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SYNCHROTRON BASED TRANSMISSION X-RAY MICROSCOPY REVEALS SMECTITE FINE STRUCTURE IN AN AQUEOUS ENVIRONMENT

Marek S. Żbik * **and Ray L. Frost**

Faculty of Science and Technology, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane Qld 4001 Australia

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*) e-mail: namer@zzz.edu.fr

A transmission X-ray microscope with 60 nm tomographic resolution has been used at beamline BL01B of NSRRC in Taiwan. 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. The TXM observations of smectites in aqueous suspension shows network of connected nano-size platelets which form a gel where highly flexible sheets 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 dimensions up to 0.5 - 2 µm. This flocked cellular structure can span all volume of 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 micrographs reveal the Na-smectite gel structure in water. In this finding, elongated smectite sheets form a cellular network, 0.6 to 1.5 µm in diameter (average 940 nm).

The smectite sample was size fractioned and sodium exchanged as described elsewhere. Solutions of aluminium and gallium 13 Keggin ions were prepared. To an aliquot of the Keggin ion solution, the sodium exchanged smectite was added in an amount which ensured the Keggin ion remained four times the CEC. The clay in Keggin ion solution was mixed overnight using a magnetic stirrer before collection, washing and drying via vacuum filtration. The Keggin ion exchanged smectite was subjected to x-ray diffraction to ensure complete exchange. A 10% w/v suspension of the Keggin exchanged smectite was prepared in filtered water. To this suspension an aliquot (3 µl/ml of suspension) of 1 mg/L gold nanoparticles (0.8-0.5 µm) was added.

Observed structural effects of smectite modified nano-clay may be explained by hydration of the exchangeable counter ions, allowing these ions to then set up an electric field double layer. It is also possible that AFM measured long-distance forces, similar to electrostatic repulsion, have a steric origin and reflect the flexibility of smectite flakes. In dense suspension hindrance of neighbour platelets would be unavoidable. The scale of squeezing of the smectite gelled structure by the AFM cantilever spring is consistent with microscopy observations as well as force measurements.

Significant differences between smectite with Na^+ and Ca^{2+} exchangeable cations may be due to the differences in the rigidity of the smectite flakes. In the case of the presented results it may 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. A 3-D space reconstruction, allowed in TXM tomography reconstruction reveals, for the first time, the cellular orientation of associated mineral sheets within aqueous based electrolyte. The reconstruction also allowed for observation of the difference in sheet thickness between single smectite flakes. Individual colloidal size particles are well visible in the presented still picture and the distinctive spongy and cellular structure can be carefully studied in this reconstruction when rotating this image. The cellular network of Na-smectite consists of highly bent elastic flakes of diameter in excess of 1 µm assembled in a continuous structure pattern. This pattern is similar to a typical honeycomb structure. The thickness of sheets assembled cells walls are below the resolution of TXM but well visible when rotating this image. A much denser gel assembled of 20 - 50 nm thick flakes was reported to build a cellular network in Ca-smectite with a cell diameter around 0.5 µm. Such flakes are stiffer and do not band to the degree observed in Na smectite gel.

Much smaller voids of ~200 nm diameter were observed between mostly randomly oriented Keggin intercalated smectite flakes when gelled as an effect of keggin addition to the smectite suspension. These flakes form compact aggregates randomly positioned in space and mostly EF orientation spanning network.