and solid volume concentration by interference of solid spheres, as originally developed by Richardson and Zaki (1954). The other approach is to focus on an individual floc and measure its settling velocity and diameter by visualizing the settling process (*i.e.* producing and recording optical images), indicating the shape, porosity, and structure of the floc. This research began in the field of water treatment technology (Tambo and Watanabe, 1979), and was developed to determine detailed floc density and structural dimensionality by improving the measurement accuracy (Nakamura et al., 1993; Adachi and Tanaka, 1997). In recent years, the physical properties of flocs in the settling process of aggregate suspensions have been the subject of many studies.

The main objectives of previous studies in this field have included analysis of fluid resistance between the wall of the settling tube and the flocs in the settling process of individual floc particles (Lall et al., 1989; Becker et al., 1996; Chhabra et al., 2003); analysis of the structures of flocs during aggregation processes (Allain et al., 1995, 1996; Gonzalez, 2001; Gonzalez et al., 2004); and elucidation of the structural changes to the flocs and changes in settling velocity caused by salt concentration, pH, and the addition of polymeric additives (Watts et al., 2000; Nasser and James, 2006; Akther et al., 2008; Bessho and Degueldre, 2009; Kim and Palomino, 2009; Mietta et al., 2011; Ji et al., 2013). The

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http://dx.doi.org/10.1016/j.clay.2017.07.024
Received 12 April 2017; Received in revised form 21 July 2017; Accepted 23 July 2017

effects on floc size and the structural changes caused by flocculant additions, such as polymeric additives, have been analyzed in recent studies of the physical properties of clay flocs (Tan et al., 2012; Nasser, 2014).

Research on floc physical properties investigated using interface settling methods have not advanced significantly since those originally conducted by Michaels and Bolger (1962). Most recent research has focused on the effects of flocculant addition on these settling properties. The interface settling method is a very simple measurement technique, but the relationship between the physical properties and the floc settling process is not clear; hence, the interface settling method has not been used to study the physical properties of flocs, such as the size and diameter. The interface settling method, however, is simpler and less costly than the visualization method. If physical properties can be observed or inferred using the interface settling method, its range of application will be greatly expanded.

In the present study, the relationship between the interface settling velocity of an aggregate suspension in a settling tube and the solid volume concentration was measured with high accuracy, and the floc size and diameter were analyzed using a newly derived interface settling velocity equation. The relationship between the physical properties and the salt concentration was also analyzed. The equation incorporates Stokes' law into the interface settling velocity formula of Michaels and Bolger (1962). Next, by visualizing (*i.e.* optically imaging and recording) the floc during the settling process, the shape, diameter, and settling velocity were measured, and the dependence of the floc Stokes diameter on salt concentration was analyzed. Lastly, by comparing the results of the visualization method with the results of the interface settling method, the applicability of the interface settling method was demonstrated by measuring the dependence of the floc Stokes diameter on salt concentration.

2. Experiments

2.1. Sample preparation

Iriki kaolinite, confirmed by X-ray diffraction tests to include small amounts of quartz, was used as the sample material. For sample preparation, the organic matter was first removed by immersing the sample in 6% H_2O_2. Second, the sample was immersed in 1 M NaCl and agitated for 24 h. Third, the supernatant solution was removed after allowing the suspension to settle. Saturated Na-type kaolinite was made by repeating this procedure several times. Next, the sample was washed repeatedly in water to remove excess NaCl until the electrical conductivity (EC) in the supernatant was 10–20 μS/cm. To remove silt such as quartz, a sample adjusted to a pH of 10 (using NaOH) and a volume concentration of 1%, with ionic strength $< 1 \times 10^4$ mol/L, was dispersed, and coarse particles with a Stokes diameter > 3 μm were removed using a settling method. Based on transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements, the average Stokes diameter of the primary particle was 260 nm. This dilute kaolinite suspension was then condensed by ultracentrifugation. The pH of this condensed kaolinite suspension was set to 10 in all instances, but the sample concentration and the bulk salt concentration were adjusted for each experiment. Based on prior research, the absolute specific gravity of kaolinite particles is 2.65, and the cation exchange capacity (CEC) is 4.1 meq/100 g (Kuroda et al., 2003).

2.2. Methods

2.2.1. Measurement of the interface settling velocity

A cylindrical glass settling tube with an inner diameter of 28 mm was used to measure the interface settling velocity. 100 cm^3 of kaolinite suspension was placed in this settling tube, and subjected to ultrasonic treatment for 5 min. After 10 cycles of inverting and swirling, the glass sedimentation tube was allowed to stand and the interface settling velocity was measured. The volume concentration of the kaolinite suspension was set to 0.001–0.005 cm^3/cm^3; in this range, the settling interface can be observed, network formation by floc contact does not occur, and plug flow is not present (Nakaishi et al., 2012). The pH of the suspension was 10 and the NaCl concentration was set to 0.03–0.2 M. All measurements were conducted at 20.0 ± 0.1 °C.

2.2.2. Visualizing the floc and measuring the settling velocity

Samples with a volume concentration of 3.0×10^{-5} cm^3/cm^3 were used for visualizing the floc and measuring the settling velocity. This volume concentration is high enough to form flocs by Brownian coagulation in dispersed kaolinite, and low enough not to form gel structures through binding of the flocs to each other. The pH of the suspension was set to 10, and NaCl concentrations of 0.03, 0.05, 0.1, and 0.2 M were used. The kaolinite suspension was subjected to ultrasonic treatment for 5 min. After 10 cycles of inverting and swirling, the floc suspension was gently drawn from the flocculator using a large cubic syringe, and introduced without vibration into the settling tube (60 mm × 60 mm × 300 mm) filled with a saline solution having the same pH and NaCl concentration. To minimize the wall effect, only the flocs that had settled at the center of the settling tube were measured by using a long focus lens. A video camera was attached to the eyepiece of an optical microscope and the settling flocs were recorded using this camera. Stokes diameter of the flocs and settling velocities were measured by checking the playback screen. Here, the magnification of the light microscope was set at 200–300 ×, and the sample temperature was 20.0 ± 0.1 °C. The reliability of this experimental system was validated by comparing the settling velocity of perfectly spherical latex particles with the settling velocity predicted by Stokes' formula (Nakamura et al., 1993; Adachi and Tanaka, 1997). The experimental

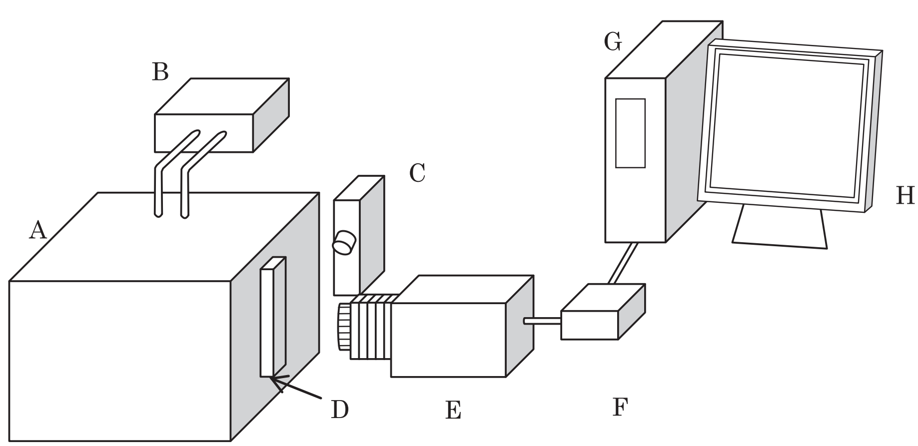

Fig. 1. Experimental setup for measuring the vertical descent velocity of a floc. A: water bath, B: constant temperature circulation, C: light source, D: glass cell, E: microscope and video camera, F: character generator, G: video recorder, H: display.