Synchrotron based transmission x-ray microscopy reveals smectite fine structure in an aqueous environment

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The unusual behaviour of smectites, the ability to change volume when wetted (swelling) or dried (shrinking), make soil containing smectites very unstable and hazardous for the building industry due to foundation movement and poor slope stability. These macroscopic properties are dominated by the structural arrangement of its finest fraction. In this work we show utilisation of a new technique called transmission x-ray microscopy (TXM) based on the synchrotron photon source. This technique enables, for the first time, the study in three dimensions, of smectite gel arranged in voluminous cellular structure and it modification by adding Al_{13} Keggin macro-molecule $[Al_{13}(O)_4(OH)_{24}(H_2O)_{12}]^{7+}$. All these observations were conducted in the natural aqueous environment.

The first experimental confirmation of smectite clay gel structure was obtained much later with the advent of transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Rosenquist (1959) published a micrograph confirming the existence of the "card house" structure. Bowles (1968), Pusch (1970) and O'Brien (1971) confirmed the presence of the honeycomb microstructure in wet clay sediments. Grabowska-Olszewska et al. (1984) using cryo-SEM investigations published a large amount of microstructural data from 86 studied samples of wet clay rocks combined with compositional and physical properties. Given the size of clay constituents, SEM was found to be the tool of choice used by scientists studying the microstructure of smectitic clays (Smart and Tovey 1982, Smart et al 2004). 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 structure (Chenu and Tessier, 1995). These artefacts result as a consequence of the low thermal conductivity of water and ice, which only allows a slow rate of heat withdrawal from the specimen. Thus the size of the gelled smectite sample must be small enough to freeze quickly limiting the inevitable damage associated with the sampling process.

Recently, a revolutionally new technique has been implemented for the study of nano-material science which is nano-tomography (Attwood, 2006). This method is based on the transmission X-ray microscopy (TXM) which works with a synchrotron photon source. This new technique has recently

been established to investigate aqueous clay suspensions. The big advantage of the TXM tomography is the possibility to observe clay microstructure in a water environment, artefact free and without sample pre-treatment. This method been recently tested in the study of another clay micro-structure modification and it usefulness in characterisation in the field of mineral processing. As an example, TXM methodology is shown in the present work in microstructure characterisation of modified clay smectite suspensions.

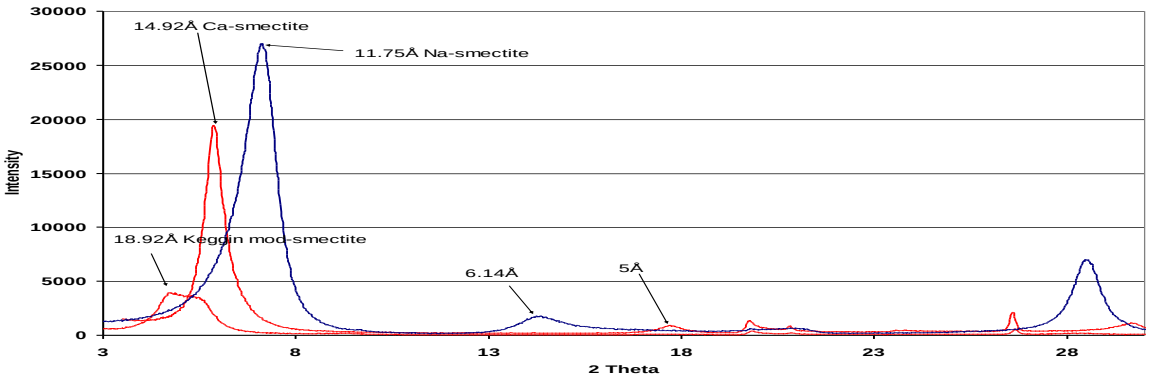

Fig 1. XRD pattern from Swy-2 montmorillonite sample modified using Na^{+}, Ca^{2+} and Keggin Al_{13}^{7+} shown significant shift in the major peak from 001 distances between smectite layers.

The transmission X-ray microscopy (TXM) with 60 nm tomographic resolution has been used in this study. This new technique however has some limitations (Zbik et al, 2008a) which were overcome and the method been recently tested in the study of different clay minerals like kaolinite (Zbik et al, 2008b) and smectite clay samples. This method shows progress in discrete structure imaging of the clay-water aggregates and in visualisation of structural modifications. These modifications may have significant impact on the microscopically behaviour of resulting, subject to modification, clay materials.

The smectite used in this study was a well known Na-montmorillonite from Wyoming (U.S.A.) obtained from Clay Mineral Repository. This sample (SWy-2) has been well described (Van Olphen and Fripiat,1979) and two samples were prepared from this original clay. First the colloidal fraction was separated by centrifugation and secondly all cations in exchangeable positions were ion exchanged with sodium Na^{+} and calcium Ca^{2+} ions. Measurements were performed in distilled water. Note that it is difficult to control Debye length in "water" because there is always some low level, 0.01 mM or less, of background electrolyte (including ions form the self-dissociation of water) that is hard to quantify or control. The most important difference in the bonding between Ca- and Na-montmorillonite sheets is that in dilute salt solutions the spacing between most of the former is restricted to 0.95 nm, whereas the spacing of the latter is unlimited (Emerson, 1983). The cluster cation $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}$ has the Keggin structure with a tetrahedral Al atom in the centre of the cluster coordinated to 4 oxygen atoms. This ion is generally called the Al_{13} ion. The Keggin ion

exchanged SWy-2 sample along with Na and Ca modified montmorillonite were subjected to x-ray diffraction to ensure complete exchange as shown in Figure 1.

Smectites naturally disperse in water forming a gel where sheets are highly flexible, individual clay sheets interact by a combination of edge attraction and basal plane repulsion and build an expanded and extremely voluminous cellular network composed of chain-like sheet assemblies as shown in presented TXM micrograph in Figure 2. In such an extended cellular network flexible smectite sheets encapsulate water within cellular voids up to 0.5-2 µm in dimension. Geometry of this network can be easily modified by shear when different and highly oriented cells may evolve. This flocked cellular structure may fill the entire vessel or be fragmented to individual flocks which differ in size. When structured clay spans a vessel the suspension is gelled; there is no free settling in this system and further compacting may proceed slowly by structural re-arrangement of the entire network. In case when shear is not present the 3-D cellular structure consists of randomly oriented smectite sheets.

In 2-D, TXM micrograph shown in Figure 2 left, elongated montmorillonite sheets in Na-montmorillonite forms cellular network 0.6 to 1.5 µm in diameter (average 940 nm). In 2-D, TXM micrograph shown in Figure 3 left, Ca-montmorillonite gel cellular structure show much smaller cells dimensions 300-600 nm. The average distances measured between smectite sheets was around 450 nm which is less than half of the cells dimension measured in Na-montmorillonite.

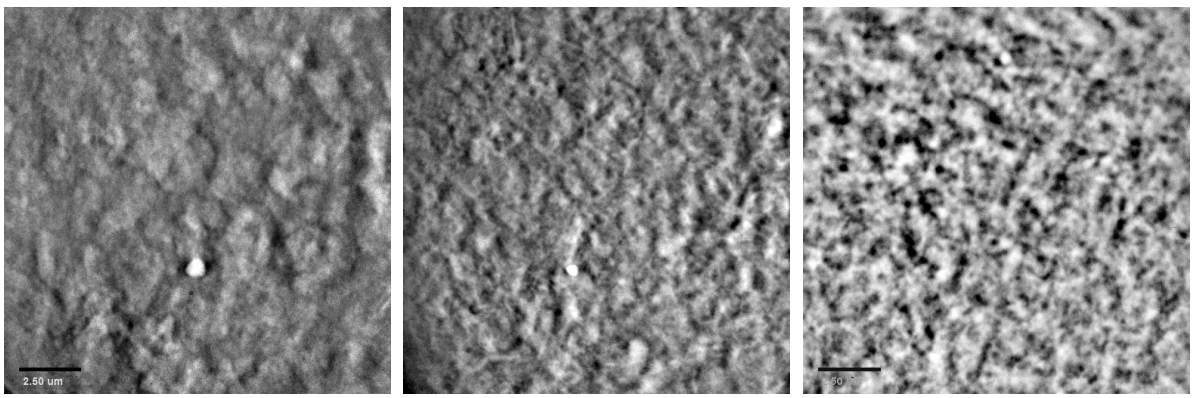

Fig 2. TXM micrographs of 5wt% (from left to right) Na, Ca, and Al_{13} treated montmorillonite colloidal gel in water; 2-D TXM micrographs. Scale bars are 2.5 um.

The 3-D space reconstruction shown in Figures 2 obtained from 2-D pictures of particles observed from angles +70 to -70 degrees (we are able to observe this gelled suspension from different angles). Such a reconstruction reveals the cellular orientation of associated mineral sheets within aqueous suspension as well as observing significant difference in sheet thicknesses between Na and Ca montmorillonite, observed from different angles.

Direct measurements of forces acting between studied Na and Ca montmorillonites were described in Zbik et al. (2008c) and show a long-range repulsion between these particles surface.

Structural changes were observed after treatment by Al_{13} Keggin where aggregates become arranged in more compacted network of thicker stacked platelet like particles about 300 nm thick building of thick face to face oriented aggregated chains. Studied in water suspension short-chained aggregates are randomly arranged and produced irregular, elongated, spongy network like shown in the 2-D TXM micrograph Figure 2 (most right image). Individual chain aggregated connecting each other, often with smaller spongy edge to edge platelets assembling short twisted chains which shaped in closed loops. Within aggregates, voids are very small and about 30% of total measured porosity belongs to voids of diameter up to 220 nm. Larger channel-like and spherical voids up to 0.5-1.5 μm in diameter are lower in number but very important in dewatering because they significantly contribute in flock permeability. Compacted chain aggregates of irregular shape are connected to neighbour similar structural elements by bridges of face to edge oriented individual thick stacked platelets and assembling spongy 3-D cellular network. Cells look clear inside and whole structure appears to be stabilised by strength of the chain assembly and friction between contacting platelets. Elongated walls of cellular pattern consist with thick (up to 300 nm) aggregates of stairstep-like arranged sheets can be observed in the 3-D computer reconstruction from tomographic investigation conducted using TXM.

Our TXM investigations reveal swollen cellular structure in aqueous montmorillonite gel with void diameters on the micrometre scale which is consistent with AFM force measurements. Na-montmorillonite with cells up to 1-2 μm in diameter where individual sheets form spacious cellular network. This network encapsulates water within impregnable honeycomb like cells. Different, coagulated aggregate type of micro-structure has been observed in Ca-montmorillonite with cells diameter ~0.4 μm and shorter and more rigid structural networking elements.

The Keggin modified smectite display significantly different microstructural type where dense smectite flakes stacked in FF and FF orientation build spongy aggregates. These aggregates are bridged to other similar aggregates in random direction, fast settling and display narrow inter-aggregate voids in resulting sediment.

Acknowledgement

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Notes