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# Smectite clay microstructural behaviour on the Atterberg limits transition

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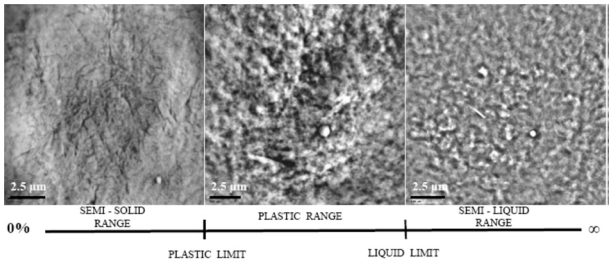
## HIGHLIGHTS

- Microstructural investigation of smectite clay in Atterberg limits was conducted.
- Clay particles form a framework with established hierarchic structural elements.
- The water loss was observed mostly from interconnected, inter-floccules voids.
- Size of intra-flock voids resulting of the water loss on liquid and plastic limits.
- Significant differences in Atterberg limits values were result of sample seasoning.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Particle space arrangement is a very important factor that determines the physico-mechanical properties of soil. Formations of three-dimensional (3D) structured networks within gelled or flocculated suspension may prevent clay particles and aggregates from building dense aggregates and by encapsulate water within the ultrathin and closed void network, lead to poor sludge dewatering. To better understand the water retention behaviour of smectite-rich clays, a microstructural investigation was conducted on Amcol Australian bentonite in aqueous suspension in near the liquid limit (LL) and the plastic limit (PL). The investigation was conducted with the aid of synchrotron-powered transmission X-ray microscope tomography (TXM), with subsequent computer reconstruction. Images from the microscopy studies were statistically analysed using the STatistical IMage ANalysing (STIMAN) system. The study found that clay particles form a spanned framework in which mineral particles, aggregates and water-filled voids assemble as hierarchic structural elements. The size of these structural elements was larger in the water suspension and subsequently became smaller as an effect of water loss in the suspension > liquid and > plastic limit conditions. The clay suspension structure was almost isometric, with a low anisotropy coefficient: $K_\alpha$ – 9%. This parameter increased to $K_\alpha$ – 17% in (LL) and increased further in (PL) conditions to $K_\alpha$ – 35%. Voids within structural elements were much smaller than the water filled inter-flock voids, with their median diameter 140 nm (suspension), 120 nm (LL) and 90 nm (PL). Significant differences in Atterberg limits values were observed between powder freshly mixed with water and a seasoned sample. Therefore, careful consideration of the sample mineral composition, clay content and genesis must be given due to preparation for geotechnical examination.



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## 1. Introduction

The term 'soil' is universally used across many disciplines of science. In general, it refers to the uncompacted layer of bedrock fragment covering the surface of the crust of planetary bodies and known by the name of a 'regolith'. Since Wesselink [1] estimated the grain size of the lunar regolith in 1948, studies of planetary regoliths have been conducted not only on Earth but also on the moon and Mars.

The term 'soil' is most commonly used in agriculture, where it can be synonymous with rich organic topsoil for plant growing, and in engineering geology (civil engineering), where soil is synonymous with the ground on or in which a range of engineering structures are built. In this sense, soil is used to support structures and embankments, as a construction material, and for other anthropogenic activities [2].

Clay-rich soils that contain more than 2 wt% of clay minerals need to be treated carefully when it comes to these activities. Clay-rich soils have different characteristics from many other regoliths and, as a result, behave differently. These characteristics often have a damaging effect on engineering structures. Generally, these soils behave as semisolids within a certain range of water content, and their physical properties change gradually as the moisture content changes. When water is added, clay-rich soils can gradually transform from a semisolid state through a plastic state to a semiliquid state. Each of these states can be determined by defined parameters, such as shrinkage limit (SL), plastic limit (PL) and liquid limit (LL). The detailed definitions of these parameters are called the Atterberg limits [3].

The Swedish scientist A. Atterberg established several specific methods for classifying and describing the behaviour of cohesive soils like clays under various moisture condition. The laboratory procedures used by Atterberg shortly after the turn of the 20th century, to determine the liquid limit and plastic limit of soil tests are in use today by soil engineers around the world.

The liquid limit and plastic limit tests define the upper and lower moisture content points at which a particular soil ceases to perform as a plastic [4,5].

The LL is determined by measuring the water content and the numbers of blows required to close a specific grove for a certain length in a standard LL Casagrande device. The PL is determined my measuring the water content of the soil when threads of the soil 3 mm in diameter begin to crumble. These two limits are vital soil characteristic because they determine how much water may be retained in the soil before liquification. The difference in the water content between these two limits is called the plasticity index (PI); it contains information about how much water can be retained in a soil before it transforms from a semisolid state to a semiliquid state. This is important because this transformation can have catastrophic consequences for engineering structures supported by the soil.

Little is known about the mechanisms behind these transformations because the clay particles are in general too small for optical observation and in the wet stage, soil samples are not suitable for investigation using most electron microscope techniques. To better understand the behaviour of clay-rich soil in the transition between semisolid and semiliquid stages, the high smectite content clay soil was investigated using a transmission X-ray microscope (TXM). Investigations were conducted in different water-capacity stages that mimicked the LLs and PLs used in engineering practice.

Structural transformations between all these stages were the subject of observation at the micro scale using synchrotron-powered TXM with subsequent computer three-dimensional (3D) reconstruction. The results of these observations from 3D space images and image sections as well as statistical image analyses were the focus of the present study.

## 2. Experimental

Commercially available Australian 'Amcol' sodium smectite, clay-rich bentonite, was chosen for this study. The product was sourced from Amcol Australia Pty Ltd., which owns and operates an Upper Jurassic bentonite mine at Miles in Queensland, approximately 375 km north-west of Brisbane [6]. From non-treated bentonite, a 2.5 wt% suspension was prepared in deionised water (DI) and was sonicated for 1-min with 50 W power. The pH was not controlled and measured approximately 8 in suspension.

Sample preparation for plastic and liquid limit condition was conducted by adding water to dry soil and working it by spatula accordingly to procedures described in [3,4,5]. The electrokinetic potential (zeta potential or $\zeta$) was measured in the clay samples using a Zetasizer (NanoSeries), manufactured by Malvern Ltd., United Kingdom. Samples of diluted suspension (~0.2 wt%) were prepared from the clay fraction and inserted into the disposable measurement cell. The zeta potential in mV and electric conductivity in mS/cm were measured in DI water. For comparison, results of the zeta potential were also measured in 0.1 M NaCl and $CaCl_2$ salt suspensions. Measurements were made following the procedures as described in Hunter [7], Lyklema [8] and Minor et al. [9].

X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert Pro, a multi-purpose diffractometer using Fe filtered Ca Ka radiation, an auto divergence slit, a 2° anti-scatter slit and a fast X'Celerator Si strip detector. The diffraction patterns were recorded in steps of 0.016° 2-theta with a 0.4 s counting time per step, and logged to data files for analysis.

Electron microscope investigations were conducted using a JEOL-2100 transmission electron microscope (TEM) operating with a 200 kV accelerating potential. A scanning electron microscope (SEM) JEOL 6040 was used to investigate samples coated in platinum film with accelerating voltage 15–20 kV. For 3D imaging, a Cryo-TEM was used with an accelerating voltage of 300 kV. The aqueous suspension samples were vitrified at liquid nitrogen temperature by rapidly plunging the samples into an environment-stable camera (stable temperature and moisture content).

TXM proved to be an efficient instrument for studying the internal structure of nano-material because of its large penetration depth and superior spatial resolution. TXM, which was used in the present study, has been installed on the synchrotron at Taiwan's National Synchrotron Radiation Research Center [10,11]. This TXM provides two-dimensional (2D) 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 to image light material that lacks X-ray absorption contrast. TXM allows the measurements of aqueous specimens because it has no vacuum requirement.

The photon energy of 8 keV was used to image the clay suspension for maximum X-ray absorption. The exposure time of a 2D image is 15 s to 4 min. 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 the azimuth angle rotating from −70° to +70° for the lateral plate specimen.

Images from the microscopy studies were statistically analysed using the STatistical IMage ANalysing (STIMAN) system [12–15] technique, which has been adapted for studying clay suspensions. This technique can extract integrated information on sample microstructures, especially on total pore (void) space and the spread of micropore sizes. It contains a subroutine for estimating filtration properties from the void space parameters. Examples of the output parameters include: examined void number; porosity (%); total void/particle area (sq. μm); total void perimeter (μm); average diameter (μm); average perimeter (μm); the form index ($K_f$) (platelet thickness to diameter); and the structure element orientation ($K_\alpha$) [16].