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Micelle-Like Microaggregate Morphology in Framework of Gelled Montmorillonite

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Abstract

Clay particles build (3-D) structured network within the aqueous suspension. Such a network prevents aggregates from settling under gravity force. It also immobilize (retain) water within a structure producing stable gel.

To better understand this phenomenon, a microstructural investigation was conducted on Wyoming montmorillonite clay suspension which was gelled by aluminium chlorohydrate. Gel morphology was studied with aid of the synchrotron-powered transmission x-ray microscope (TXM) and cryogenic scanning electron microscope (Cryo-SEM).

New type of globular micro-morphology and the particle space arrangement was observed. For the first time, globular micro-aggregate morphology was found where flexible smectite flakes were curled to build globular aggregates. These aggregates were assembled onto multilayer, micelle-like globular superstructure. This new smectite gel micro-morphology may be similar to earlier described pseudoglobular microstructure model observed in eluvial and hydrothermal clay deposits.

Introduction

The phenomenon of particle framework formation has been predicted since works carried out by McEwen in 1950 [1]. The study of microstructure can be dated to before the electron microscopy method of Terzaghi [2] and Casagrande [3], and the classic 'house of cards' model of microstructure was suggested by Goldschmidt in 1926 [4]. The first experimental information about clay microstructure was obtained with the advent of transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [5,6,7].These microscope tools enable for the first time to visualize natural behavior of clay particles in aqueous environment.

The formation of the fabric-like particle network with strong structural frameworking in the Wyoming clay suspension was proposed in 1950's by McEven and Pratt [8]. Despite numerous studies around the world, the subject is still poorly understood because of its complexity and the difficulty presented by the minute in size particles. To enrich knowledge in this field, the present study was dedicated to investigate the microstructure of gelled smectite flocks within aqueous suspension.

Smectite, like Wyoming montmorillonite, are common clay minerals in soils. Their presence in aqueous suspension is the primary cause of slow settling and water clarification problems. Particles reassembly plates of flakes that are generally fine, with equivalent diameters of 5-200 nm in with a high aspect ratio [7]. Owing to the electric charges present at the mineral surfaces (basal and edge sites) within an aqueous solutions, 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 [8]. The electric charge on the mineral interface is compensated by the adsorption of cations from the solution [9]. Smectites characterized by 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 [10,11], 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 of spherical particles. In platy minerals such a charge, leads to structure building phenomenon within the aqueous suspensions.

Most recently, formation of ribbon like structured networks was described within clay suspension [12]. Such a structure hinders involved particles, caused suspension gelling and subsequently prevent aggregates from settling [12-15].

Most of previous studies which involved electron microscopes (EM) were conducted on the vacuum dried samples. Present contribution show results of insitu examination of gelled suspension within aqueous environment. To achieve this, the state of art Transmission X-ray microscopy (TXM) based on the synchrotron photon source was used. Such an approach was needed to better comprehend montmorillonite behavior in water. TXM results were complemented using Cryo-

SEM/FIB electron microscope which works on vitrified gel sample in liquid nitrogen temperature.

Methods

The smectite sample used was SWy-2 sodium montmorillonite, which is a well-known Na-bentonite sample from Wyoming, obtained from the Clay Minerals Society [16]. This bentonite is of the chemical formula $Na_{0.33}[Al1.67Mg_{0.33}(O(OH))_2(SiO_2)_4]$. Smectite before treatment was soak in 0.1 M NaCl solution overnight and washed by DI water in dialyze tubes. Resuspended smectite sample was repeatable centrifuged on spinning speed 4000 rev/min to separate any sediment. Only colloidal fraction which retained in supernatant was used to further treatment and investigations.

Smectite water suspension was treated by adding aluminium chlorohydrate 50% solution until smectite negative charge was neutralized. This aluminium salts having the general formula $Al_nCl_{(3n-m)}(OH)_m$ and is extensively used in deodorants and antiperspirants and as a coagulant in water purification.

The aluminium chlorohydrate ten times diluted in water solution was titrated into montmorillonite aqueous suspension in sol form, until it rapid transformed into gel. The electrokinetic potential was monitored by Zetasizer (nanoSeries) manufactured by Malvern Ltd. in United Kingdom.

Zeiss Auriga 60 Cryo-SEM/FIB was used in studying vitrified gel sample accordingly to procedure [17].

Transmission X-ray microscopy (TXM) proved to be an efficient instrument in studying internal structure of nano-material owing to its large penetration depth and superior spatial resolution. TXM, which was used in the present study, was installed on synchrotron of NSRRC in Taiwan [18]. This TXM provides two-dimensional imaging and 3D tomography at an energy of 8–11 keV, with a spatial resolution of 50–60 nm and with the Zernike-phase contrast capability for imaging light material that lacks X-ray absorption contrast. TXM allows the measurements of aqueous specimens owing to having no vacuum requirement.

The photon energy of 8 keV was used to image the clay suspension for the maximum X-ray absorption. The exposure time of a 2D image is from 15 seconds to 4 minutes. 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 first order diffraction mode with azimuth angle rotating from -70° to +70° for our lateral flake specimen.

Images from all microscopy studies were statistically analyzed using the Statistical Image Analyzing (STIMAN) technique [19,20], which was adopted for the study of clay suspensions. This technique can extract integrated information on sample microstructure, and calculate aggregate sizes.

Results

General characterization of studied sample was described in [14]. The TEM and AFM micrographs represent relatively large, flexible sheets/flakes of lateral dimension ~800–1000 nm and a thickness of ~1–10 nm. The extreme thinness and flexibility of the flake-shaped particles accounts for the considerable plasticity of this mineral. The flakes are very thin and flexible, displaying numerous wrinkles and rough, highly transparent edges, as observed in the SEM micrograph.

EDX analyses show typical 2:1 smectitic Al/Si picks ratio and the presence of Na, Al, Si, Ca, and Fe elements. The XRD results show almost pure smectite composition with a small admixture of quartz. The sample treated in the NaCl solution displays a major 001 peak at d-space 12,31Å, and after glycol treatment this produces a narrower and higher peak with shifts toward a larger d-space 17,16 Å. Clay treated in the $CaCl_2$ solution produces a strong and narrow peak with d-space 15,11 Å shown in [14].

TXM micrographs, such as that displayed in Figure 1a, shows full flocculated microstructure. Flocculated framework in this scale display globular aggregates interconnected with each other. Most aggregates looks rather spherical in shape and others more elongated. All aggregates in observed area have diameter between 1 to 2 μm and looks highly porous inside.
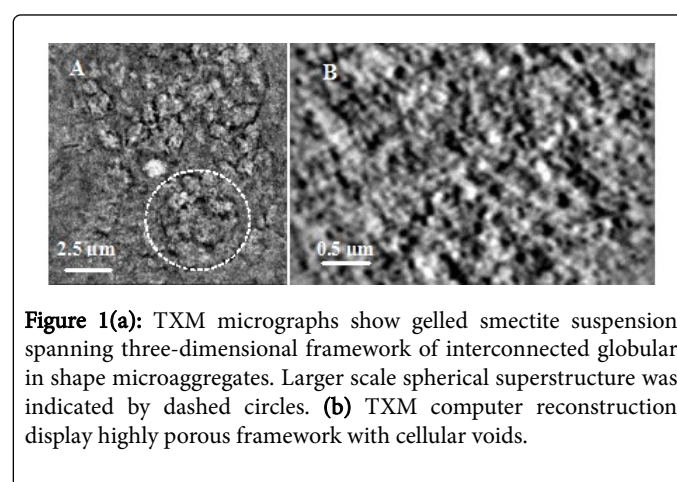

Figure 1(a): TXM micrographs show gelled smectite suspension spanning three-dimensional framework of interconnected globular in shape microaggregates. Larger scale spherical superstructure was indicated by dashed circles. **(b)** TXM computer reconstruction display highly porous framework with cellular voids.

Larger scale spherical superstructure was frequently observed in TXM micrographs. That displayed on a micrograph Figure 1a by dashed circles. These micelle-like globular superstructures display multilayer, onion style internal texture. Under high magnification micrographs from computer reconstruction of TXM images the detailed morphology of highly porous framework can be seen (**Figure 1b**). Total observable porosity is about 70 %. Interconnected into dense spanned network smectite flakes in many places forms circular aggregates mostly empty, filled by water.

Statistical parameters of observed framework were calculated from TXM images using image analyzing technique [19, 20]. The aggregate size distribution graph shows strong and broad aggregate distribution maximum between 1 and 3 μm with average aggregate diameter 850 nm (**Figure 2**). Graph show multimodal particle distribution but microscope resolution limits didn't allow studying highly porous inner-aggregate area.

Observations of vitrified suspensions using cryogenic scanning electron microscopy (Cryo-SEM) were shown in micrographs in Figure 3. Figure 3a clearly displayed globular flocculated microstructure. Individual smectite aggregates display spherical morphology with diameter 1 to 2 μm. All these globular aggregates were densely packed in similar way as been observed in TXM images. Some these spheres were partly broken and display empty interior. More complex morphology can be seen in selected aggregates vitrified and partly sublimed in vacuum (**Figure 3b**). These, partly broken globular aggregates show flexible smectite flakes curled spherically or elaborately spindle like elongated shapes with vitrified water ice encapsulated inside. Many observed larger spherical aggregates display

grape like composition of multiple submicron in diameter smectite spherules.

In our previous studies flocculated smectite aqueous suspensions was observed in the aqueous solutions of varied ionic strength [12-15]. All studied aqueous-clay systems displayed high to low negative electrokinetic potential, usually between -61 to -12 mV. The structure-building phenomenon observed during subsequent TXM and Cryo-SEM investigation was believed to have been triggered by several factors and resulted in suspension coagulation forming easily pourable gels, we call "light gel" of semi-liquid properties. In contrast, in our present study conducted on samples which electrokinetic potential was reduced to about zero mV, highly viscous "hard-gel" was obtained with semi-plastic properties. In literature, similar gels can be found under name of "hydro-gel".

Usually, the ionic strength of the solution, dry mass density that exceeds the critical coagulation concentration and presence of nanoparticles [21] found to cause of suspensions to gel. In such a case, where particles carry high electrical charge, they most probably found equilibrium in contacting each other in the primary energy minimum which resulting in semi-liquid, "light gel" formation. The presence of the extremely small particles (nano-colloids) in a suspension was reported to enhance sample flocculation [22]. It was found that a concentration of only 1–1.5 vol. % of nanoparticles was required to produce the space-filling gel network.
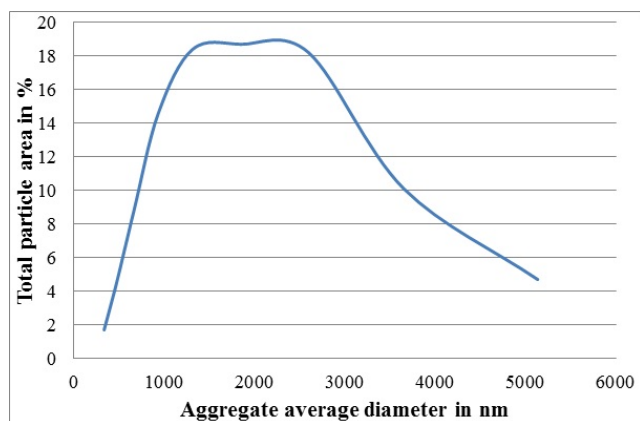

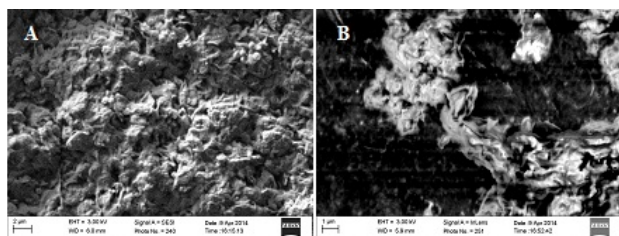**Figure 2:** Microaggregate size distribution from TXM micrographs.

Figure 3: Cryogenic scanning electron microscope micrographs show **(a)** Packed globular aggregates, many spherical in morphology. **(b)** Sophisticated spherical and spindle like aggregates of curled smectite flexible flakes.

In our present investigation, the majority of the sample was montmorillonite nanoparticles placed in optimum quantity aluminium chlorohydrate, where the clay particle electrokinetic potential was reduced to zero, so no electrostatic repulsion was acting between particles [23,24].

Nanoparticle presence and lack of repulsive electrostatic forces acting between smectite flakes were most likely responsible to form the spanned network of unique microstructure as shown in TXM micrographs. Observed microstructure of the "hard gerl" (hydrogel) was completely different in comparison with the low viscosity "light-gel" microstructure observed before [12-15].

In the previous study, "light gel" produced from the same Wyoming montmorillonite sample [14] the flock dimension calculated from TXM stereo images using STIMAN technique, gives median value 312 nm in water and the NaCl solution and 483 nm in the $CaCl_2$ solution. In our present study, newly observed microstructure within the "hard gel" show globular flocks average diameter was twice larger than in the "light gel". Also the flocks dimension range increased from 2.35-3.4 μm observed in the "light gel" [14] to almost 6 μm as seen within limits of our observation frame in the "hard gel". Obtained "hard gel" proof to be strong, dense and stable, displaying semi-plastic behavior for very long time. Probably particles within observed framework contacted each other within the secondary energy minimum.

Instead 'net of flakes' clay structural model [14,15], in which clay particles contact each other in EF and EE pattern and form short and long ribbons, the commonly observed texture in aluminium chlorohydrate modified "hard-gel" were curled smectite flakes into spherical aggregates. These spherical aggregates were interconnected into multiple spherical superstructures assembled spanned network of globular pattern. Such a pattern can be associated with previously described "pseudoglobular structure model" found commonly in eluvial and hydrothermal clay deposits [25]. Here for the first time this type of microstructure has been observed in gelled montmorillonite suspension. The mechanism behind this curling phenomenon is unknown and need to be studied.

Observed in TXM strongly-built circular aggregates are assembled in a robust multilevel globular framework of gelled suspension. These globular, mostly empty spherical aggregates form larger circular micelle-like superstructures. Such structures were observed in present TXM and the Cryo-SEM study. The water-encapsulating cellular voids, observed within the gelled suspension, were mostly far below 2 μm in diameter and most of the water was retained within the observed network and was permanently immobilized within these micro-pores. This phenomenon could explain why hydrogel can retain water without it significant loose, can also be employed to build watertight membranes and moisture rising base for pharmaceutical and cosmetic industries. Results of present study may explain why dewatering of such gelled system can be so complex and difficult task.

These findings on clay particle space arrangement within smectite-rich suspension may play a crucial role in the understanding of clay mineral suspension behavior and its aggregating nature. Such an understanding is important in designing the most suitable methods for water, cosmetics and pharmaceutical carriers, for faster particle settling, for water purification and mine tailing dewatering.

Conclusions

As the result of present investigations, new, never seen before, completely different particle architecture was observed within montmorillonite gel prepared in reduced to zero electrokinetic potential. In such a system no repulsion shall exists between individual particles. Resulting highly viscous gel, obtained in such an environment we call "hard-gel, or hydrogel". Such a gel microstructure differs from observed gel microstructure which forms within suspension of highly charged particles. Hydrogel microstructure permanently retains water, makes it stable and display semi-plastic behavior. Particles within observed framework of hydrogel are contacting probably in the secondary energy minimum in comparison with highly charged particles gelled by contacting particles in primary energy minimum.

For the first time, new globular flock morphology was observed where flexible smectite flakes were curled and build globular aggregates. These aggregates in many places were observed to assembly multilayer, micelle-like globular superstructure.

Average diameter of aggregates observed in studied sample was 850 nm with broad range of aggregates from 0.2-6 μm. Maximum aggregate range was between 1-2 μm.

Globular smectite aggregates looks mostly empty inside and tightly encapsulate water. This may explain it extremely good water retention capability which may be used in membrane technology, pharmaceutical applications, cosmetics industries and others.

Observed smectite gel micro-morphology may be similar to earlier described pseudoglobular microstructural model described in eluvial and hydrothermal clay deposits.

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