Transmission X-ray microscopy reveals the clay aggregate discrete structure in aqueous environment

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Abstract
The utilization of new transmission X-ray microscopy (TXM) using the synchrotron photon source enable for the first time the study in three dimensions microsize clay particles in aggregates in their natural aqueous environment. This technique makes possible remarkable accurate images of nanosize mineral interparticle structure which forms a new nanocomposite. The Birdwood kaolinite/LDH aggregates observed in the TXM are much more compact than observed before in pure Birdwood kaolinite suspension and similar to aggregates formed after treatment by positively charged surfactant. Kaolinite/LDH aggregates in water reveal complex structure of larger kaolinite platelets connected together by gelled nanoparticles which are most probably LDH colloidal plates. Comparisons of the transmission electron microscope (TEM) and TXM techniques show similarities in particle morphology. The ability to study particles and aggregates in their natural aqueous environment and in 3-dimensions make this technique superior to the TEM technique.

Keywords: Clay aggregates; Transmission X-ray microscopy; Kaolinite; Hydrotalcite; Halloysite

1. Introduction
The success of clays in many different applications for thousands of years in the development of human technology has its success in its ability to build within clay aggregates complex microstructures in which mineral particles interact in an aqueous environment with each other and with other components such as organic molecules. Clay particles are minute mineral particles often less than a fraction of a micrometer in dimension and often on a nanoscale. The clay particles are thin plates with diameter to thickness ratio (aspect ratio) around 10 and they are important components of the colloidal fraction of the most soil and mine waste (tailings) suspensions.

Because of this minute size, clay particles may be stable in aqueous suspensions causing water turbidity, are extremely difficult to handle and cause clay rich mine tailings difficult to dry.

These difficulties in mine tailing dewatering is caused by the way in which the water is encapsulated into the specific cellular structure which makes the clay sludge very resistant to drying (dewatering). These generate serious problems in the mining industry where tailings ponding is expensive because of the vast land surface areas required and sometimes become dangerous when spills occur.

Clays, because of their large surface area were also successfully used in cleaning water from unwanted pollution by heavy metals and organic compounds. Also these clays were used frequently in stabilizing oil in water suspensions in many petroleum products as well as in the cosmetic industries.

Clay behavior is not yet completely understood and this knowledge possibly has its roots in the quantum chemistry because of the small particle dimensions and molecular distances of their mutual interactions. The colloid stability theory named from the authors names (Derjaguin–Landau–Verwey–Overbeek) the DLVO theory [1,2] based on the balance of electrostatic and van der Waal’s forces are the most accepted mechanism to describe clay particle interactions in dilute sus-
pension. In effect, because of this complicated interaction between nanoscaled clay particles, a complex microstructure is created in the suspensions [3]. This microstructure determines all the clay complex properties.

To change clay particle behavior in colloidal suspensions it is necessary to alter electrostatic charges on the mineral interfaces using a surfactant, some of which may be hazardous in the natural environment. Another way of reduction the kaolinite surface charges is by using oppositely charged colloidal particles like commonly synthesized layered double hydroxides (LDHs). The LDHs are colloidal platelet like particles and are positively charged. This charge is opposite to most common clay minerals, which are negatively charged. Such new materials composed of the oppositely charged particles may produce new nano materials whose behavior will be determined by structure of clay–LDH complexes.

Clay structures have been studied since first the scanning electron microscopy (SEM) application and recently in vitrified suspensions using cryo-SEM technique. SEM technique however can show clay particle arrangement on the fractured surface in a two-dimensional perspective. Recently developing transmission X-ray microscopy (TXM) based on the synchrotron source of photons offers a new opportunity to study clay particle interactions and aggregate structures in three-dimensional tomography reconstruction. Some limitation of this technique, previously observed in the early stages of these investigations has been subsequently resolved.

2. Experimental

Transmission electron microscope Philips-200 was used in this research and samples were prepared accordingly with procedure described in Ref. [4]. Results of the TEM investigation of studied clay samples are compared with the results obtained from the relatively new technique of TXM in an effort to find limitations and advantages of new technique in studying clay aggregates in an aqueous environment.

Transmission X-ray microscope with 60 nm tomographic resolution has been installed at beamline BL01B [5,6] of NSRRC in Taiwan with a superconducting wavelength shifter source, which provides a photon flux of $5 \times 10^{12}$ photons/s/0.1% bw in the energy range 5–20 keV. X-rays generated by a wavelength shifter are primarily focused at the charge coupled detector by a toroidal focusing mirror with focal ratio nearly 1:1. A double crystal monochromator exploiting a pair of Ge (111) crystals selects X-rays of energy 8–11 keV. After the focusing mirror and double crystal monochromator, the X rays are further shaped by a capillary condenser. Its entrance aperture is about 300 µm, with an end opening about 200 µm and is 15 cm long. This capillary condenser gives a reflection angle of 0.5 mrad with respect to the propagation direction. The condenser intercepts the impinging X-rays and further focuses them onto the sample with a focusing efficiency is as high as 90% due to the internal totally reflecting nature inside the capillary. The zone-plate is a circular diffraction grating consisting of alternating opaque and transparent concentric zones. In the microscope, the zone-plate is being used as an objective lens magnifying the images $44 \times$ and $132 \times$ for the first-order and third-order diffraction mode, respectively. Conjugated with a $20 \times$ downstream optical magnification, the microscope provides total magnification of $880 \times$ and $2640 \times$ for first-order and third-order diffraction mode, respectively. The phase term can be retrieved by the Zernike’s phase contrast method being introduced in light microscopy since 1930s. The gold-made phase ring positioned at the back focal plane of the objective zone-plate retards or advances the phase of the 0th-order diffraction by $\pi/2$ resulting a recording of the phase contrast images at the detector.

Birdwood kaolinite from South Australia and Georgia kaolinite (KGa-1b) from USA were studied. Sample KGa-1 obtained from the Clay Mineral Society is well-ordered kaolinite quoted at 97% purity. KGa-1 sample was described in details [7] and composition and properties of the kaolinite from Birdwood was described in [8,9]. Samples were studied in 0.001 M NaCl solution at natural pH (~8.5). Two-dimensional (2-D) examinations were conducted on 100 µm thick kaolinite suspensions placed in frame and covered by Kapton© tape windows. The three-dimensional (3-D) tomography examinations were conducted on kaolinite suspensions inserted into 150 µm diameter Kapton© capillaries. 3-D tomography was reconstructed based on 141 sequential images taken in first-order diffraction mode with azimuth angle rotating. The studied kaolinite samples of chemical composition, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ were mixed with 10 wt% LDH (layered double hydroxide) of the chemical composition $\text{Mg}_6\text{Al}_2[\text{OH}]_{16}[\text{CO}_3]_3\cdot 4\text{H}_2\text{O}$ which was synthesizes in our laboratory by the coprecipitation method.

3. Results and discussions

Transmission electron microscopy micrographs reveal in sample KGa-1 kaolinite crystals in the form of larger stacks and defoliated pseudo-hexagonal in shape plates a few micrometers in size (Fig. 1A). The large stacks, shown in the center of TEM micrographs in Figs. 1A and 1C is ~2 µm wide and ~1.5 µm thick and is very typical for this kaolinite coarse fraction. The aspect ratio of such particles are low (~1.3) and consists of partly delaminated more fundamental large kaolinite crystals of ~70 nm thick. This large kaolinite stack is surrounded by fine kaolinite platelets, with distinctive pseudo-hexagonal plate symmetry, usually less than 200 nm in diameter and ~25 nm thick with typical aspect ratio around 8. Flakes of diameter 20–50 nm are visibly attached to the surface of large kaolinite stack. These flakes do not show any particular symmetry and based on their morphology we assume they are LDH particles which we add to kaolinite suspension. LDHs particles have remarkably different morphology in comparison to kaolinite platelets. They are reassemble small platelets irregular in shape and are usually 50 nm in diameter as shown in TEM micrograph (Fig. 1B).

EDX spectra of this sample are typical for kaolinite Al, Si content which is characteristic of this kaolinite. These kaolinite crystals show regular hexagonal arrangement in electron diffraction patterns proving its crystalline structure [7–9]. LDH addition EDX spectra of this sample show high uniformity
where Mg (from LDH) is detected in all areas additional to the Al, and Si (from kaolinite).

Similar stacks as described above from TEM micrographs can be seen in micrographs from the TXM (Fig. 1C) where the stacking is strongly visible and the individual spacing can be measured (70–100 nm). The 3-D space reconstruction shown in Fig. 2 was obtained from 2-D pictures as shown in Fig. 1C, of particles observed from angles +70° to −70° (as we are able to observe this stacking particle from different angles). Such a reconstruction reveal for the first time the mutual random orientation of associated stacks in aggregates within aqueous based electrolyte as well as observing the stacking sequences within individual crystals, observed from different angles. This was not possible to investigate in the TEM micrographs where only separate particles were observed in the dried substrate in vacuum environment.

In micrographs (Fig. 1A) where kaolinite was mixed with LDHs the significant numbers of LDHs particles adhere to larger kaolinite crystal surfaces. Also small LDHs particles adhere to the surface of stack as may be observed in Figs. 2 and 3A, and getting into voids in-between individual platelets within stacks itself. The LDHs nanoparticles in TXM micrograph is apparently less clear in comparison to the TEM micrographs because of Brownian motion which affect to a larger degree smaller particles than the crystals from the coarser fraction. It should also be noted that the dimension of LDHs particles lay close to resolution limit of this microscopic technique.

Very dense packing by LDHs nanoparticles as observed in the TEM micrographs of the kaolinite surface suggests strong bonding between both mineral phases. These TEM micrographs may prove formation of kaolinite–LDHs complexes. However because the TEM micrographs were produced from samples which were dried prior to observations being conducted, little may be learnt about mutual structural arrangements between particles in the real aqueous based suspension.

In Fig. 3B, three-dimensional arrangements of the fine fraction of Birdwood kaolinite platelets can be seen with nanoparticles of LDHs in-between playing the role of a bonding medium between kaolinite platelets. Presented micrograph is one of 250 photos taken before 3-D reconstruction which has been performed to observe this microaggregate from different angles. In this micrograph, kaolinite platelets are oriented by edges...
towards larger crystal planar wall surfaces (edge to face orientation EF) which are remarkably different from micrographs of pure Birdwood kaolinite suspensions as reported in references [9,10] where kaolinite platelets are arranged in edge to edge orientation (EE). LDHs particles form networks with kaolinite platelets spanning kaolinite platelets to form aggregates where kaolinite platelets are arranged mostly in an EF pattern. In Ref. [10] it was reported that aggregates formed similar EF arrangements in a similar pattern after surface charge reduction by positively charged surfactant. Observed aggregates in kaolinite–LDHs complexes are also less porous than these observed in pure kaolinite suspensions as described in [9,10] where chains of EE oriented platelets forms cellular-like structure. Kaolinite platelets in aggregates like observed in Fig. 3B are bonded with LDH nanoparticles. These nanoparticles form gelled structure between larger kaolinite platelets which can be recognizable by their pseudo-hexagonal symmetry. Such a gel, for the first time can be observed in the water environment in aid of TXM method only. This gel formed from LDH nanoparticles between larger kaolinite platelets bonding all mineral phases into larger aggregates. This ability gives potential in commercial utilization for encapsulate and retain larger molecules. It also can be used in water treatment as well as in fine particles aggregation for faster suspension dewatering and improve sedimentation.

4. Conclusions

Comparisons of the images obtained using TEM and TXM techniques show similarities in particle morphology which validate TXM as useful tool in micromorphological observations. Ability to observe particles and aggregates in their natural aqueous environment and in three-dimensions make this technique a superior compared with the TEM technique.

Observed kaolinite/LDH complex aggregates are composed of clay platelets covered by nanoparticles of LDH. This adhesion of LDH nanoparticles to clay platelets basal surfaces is probably, because particles are oppositely charged of electrostatic nature. The Birdwood kaolinite/LDH aggregates observed in the TXM are much more compact than observed before in pure Birdwood kaolinite suspension [10] and similar to aggregates formed after treatment by positively charged surfactant. In the aqueous suspension kaolinite/LDH aggregate consists of larger kaolinite platelets connected together by gelled nanoparticles, most probably LDH colloidal plates.

Because TXM based on the synchrotron photon source is relatively new and is in rapid development, in this work we report the first attempt to study clay aggregate structure in an aqueous environment. The images may be not giving very impressive micrographs as compared with other well established techniques such as TEM, but enable us to observe clay aggregates within water, which has never been previously possible. Most importantly, this technique allows us to conduct observations inside clay aggregates within water environment and from

Fig. 2. 3-D reconstruction of the kaolinite stack from coarse fraction of Georgia kaolinite sample (KGa-1) as seen within the aqueous solution. Stacking is visible as well as fine fraction of kaolinite and LDH particles adhered towards stack edges which are more clearly visible when picture is rotated. Dimension of cube is $\sim 2 \times 4 \mu m$.

Fig. 3. Birdwood kaolinite–LDHs complexed particle (A) by using TEM and (B) by using transmission X-ray microscopy.
different angles which was not available using different techniques except perhaps, the new cryo-TEM tomography technique. Cryo-TEM attempts to study the structure after quickly freezing the sample, but is hampered because the freezing can lead to the formation of a number of artifacts. The SEM may also be used to make 3-D imaging in stereoscopic images, but these images give only the outermost morphology and it is impossible using SEM to observe particle aggregate internal structure through water in which clay particles can be observed easily by TXM. Also the ability to observe aggregates in the aqueous environment is the big advantage of TXM as it is not possible using the TEM technique. The TXM technique also potentially enables observation in slow dynamic systems, where mutual arrangements between particles may change with time. This ability is also unique to TXM technique and makes it superior to other techniques like cryo-TEM or cryo-SEM techniques where samples are vitrified prior to observations and any dynamics in this sample cannot be studied.

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References