Evaluation of microfabric of clay using atomic force microscopy

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The term 'microfabric' (geometric arrangements of particles) was first used in the late 1960s to study features of the soil that cannot be seen with the naked eye; which includes the orientation of particles, particle size and shape, stratification and voids. It is generally believed that electron microscopy (SEM, TEM) is the only technique that can reveal particle arrangements directly. In the present study, a novel and more advanced technique, atomic force microscopy (AFM) is introduced to evaluate the microfabric of cohesive soil which is an important parameter to decide the shear strength behaviour of the soil. AFM has several advantages over SEM/TEM for characterizing particles at the sub-micron range: (i) AFM gives 3D images and 2D images with *Z* information, providing quantitative measurements of the soil microfabric using SPIP software; (ii) AFM images can be obtained in all environments – ambient air, liquid and vacuum. This article focuses on the use of AFM for evaluating the variation in particle size distribution, angle of orientation of particles, particle size and shape, and aspect ratio of particles due to the change in the microfabric of clay.

Keywords: Angle of orientation, atomic force microscopy, clay, microfabric.

THE particle arrangements in cohesive soils remained largely unknown until the development of suitable optical microscopy, X-ray diffraction (XRD) and electron microscopic techniques in the mid of 1950s, which made direct observations possible. In the late 1960s, interest of researchers was focused on clay particle arrangements and their relationships to mechanical stability of the soils. The term 'microfabric' was then used for the study of those features of soil that cannot be seen with the naked eye. The electron microscope has been most rigorously used in identifying particle arrangements directly[1–4]. Although the resolution used for these studies was found to be reasonably good (for TEM 20 Å and SEM 100 Å), the main problem was in the sample preparation for cohesive materials like clay. These techniques are capable for studying only the extremes of microfabric (dispersed and flocculated), not the microfabrics between the extremes (intermediate microfabrics). The present study focuses on the intermediate microfabrics (microfabrics between the extremes), which are more common in real-life geotechnical problems. All microfabric identification techniques developed in the past using SEM, TEM and XRD would result in a relatively crude method for the identification of intermediate microfabrics of cohesive soils. Thus, an advanced technique using atomic force microscopy (AFM) has been introduced in the present study to evaluate the intermediate microfabrics of clayey soil. This included the orientation of particles, particle shape, particle size distribution, stratification, voids and so on.

Over the last few years, many researchers[5–8] have investigated and confirmed the fact that the microfabric or particle arrangement in clayey soil could significantly influence its overall engineering behaviour, e.g. consolidation characteristics, permeability, shear strength, sensitivity, etc. All these studies were performed only on extreme microfabrics (dispersed, flocculated) using triaxial tests, SEM, TEM, XRD, etc. The effect of intermediate microfabric on the interpreted engineering behaviour of soil is still unknown.

AFM is a powerful device for imaging clay and other mineral surfaces at the sub-micrometre and sub-nanometre range[9]. This is a novel technique which is gradually gaining importance. In the present work, AFM was used to evaluate the geometric arrangement of particles (microfabric) of kaolin clay at the submicron range, and samples with different microfabrics were prepared using different concentrations of dispersing electrolytic agent (calgon: sodium hexa-meta phosphate). The particle size and shape, particle size distribution, angle of orientation of particles, and aspect ratio of the particles were evaluated for kaolin clay samples with varying microfabrics. 3D images of the clay samples were also obtained to supplement the results.

Previous investigations

AFM has evolved as a promising device to explore the mineral surface, visualize the sorption of organic substances, determine morphology, measure size and thickness of clay-sized particles, and measure growth, dissolution, heterogeneous nucleation and redox processes[10,11]. However, the use of this technique has not been explored properly for soils. The high heterogeneity, imperfect mineral cleavage

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and complex composition of soil materials and the complex resulting force measured by the tip–sample interaction seemed to be the most difficult aspect when applying AFM to soils. Heil and Sposito[12] studied the influence of organic matter on the flocculation of illite soil colloids with AFM device using a geologic specimen illite and the clay fraction of a coarse loamy soil. The differences in particle morphology and surface features between the soil and illite were identified, which indicated the presence of surface roughness that could inhibit flocculation of the soil particles. The contact-mode AFM equipment to analyse smectite/illite particle morphology with careful attention to sample preparation and imaging has shown that AFM can be used to determine the dimensions of the particles with an accuracy of ± 1.5 Å for particle thickness in the order of several nanometres and the *X–Y* dimensions of less than 100 nm. Particle thickness measurements were found to agree well with measurements on the same samples by TEM and XRD. Until the advent of high-resolution field emission scanning electron microscopes, most SEM papers describing kaolinite morphology had relatively poor resolution (practically 100–500 nm) and used electro-conductive coatings (10–30 nm thick). Together with the two dimensional nature of the SEM/TEM technique, this was limited to the qualitative information largely with the description of shape and aggregate structure. The availability of AFM has now provided a second imaging technique for the study of surface morphology with atomic resolution on ideal surfaces[13,14]. Studies have shown that AFM can also produce quantitative measurements of clay morphology[15] in an aqueous solution as well as *in situ* dissolution of clay minerals.

AFM and its advantages over other methods

AFM is an excellent technique for visualizing particles with sizes ranging from 1 nm to 10 μm (http://nanoparticles.pacificnano.com/pdf/quantity.pdf), and for clay particles of size less than 2 μm. Thus the AFM technique can be used for all types of clays. A major advantage of AFM is its simplicity of operation and that it requires minimal sample preparation. TEM is well known for time-consuming and complicated sample preparation. SEM samples are easier to prepare; however, the requirement of sample coating adds some difficulty and the coating procedure may also cause irreversibly change or damage to the sample. AFM samples do not need to be coated, which makes sample preparation easier for the user. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. In comparison to the traditional techniques (SEM and TEM) for sub-micron particles, AFM can give 3D images and 2D images with *Z* information through colour intensity, providing the opportunity to obtain quantitative measurements of microfabric of cohesive soils using SPIP software. SEM and other methods can give only qualitative information about extreme microfabrics (dispersed, flocculated). However, the intermediate microfabric is difficult to identify using these methods without quantitative measurements of particle orientation because there is a large difference in the geometric arrangements of particles in extreme microfabrics; and qualitative analysis is often sufficient in that case[8].

AFM device and its functioning for cohesive soil samples

All the experiments were performed on PicoScan-AFM (Molecular Imaging Inc; now known as Agilent Technologies) which consists of a microscopic head, piezoelectric tube, scanner inside the glass block assembly and a silicon chip[11,15] (Figure 1). The silicon chip (NSC-36 series) has three rectangular micro-scale cantilevers coated with silicon nitride (Si_3N_4) and the thickness of the chip was 0.4 mm. Each cantilever (NSC36/AIBS/50) has a silicon tip with radius of curvature less than 10 nm. The tip height was between 15 and 20 μm.

In the present study, 'non-contact mode' was used while scanning the sample surface, because 'contact mode' can damage both the silicon tip and the surface of the cohesive soil sample due to high frequency (54.59 kHz) of the cantilever. The AFM apparatus had two types of mode for working, 'constant force mode' and 'constant height mode'. Use of 'constant height mode' was found to be more appropriate for the study of clay microfabric due to its cohesive nature. The data processing of AFM images was handled by the Scanning Probe Image Processor (SPIP, version-4.5.2.0 released 31 July 2007) data analysis package. Grain analysis module and 3D visualization studio module of SPIP software were used in the present study. The *X*, *Y*, *Z* values of different points on a particle were determined using the 'watershed method' as suggested by the SPIP software, because particles were glued to each other due to the cohesive nature of clay.

Two-dimensional AFM images containing discrete particles of soil and *Z* information through colour intensity were used in the SPIP software analysis. A typical 2D AFM image used is shown in Figure 2. During the analysis, the software considered all the particles as contours and determined the *X*, *Y*, *Z* coordinates, length, size, centre of the particle, etc. All these values were obtained by analysing 2D AFM images using the following steps: (i) choosing a reference line for a given 2D image while scanning it using the AFM device, (ii) identifying each particle as a contour and providing the *X*, *Y*, *Z* coordinates of the points at a certain interval in a given contour (particle) from the chosen reference line, and (iii) providing the maximum and minimum values of *Z* and length of a given contour (particle). These parameters were then used to evaluate

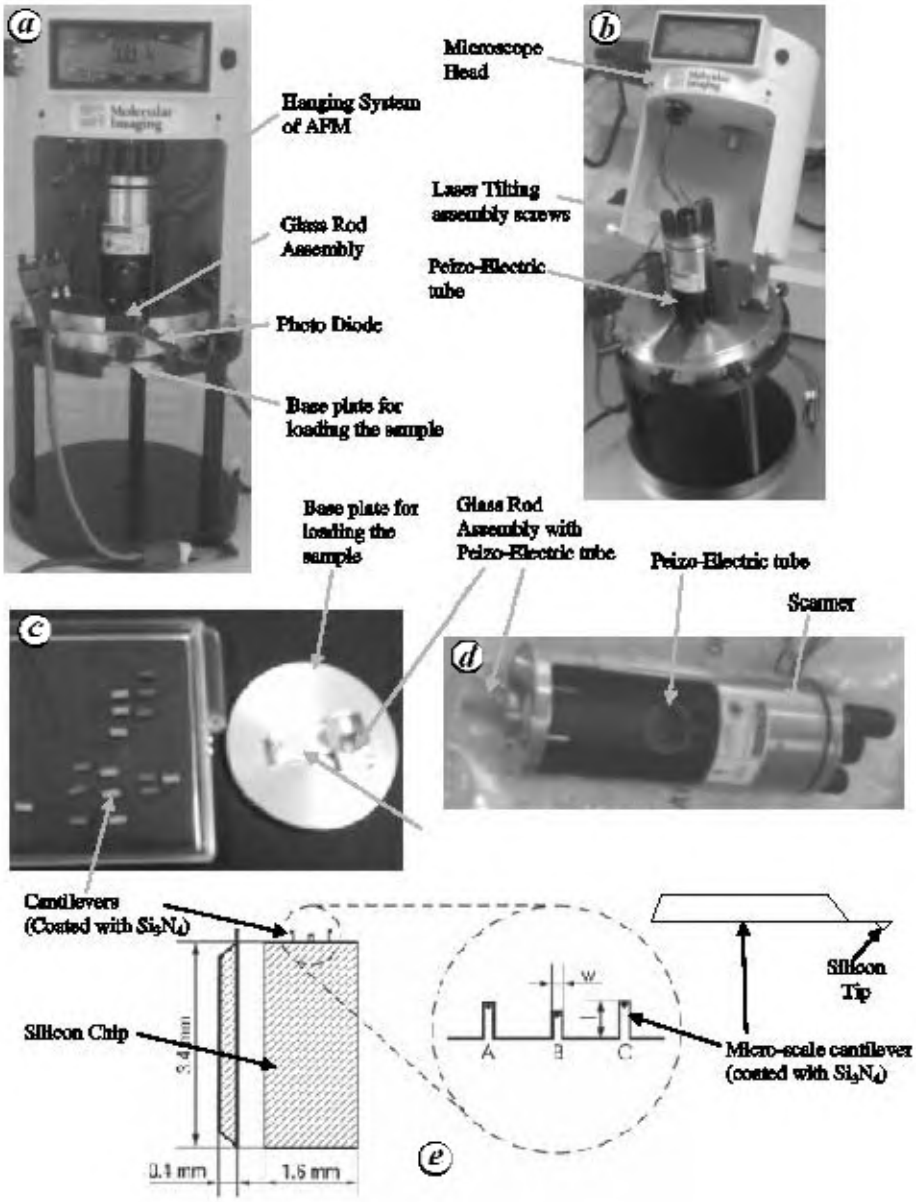

Figure 1. Atomic force microscopy (AFM) apparatus used in the present study. ***a***, Complete set-up of AFM. ***b***, Set-up after removing the glass block assembly. ***c***, Micro-scale cantilevers, and glass block assembly. ***d***, Peizo-electric tube. ***e***, Schematic diagram of silicon chip, micro-scale cantilever and its silicon tip.

the particle size distribution, angle of particle orientation, particle size and shape, and aspect ratio of particles of the soil to identify its microfabric.

Material properties and sample preparation

The present study was carried out on commercially available kaolinite clay, obtained from English Indian Clays Ltd, Kerala, India. The kaolin clay used in this study had a liquid limit of 65%, plastic limit of 30%, plasticity index of 35% and a specific gravity of 2.6.

A series of tests were performed on glass-slide samples of kaolin clay with 0, 1, 2 and 4% electrolytic agents (Calgon) respectively. Hydrometer method was used to prepare the clay slurry, which was used to obtain glass-slide samples[16]. The clay slurry was prepared by mixing 40 g of powdered clay with 125 ml de-ionized water and 0, 1, 2, 4% Calgon according to the requirement. Additionally, de-ionized water was added to finally obtain 1000 ml solution[16]. A thin layer of clay slurry was placed on the glass slide and it was kept at room temperature for drying.

Results and discussion

The microfabric or geometric arrangement of particles within the clay mass depends on the following: (i) the space between two particles and (ii) the angle between two particles[10]. The first causes a change in void ratio of soil mass and the second causes a change in the anisotropy of soil mass, and these parameters play an important role in the engineering behaviour of soils. The present study focuses on the variation in particle size distribution, angle of orientation of particles, and aspect ratio of particles due to change in the microfabric. These microfabrics of clay samples were obtained by changing the amount of electrolytic agent (Calgon) in the clay slurry. The possibility of the change in shape and size of the clay particles due to the presence of dispersing agent (Calgon) was also evaluated. In principle, the dispersing agent should only break the clusters of the particles and disperse them without affecting the original size and shape of the clay particle. Four different types of microfabrics of kaolin clay were prepared using Calgon 0, 1, 2 and 4% Calgon respectively. Then 2D and 3D images were obtained for all these samples at a resolution of 2000 nm using AFM device. The 2D AFM images were then analysed using SPIP software to obtain quantitative measurements of microfabric of clay.

Particle size distribution

Figure 3 illustrates the relationship between size of clay particles and their distribution within the soil sample. The size of the particles was calculated using SPIP software and percentage finer of the particles was then calculated based on their sizes. Percentage finer (in % by number of particles) has been plotted on the ordinate using arithmetic scale and the size of the clay particles (in nanometre) on the abscissa using a logarithmic scale. Percentage finer is the cumulative number of particles, as a percentage of the total number of particles available in the sample, of all particles smaller than any given particle size. A semi-logarithmic plot has the merit that soils of equal uniformity exhibit the same shape of particle size curves, irrespective of the particle size fractions present in the soil. The slope of the curve indicates the gradation of the soil or the particle size distribution. All the kaolin clay samples (with 0, 1, 2 and 4% Calgon) exhibited uniform gradation of the particles. Clay particles were observed to be slightly finer with increasing amount of calgon in the sample, i.e. clay particles were observed to be finer in 4% calgon sample than the other samples. This indicates the breaking of the group of particles and separating the clay platelets from each other due to the effect of dispersing agent.

Inclination of particles

Figure 4 shows the relationship between angle of orientation of clay particles, and the cumulative number of particles, as a percentage of the total number of particles available in the sample, of all particles oriented at smaller angle (from horizontal axis) than any given angle of orientation of the particle. Inclination of clay particles was obtained by calculating the angle of orientation (θ) along the maximum length of the particle using maximum and minimum values of Z of a particle and length of the particle (Figure 5). All these values were obtained using the SPIP software. Most of the particles (90%) in the sample with 2% calgon were observed to be orientated at an angle lower than 20° (from the horizontal), indicating the parallel-type particle orientation or dispersed microfabric. However, the sample with 0% calgon had only 35% of particles oriented at an angle lower than 20°. Angle of orientation curve was observed to be moving in an upward direction as the amount of dispersing agent (calgon) increased up to 2%. For 4% calgon, the curve moved downwards and showed values close to the that for 1% calgon,

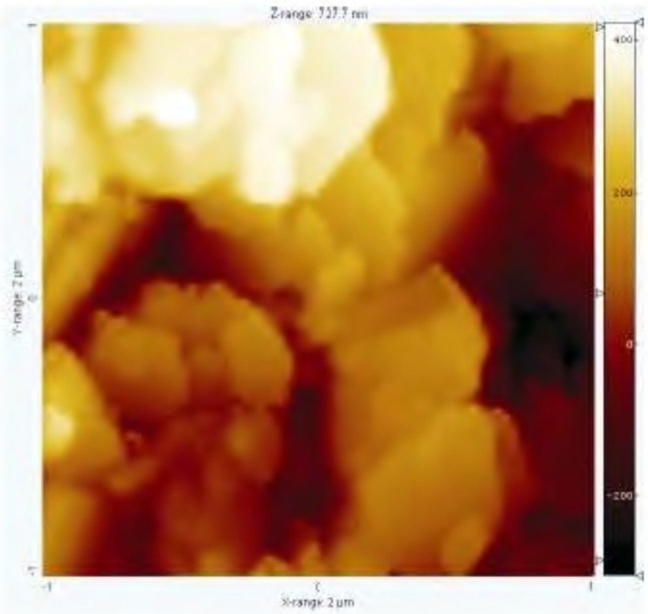

Figure 2. A typical 2D AFM image of kaolin clay sample used in SPIP software analysis.

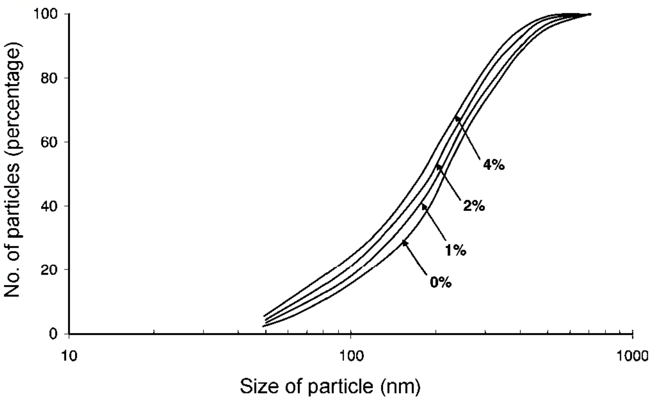

Figure 3. Particle size distribution curves for kaolin clay with different calgon content.

indicating that the highest level of dispersion of clay particles was already achieved at 2% calgon. This was validated by 3D images of the samples with 0, 1, 2 and 4% calgon, as shown in Figures 6 *a–d* respectively. Figure 6 suggests the formation of intermediate microfabric for samples with 1 and 4% calgon, and extreme microfabric for 0 and 2% calgon samples (flocculated and dispersed respectively).

The crystal structure of clay minerals shows that clay particles are negatively charged, and in the presence of water, cations concentrate near the surface of clay particles[5]. The potential established as a result of interaction of adjacent charged particles is the deciding parameter for clay particles to be oriented in a certain type of geometric arrangement or microfabric. If the electrolytic environment of a clayey soil is changed by adding a dispersing agent, the potential energy is increased. The positively charged ions in the solution concentrate near the surface of the clay particles in an attempt to balance the net negative charge with high inter-particle repulsion force, thereby resulting in a dispersed microfabric (face-to-face particle contact). The net force at a given separation distance is the algebric sum of the repulsive and attractive forces acting at that distance. Since van der Waal's (attraction) force is insensitive to the properties of the separating medium while the repulsive forces are sensitive, it follows that the net force of interaction between the clay particles can be varied directly by varying the properties of the medium[5]. When the magnitude of the inter-particle repulsion force become lower than the van der Waal's force of attraction, the particles move towards each other and make face-to-edge particle contact[8]. In the present study, the dispersive behaviour of kaolin clay was observed to increase with increasing amount of calgon (dispersing agent) ranging from 0 to 2%. However, 4% calgon sample (or after 2% calgon) showed a decrease in dispersive nature of the soil. This observation could be explained by the argument that the inter-particle force becomes smaller than the van der Waal's force in the 4% calgon sample, making the particles come closer to each other and form face-to-edge particle contacts. It is important to note that face-to-face particle contacts were already present in the sample due to the presence of calgon, but the extra calgon changed the ratio of inter-particle force and van der Wall's force based on the double layer theory concept[5], which also allowed the particles to make face-to-edge contacts; this exhibited the intermediate microfabric of the soil similar to 1% calgon. Intermediate microfabric can be defined as the geometric arrangement of particles which has both types of particle contacts, face-to-edge and face-to-face; and the ratio of these particle contact within the soil decides its closeness to the extreme microfabrics of that soil.

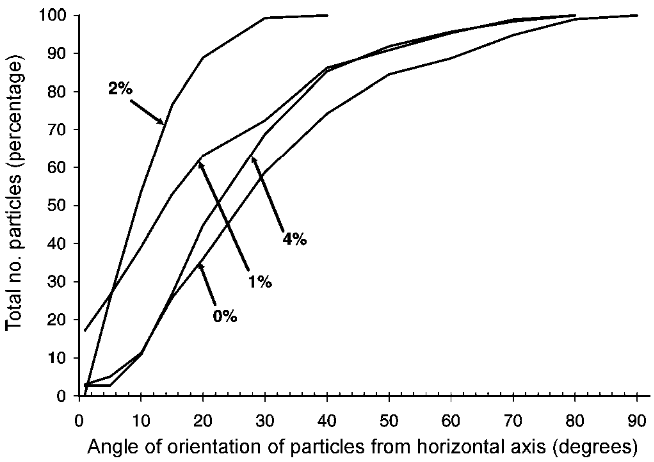

Figure 4. Angle of orientation of clay particles for samples with varying calgon content.

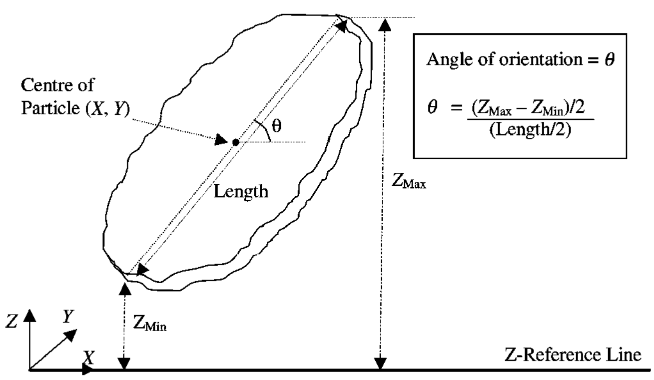

Figure 5. Schematic diagram of a clay particle for calculation of angle of orientation.

Sachan and Penumadu[8] showed the geometric arrangement of particles in kaolin clay samples with 0 and 2% calgon by evaluating SEM images of the samples. They showed that the sample with 0% calgon had particles oriented in all possible directions with equal probability (flocculated microfabric), whereas the sample with 2% calgon had particles oriented parallel to each other (dispersed microfabric). Sachan and Penumadu[4,8], and Sachan[17] reported that the contact between two particles (particle-to-particle contact) was 'face-to-face' in dispersed microfabric and 'face-to-edge' in flocculated microfabric. Similar behaviour of kaolin clay for 0 and 2% calgon was observed in the present study, as shown in the 3D images of the samples (Figure 6 *a* and *c*).

Aspect ratio of particles

The aspect ratio refers to the ratio of length and width of the clay platelet, and these values were obtained with measurements using SPIP software. Figure 7 shows the relationship between the aspect ratio of the clay particles and the number of particles (in percentage) available in the sample for a given range of aspect ratios. The kaolin clay samples with 1 and 2% calgon showed similar pattern, indicating that the particles with aspect ratio in the

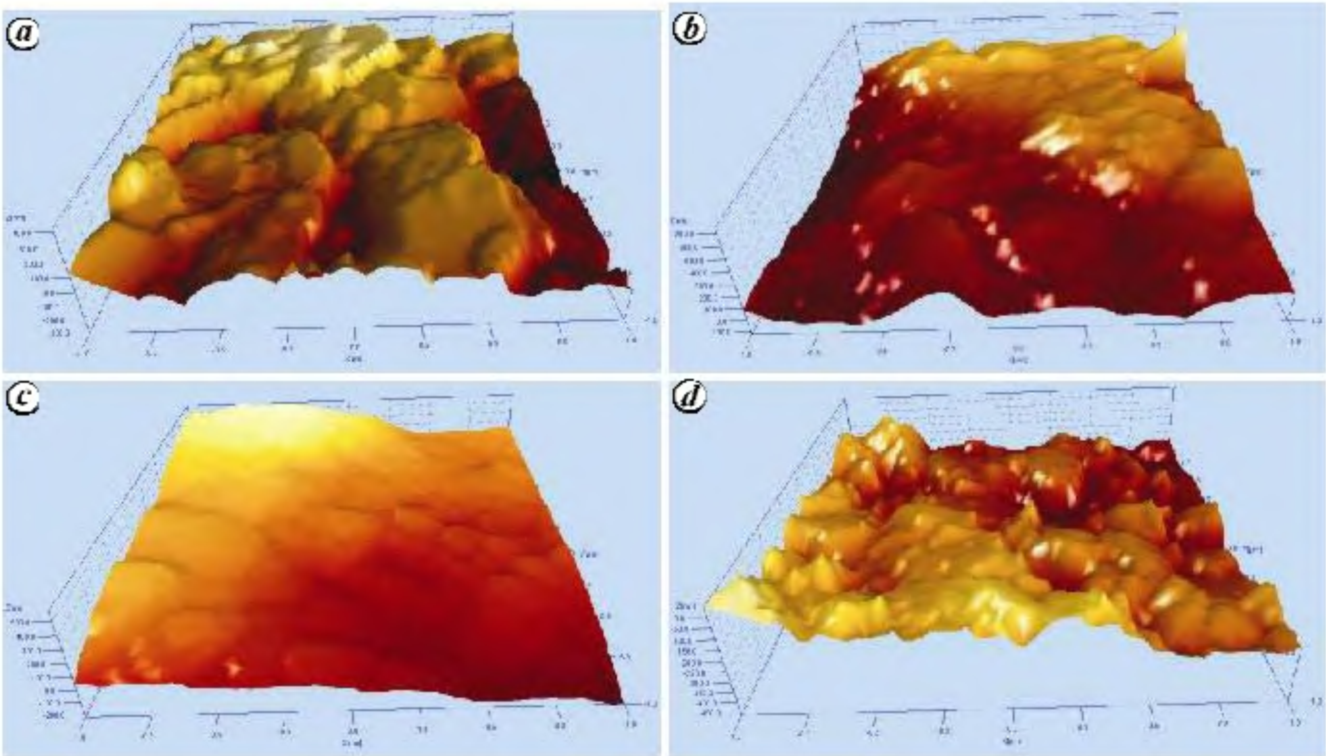

Figure 6. Three-dimensional image of kaolin clay sample with 0% calgon (***a***), 1% (***b***), 2% (***c***) and 4% (***d***) using AFM technique.

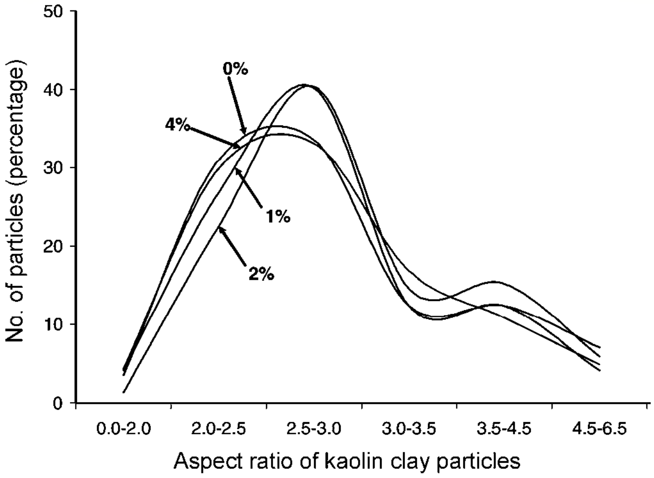

Figure 7. Aspect ratio of kaolin clay particles for samples with different calgon content.

range 2.5–3.0 were largest in number and only few particles with aspect ratio in the range 0.0–2.0 were available in the samples (Figure 7). Although samples with 4% calgon showed the finest particles in comparison to the other concentrations of calgon, these particles showed aspect ratio following the pattern of a curve similar to the sample with 'no calgon' (0% calgon).

Shape of clay particle

Figure 8 shows the relationship between the standard deviation of the Z values of different points at the particle from the reference line of the AFM image chosen by SPIP software and the range of Z, which is the difference between the maximum and minimum value of Z of a particle. The SPIP software chooses a reference line for each image while scanning it using the AFM device. It identifies each particle as a contour and provides the X, Y, Z coordinates of the points at certain intervals in a given contour from the chosen reference line and provides the maximum and minimum values of Z and standard deviation of all Z values of a given contour (particle). The range of Z for a given particle can be considered as one of the deciding factors for its orientation within the soil mass (Figure 5). SD of the Z values of a given particle can be considered as a function of the surface curvature of the particle, as it considers the Z values of different points on the X–Y plane. The slope of the curves for all four cases (0, 1, 2 and 4% calgon) was observed to be similar, indicating 'no effect' of calgon on the surface of curvature of the particles of kaolin clay.

Relationship between particle size and Z-range of the particle

Figure 9 exhibits the relationship between range of Z and size of particles for kaolin clay samples with varying calgon content (0–4%). The size of the particles increased with increase in the value of range of Z, indicating that the large-sized clay particles align themselves at a larger angle (large value of Z range), and this was found to be true for

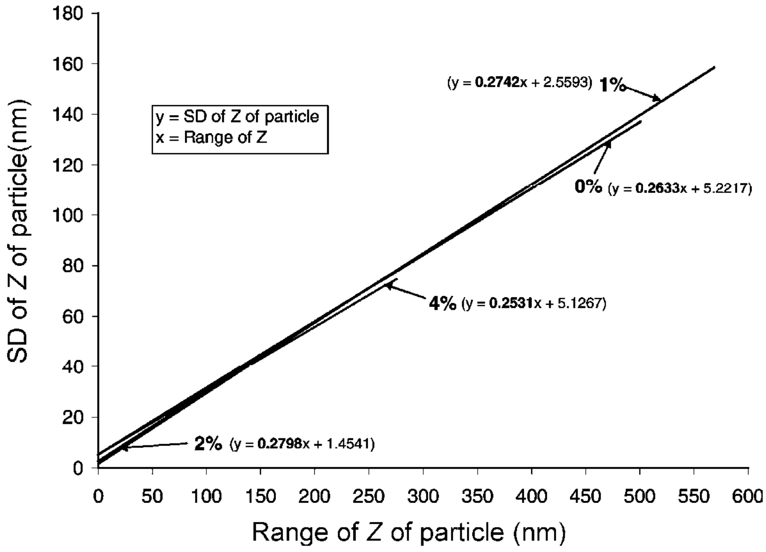

Figure 8. Standard deviation of Z values of the clay particle with respect to its range of Z.

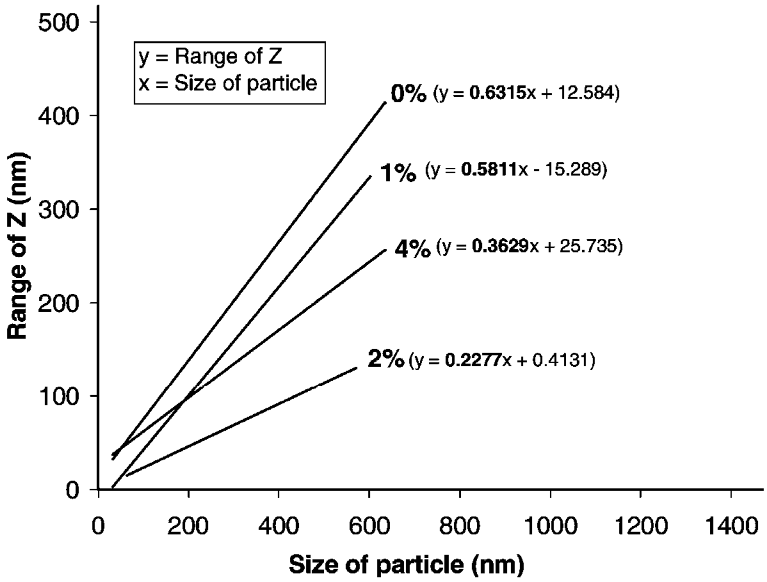

Figure 9. Relationship between the range of Z of clay particle and its size.

all the clay samples (0, 1, 2 and 4%). The maximum value of range of Z for 2% calgon sample was observed to be significantly lower than that for 0, 1 and 4% calgon, making the clay particles orient themselves at lower angles in the 2% calgon sample than the others. This led to the formation of a large number of 'face-to-face' particle contacts in 2% calgon sample and thus the dispersed microfabric of clay. The number of 'face-to-face' particle contacts was observed to increase as the amount of calgon increased (from 0 to 2%). But this number was found to decrease for 4% calgon sample, showing its intermediate microfabric. From the findings of this study, the microfabric for 0% calgon sample could be termed as 'flocculated microfabric', for 2% calgon sample as 'dispersed microfabric', and 1 and 4% calgon samples as 'intermediate microfabric'. Samples with 1 and 4% calgon were observed to have both types of particle contacts in a large number, indicating that they lie between the dispersed and flocculated microfabrics.

Conclusion

A novel and advanced technique using AFM has been proposed to evaluate the microfabric (geometric arrangement of platelets) of cohesive soil. A series of AFM tests were performed on glass slide samples of kaolin clay with different microfabrics, prepared using 0, 1, 2 and 4% respectively of the dispersing agent respectively. PicoScan AFM with 'non-contact mode' was used to obtain the 3D and 2D images of the clay sample with *Z* information, which was analysed using SPIP software for data processing of the images. Key observations from this study are summarized as follows:

(1) The proposed method using AFM has the potential to become a routine tool for obtaining quantitative measurements of microfabrics of clay using SPIP software, which also provides the 3D images of the sample.

(2) Most of the particles (90%) in the 2% calgon sample were observed to be aligned at an angle lower than 20°. However, this was 35% in the 0% calgon sample, indicating their microfabrics as dispersed and flocculated respectively.

(3) 'No effect' of calgon was observed on the surface of curvature of the clay particles.

(4) The microfabric of kaolin clay for 0% calgon was evaluated as 'flocculated microfabric', 2% calgon as 'dispersed microfabric', and 1 and 4% calgon as 'intermediate microfabric'; which was also verified by their 3D images.

1. Gillot, J. E., Fabric of Leda clay investigated by optical, electron-optical, and X-ray diffraction methods. *Eng. Geol.*, 1970, **4**, 133–153.
2. Mitchell, J. K., *Fundamentals of Soil Behaviour*, John Wiley, 2nd edn, 1993.
3. Bai, X. and Smart, P., Change in microstructure of kaolin in consolidation and undrained shear. *Geotechnique*, 1997, **47**, 1009–1017.
4. Sachan, A. and Penumadu, D., Identification of microfabric of kaolinite clay mineral using X-ray diffraction technique. *Geotech. Geol. Eng.: Int. J.*, 2007, **25**, 603–616.
5. Nagaraj, T. S., Soil structure and strength characteristics of compacted clay. *Geotechnique*, 1959, **14**, 103–114.
6. Sridharan, A., Rao, S. and Rao, G., Shear strength characteristics of saturated montmorillonite and kaolin clays. *Soils Found.*, 1971, **11**, 1–22.
7. Yimsiri, S. and Soga, K., Micromechanics-based stress–strain behaviour of soils at small strains. *Geotechnique*, 2000, **50(5)**, 559–571.
8. Sachan, A. and Penumadu, D., Effect of microfabric on shear behaviour of kaolin clay. *J. Geotechn. Geo-environ. Eng.*, 2007, **133(3)**, 306–318.
9. Binnig, G., Quate, C. F. and Gerber, Ch., *Phys. Rev.*, 1986, **56**, 930.
10. Scheidegger, A. M. and Sparks, D. L., A critical assessment of sorption desorption mechanisms at the soil mineral/water interface. *Soil Sci.*, 1996, **161**, 813–831.
11. Sharp, T. G., Oden, P. I. and Buseck, P. R., Lattice scale imaging of mica and clay (001) surfaces by atomic force microscopy using net attractive forces. *Surf. Sci. Lett.*, 1993, **284**, L405–L410.
12. Heil, D. and Sposito, G., Organic matter role in illitic soil colloids flocculation: III. Scanning force microscopy. *Soil Sci. Soc. Am. J.*, 1995, **59**, 266–269.
13. Hochella Jr. M. F., Mineral surfaces: their characterization and their chemical, physical and reactive nature. In *Mineral Surfaces. Mineral Society Series 5* (eds Vaughan, D. J. and Pattrick, R. A. D.), Chapman and Hall, London, 1995, pp. 17–60.
14. Smart, RStC., Minerals, ceramics and glasses. In *Problem-Solving Methods for Surfaces and Interfaces* (eds Riviere, J. C. and Myhra, S.), Dekker, London, 1998.
15. Bickmore, B. R., Hochella Jr. M. F., Bosbach, D. and Charlet, L., Methods for performing atomic force microscopy imaging of clay minerals in aqueous solutions. *Clays Clay Miner.*, 1999, **47**, 573–581.
16. IS:2720 Part (IV), Methods of test for soils; grain size analysis, 1994.
17. Sachan, A., Variation in geometric arrangement of particles in kaolinite clay due to shear deformation using SEM technique. *Curr. Sci.*, 2007, **93**, 515–522.

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