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The formation of a structural framework in gelled Wyoming bentonite: Direct observation in aqueous solutions

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ABSTRACT

Hypothesis: Particle space arrangement is a very important factor that determines the physico-mechanical properties of soil. Formations of three-dimensional (3D) structured networks within gelled or flocculated suspension may prevent clay particles and aggregates from settling under gravity force and by encapsulate water within such a network, lead to poor sludge dewatering. To better understand this phenomenon, a microstructural investigation of a smectite clay (SWy2) suspension was conducted.
Experiments: SWy-2 was diluted in water and a moderately salty aqueous solution and was studied with the aid of a synchrotron-powered transmission X-ray microscope (TXM) and cryogenic transmission electron microscope (Cryo-TEM). Observations of mutual particle arrangement in 3D spaces were conducted within a natural water environment after vitrification without drying.
Findings: A new type of micro-architecture in particle space arrangement was observed. Smectite flakes were mostly in edge-to-edge (EE) contact and formed a 3D network, confirming a "net of flakes" structural model. Clay particles form a complex and multi-hierarchic flocculated structure with characteristic cellular chained networking. Chained aggregates build cellular elements, encapsulating water inside closed voids. Increasing ionic strength results in the development of multi-hierarchic voids categories, with most water retained within nano-pores.

1. Introduction

Particle space arrangement is a very important factor that determines the physico-mechanical properties in soil. These properties play a major role in dams, footings and other engineering projects in which soil strength or permeability is crucial to the performance of a structure. As most soil mineral particles cannot be shredded by natural factors beyond a certain size, they are not present in the soil size fraction below 2 μm. Particles observed below this size limit are mostly secondary minerals that belong to the sheet silicates and are known as clays. The structure of clay-rich soils is important to a range of engineering tasks, especially those dealing with soil dewatering and stabilization. As soil structure depends on the primary particle aggregating in aqueous suspension, primary aggregating processes are the subject of increasing research interest. This study focuses on the structure of aggregates and flocks within clay-rich suspension. To avoid misunderstanding of the terms "structure" and "texture," we follow the most recent definition of "soil structure" by Osipov and Sokolov [1] as "space arrangement of all soil constituents characterized by a set of morphometric, geometric and energy parameters. It is defined by qualitative composition, quantitative ratio of all soil components and interaction between them." However, as soil macroscopic physical behavior is governed by their constitution on a microscopically small scale, we use the term "soil microstructure" in this study.

Despite numerous studies around the world, the subject is still poorly understood because of its complexity and the difficulty presented by the minute size. To enrich knowledge in this field, the present study is dedicated to investigating the microstructure of gelled smectite flocks within moderately salty aqueous uspensions. The findings from these observations may be used to improve water recovery technology primarily in mine-tailing dewatering projects.

Kaolinite, illite and smectite are the most common clay minerals in soils. Their presence in aqueous suspension is the primary cause of slow settling and water clarification problems. Clay particles are plates of flakes that are generally fine, with equivalent diameters of 200–1000 nm in kaolinites and 5–200 nm in

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smectites with a high aspect ratio [2]. Owing to the electric charges present at the mineral surfaces (basal and edge sites) within an aqueous solution, clay particles have the ability to form complex aggregates and networks. This behavior depends on water and clay chemistry as well as the packing density of clay particles [3]. The electric charge on the mineral interface is compensated by the adsorption of cations from the solution [4]. Smectite, the most dispersed member of the clay mineral group, represents a 2:1-type layer silicate. The layered smectite structure consists of an octahedral alumina sheet sandwiched between two tetrahedral silica sheets. With the expandable structure comprising sheets carrying an excess negative layer charges are linked by weak van der Waals forces. Because of this they may easily expand in water and form nanosuspension.

Contemporary approaches to describing the behavior of dilute clay suspensions are based on the DLVO theory of colloid stability [5,6], where competing electrostatic and van der Waals forces generally determine whether particular colloidal clay suspensions will be stabilized (in sol form) or coagulated (in gel form). Chemical changes in the aqueous environment may reduce the electric charge at the mineral interface and in consequence collapse the electrical double layer and allow particles to approach each other closely enough for short-range van der Waals forces to bond them into larger aggregates. This process significantly increases the settling rate.

Given the size of clay constituents, the electron microscope (EM) was found to be the tool of choice used by scientists studying the microstructure of clays [7,8]. Development of concept about microstructure in clays can be dated back much earlier than the advent of electron microscopy methods and initiated many ideas [9–11]. The formation of a fibrillar network of particles and existence of a structural framework in sols of Wyoming was proposed in 1950s by McEwen and Pratt [12,13] The first experimental information about clay particle mutual arrangements was obtained with the advent of the transmission electron microscope (TEM) and scanning electron microscope (SEM) [3,14,15].

In terms of their settling, dewatering and filtration performance, some species of clay are quite responsive to changes in water quality, exchangeable cations concentration, flocculants type and dosage, and the treatment procedure adopted, while others remain relatively inert. The most likely cause of these differences in performance is the formation of structured networks within gelled or flocculated suspension of clay platelets may hinder particles, preventing their movement when settling in gravity force. Microstructural patterns within clay-rich suspension and sediments may not only cause settling difficulties but also in some way encapsulate water, which causes a major problem in clay-rich sludge dewatering [16–19]. The present study investigated smectite suspension microstructure in water and a medium salty aqueous environment to better understand this floccule-building phenomenon.

2. Materials and methods

The smectite used in this study was SWy2, which is a well-known Na-bentonite sample from Wyoming, obtained from the Clay Minerals Society. This bentonite is of the chemical formula $Na_{0.33}[Al_{1.67}Mg_{0.33}(O(OH))_2(SiO_2)_4]$ with high smectite content (sodium montmorillonite). SWy2 has been well described [20] and 2.5 wt% suspensions were prepared from this original clay sample in deionized (DI) water and in 0.1 M NaCl and $CaCl_2$ aqueous solutions. The suspension was sonicated 5 min with 50 power W prior to investigations. The pH was not controlled and measured in suspension at around 8.

Electrokinetic potential (Zeta potential or ζ) was measured on the clay samples using Zetasizer (NanoSeries), manufactured by Malvern Ltd., UK. Samples of diluted suspension (~0.2 wt%) were prepared from the clay fraction and inserted into a disposable measurement cell. Zeta potential in mV and electric conductivity in mS/cm were measured in DI water and 0.1 M NaCl and $CaCl_2$ salt suspensions, as described in [21–23].

X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert Pro, multi-purpose diffractometer using Fe filtered Ca Kα radiation, autodivergence slit, 2° anti-scatter slit and fast X'Celerator Si strip detector. The diffraction patterns were recorded in steps of 0.016° 2-theta with a 0.4-s counting time per step, and logged to data files for analysis.

An EM investigation was conducted using a JEOL-2100 TEM with 200 kV accelerating potential. The SEM JEOL 6040 was used to investigate a sample coated in platinum film with accelerating voltage of 15–20 kV. For 3D imaging, the cryogenic transmission electron microscope (Cryo-TEM) was used with accelerating voltage of 300 kV. The aqueous suspension samples were vitrified into the liquid nitrogen temperature by rapid plunging samples in an environment-stable camera (stable temperature and moisture content).

The transmission X-ray microscope (TXM), which was installed on an National Synchrotron radiation Research Centre (NSRRC) synchrotron in Taiwan [24,25], proved to be an efficient instrument in the interior three-dimensional (3D) structure of nanomaterial owing to its large penetration depth and superior spatial resolution. The TXM provides two-dimensional (2D) imaging and 3D tomography at energy 8–11 keV with a spatial resolution of 50–60 nm, and has a Zernike-phase contrast capability for imaging light material that lacks X-ray absorption contrast. A photon energy of 8 keV was used to image the clay suspension for maximum X-ray absorption. The exposure time of a 2D image is from 15 s to 4 min, depending on the spot size used. By acquiring a series of 2D images with the sample rotated stepwise, 3D tomography datasets were reconstructed based on 141 sequential image frames taken in the first-order diffraction mode with azimuth angle rotating from −70° to +70° for our lateral plate specimen.

The imaging and force measurements were conducted using a Nanoscope III atomic force microscope (AFM), Digital Instruments Santa Barbara, USA, in the force mode, utilizing a scan head (JA) and standard fluid cell with a scan rate of 1 Hz used for measurements. The AFM cantilever was triangular, tipples, silicon nitride with a spherical colloidal probe (2.5 μm in diameter) purchased from NOVASCAN. The spring constant was nominal, 0.12 N/m. To record forces acting on a spring, the clay-coated flat substrate surface was displaced in a controlled manner toward and away from the colloidal probe in aqueous solutions.

Images from all microscopy studies were statistically analyzed using the Statistical Image Analyzing (STIMAN) technique [26–29], which was adopted for the study of clay suspensions. This technique can extract integrated information on sample microstructure, especially on total pore (void) space and the spread of micro-pore sizes. It contains a subroutine for estimating filtration properties from the void space parameters. Examples of the output parameters include the following: number of voids analyzed; porosity (%); total void/particle area (sq. μm); total void perimeter (μm); average diameter (μm); average perimeter (μm) and the form index (K_f), which is the ratio of platelet thickness to its diameter. Form index is 1 for perfectly round isometric particles and near 0 for string-like, elongated particles. In this study we limit the use of the STIMAN technique to obtaining statistical information about porosity, average diameter of particles and pore distribution according to their total area from 2D micrographs. The 3D STIMAN technique was also used to estimate flock size within suspension—two consequent TXM images with known rotation angle difference, these investigations were able to measuring structural elements dimension in the 3D arrangement.