Transmission X-ray Microscopy (TXM) Reveals 3-D Nano-structure of Clay-water Suspension

The unusual behaviour of smectites, their ability to change volume when wetted (swelling) or dried (shrinking), makes soil rich in smectites very unstable and dangerous for the building industry due to possible or likely movement of building foundations and poor slope stability. These macroscopic properties are dominated by the structural arrangement of smectites finest fraction. Here, we show in three dimensions how the swelling phenomenon in smectite, caused by a combination of hydratation and electrostatic forces, may expand dry smectite volume over 1000 times. A new technique, Transmission X-ray Microscopy, makes it possible to investigate the internal structure and 3-D tomographic reconstruction of the clay aggregates. This reveals, for the first time, smectite gel arrangement in voluminous cellular tactoid structure, within a natural aqueous environment.

Beamline

01B1 SWLS-X-ray Microscopy

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Clay minerals (kaolinites and smectites) are commonly found as components of soils from temperate to hot climates. They are formed as the result of weathering of minerals in granites (kaolinites) or volcanic glass abundant in ash-beds and basic rocks (smectites). Kaolinites are used in cosmetic and paper coating industries. Smectites are useful for dam bed impregnation, to improve water retention properties and as a drilling mud to seal the cut, thus preventing fluid loss. They are also popular stabilising additives in engine oils, cosmetics, and the pharmaceutical and chemical industries.

Clay's unusual macroscopic properties are dominated by its structural arrangement and the morphology of its finest fraction. Most clay minerals are extremely dispersed and exhibit very high surface area. The first attempt to describe the microstructure of clays was made by Terzaghi[1] who proposed the "honeycomb model" as the structural basis of water saturated clays. The first experimental confirmation was obtained with the advent of electron microscopy. Sample preparation methods available for such investigations, like partial freeze drying, critical point-drying and cryo-fixation, have been found to introduce many artefacts especially when applied to the study of smectite-rich clay aqueous structure. 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.

A transmission X-ray microscope with 60 nm tomographic resolution has been installed at beamline BL01B[2] of NSRRC in Taiwan as shown in Fig. 1. This device has a superconducting wavelength shifter source which provides a photon flux of 5×10^{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

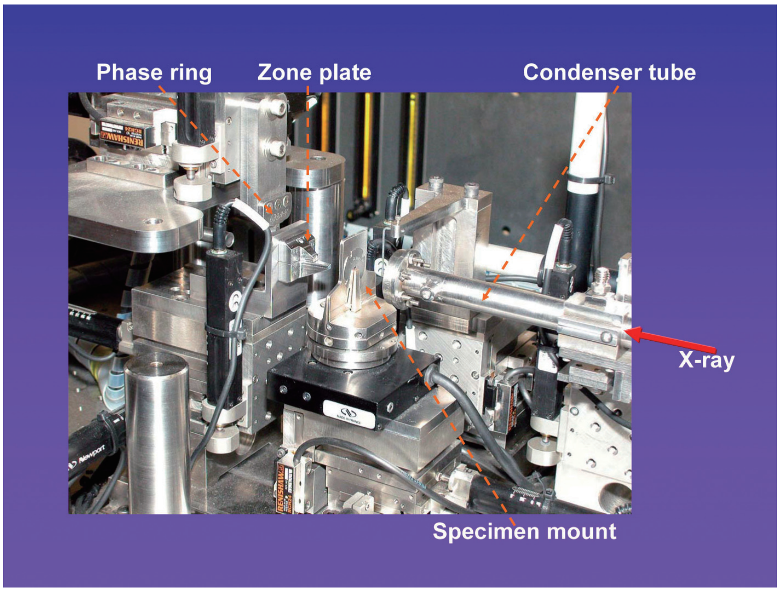

Fig. 1: Schematic arrangement of 01B1 beamline.

light microscopy since the 1930s. The gold-made phase ring positioned at the back focal plane of the objective zone-plate retards or advances the phase of the zeroth-order diffraction by $\pi/2$, resulting in a recording of the phase contrast images at the detector.

The TXM observations of smectites in aqueous suspension shows a network of connected nano-size platelets which form a gel where highly flexible sheets[3] are interacting with each other by a combination of edge attraction and basal plane repulsion. These build an expanded and extremely voluminous cellular network composed of chain-like sheet assemblies. In such an extended cellular network flexible smectite sheets may encapsulate water within cellular voids of

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 passing through 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 of as high as 90% due to the 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× and 132× for the first order and third order diffraction mode, respectively. Conjugated with a 20× downstream optical magnification, the microscope provides total magnification of 880× and 2640× for first order and third diffraction order mode, respectively. The phase term can be retrieved using the Zernike's phase contrast method that was introduced in

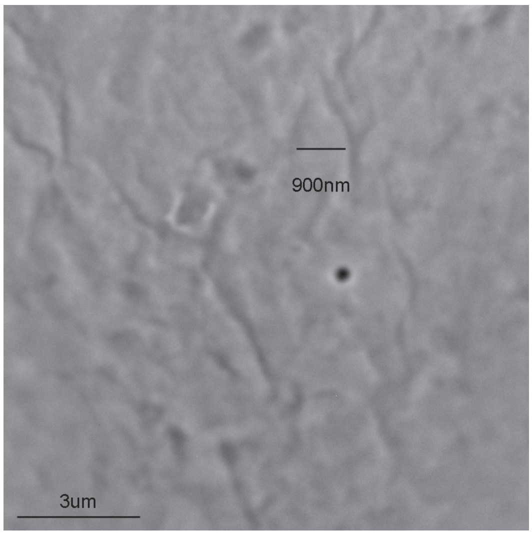

Fig. 2: TXM micrographs of 5wt% montmorillonite colloidal gel cellular structure around 900 nm in diameter in water Na saturated at exchangeable position: large cells and thin walls are visible.

dimensions up to 0.5-2 μm. This flocked cellular structure can span all the volume of the clay slurry. In such a case the suspension is gelled; there is no free settling in the system and further compacting may proceed slowly only by structural re-arrangement of the entire network. In a 3-D structure and in the absence of sheer, smectite sheets are not oriented in any particular direction and therefore, their most probable orientation in the volume of suspension is random.

In 2-D, TXM micrograph shown in Fig. 2 reveals the Na-smectite gel structure in water. In this micrograph, elongated smectite sheets form a cellular network, 0.6 to 1.5 μm in diameter (average 940 nm).

Direct measurements of forces acting between the studied Na-smectite basal surfaces showed:[3] (a) there is a long-range repulsion between these two surfaces; (b) the decay of the force is quasi-exponential; and (c) there is no adhesion between these surfaces. The long range repulsive forces for Na-smectite have been detected from distances of over 1000 nm of the surface separation. Strangely, these numbers correspond to the cellular dimensions observed in TXM 3-D reconstruction shown in Fig. 3 as well as in the 2-D TXM micrograph.

Observed structural effects may be explained by hydratation of the exchangeable counter ions, allowing these ions to then set up an electric field double layer. It is also possible that these long-distance forces similar to electrostatic repulsion, have steric origin and reflect the flexibility of smectite flakes. In effect, hindrance of other platelets due to the interaction between two concerned platelets would be unavoidable. If this mechanism is responsible for a measured in AFM and observed in TXM structure building phenomenon measured in AFM and observed in TXM, it reflects squizzing by AFM cantilever spring. This squizzing of the smectite gelled structure has dimensions that are consistent with microscopy observations as well as force measurements.

Significant differences between smectite with Na^+ and Ca^{2+} exchangeable cations, which has been reported in[3] may be due to the differences in the rigidity of the smectite flakes. The presented results suggest that thicker and more rigid flakes made with Ca^{2+} exchangeable cations will build much smaller cellular structures than the thinner, more flexible smectite flakes made with Na^+ exchangeable cations. However, the nature of the long distance repulsive force responsible for enormous swelling between flakes which build the Na-Smectite cellular structure, remains obscure.

The 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 smectite gel structure in an aqueous environment. The images may not be giving very impressive micrographs as compared with other well established electron microscopy techniques, but enable us to observe clay aggregates within water, which has never been previously possible. A 3-D space reconstruction as shown in Fig. 3 was obtained from 2-D images of particles observed from angles +70 to -70 degrees where the gelled suspension is able to be observed from different angles. Such a reconstruction reveals for the first time, the cellular orientation of associated mineral sheets within aqueous

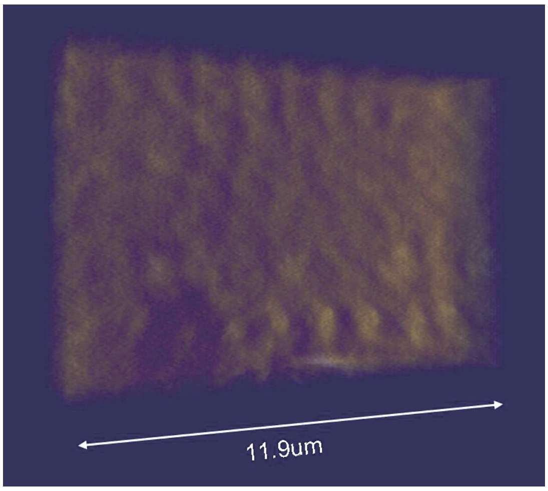

Fig. 3: 3-D reconstruction of the montmorillonite gel Na sorption complex, sample as seen within the aqueous solution.

based electrolytes. The reconstruction also allowed for observation of the difference in sheet thickness between single smectite flakes[3]. This can be done from different angles. Individual colloidal size particles are well visible in still picture and the distinctive spongy and cellular structure can be carefully studied when rotating this image. Cellular network of Na-smectite as observed in Fig. 3 consists of highly bent elastic flakes of diameter in excess of 1 μm, assembled in a continuous structure pattern of the smectite gel, which is similar to typical a honeycomb structure. The thickness of sheets assembled cells walls are below the resolution of TXM but well visible when rotating this image. Much denser gel assembled of 20-50 nm thick flakes was reported in[3] to build cellular network in Ca-smectite with cell diameter around 0.5 μm. Such flakes are stiffer and do not band to the same degree observed in Na-smectite gel.

Disputes about the nature of long range repulsion have remained. However, the presences of such forces are supported by our TXM and SEM micrographs and AFM force measurements in Na and Ca smectite samples. A cellular tactoid model with a honeycomb structure has been proposed[3]. In this model combination of repulsion between negatively charged basal surfaces and attraction of positively charged edges towards negatively charged basal surfaces creates the swollen cellular tactoid structure. This structure is unique to smectite and especially to smectite gel with Na sorption complex as a result of the high flexibility of thinner sheets. The formed structure may correspond to the well known Terzaghi "honeycomb" structure, described for more rigid, platelet shaped minerals such as kaolinite.◆

Publications

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