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USE OF ATOMIC FORCE MICROSCOPY FOR EXAMINING WET CLAY

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Abstract—Clays and their composites have been widely used for secondary containment walls for underground storage tanks and landfills. The pore-size changes occurring in the clay have a profound effect on its permeability. This study presents a new method for evaluating the use of an atomic force microscope (AFM) for studying wet clay in a non-aqueous state in order to determine the pore-size of clay at various water contents, a type of study typically performed by the more expensive environmental scanning electronic microscope. The method consists of mounting a sponge saturated with water under the sample in order to prevent drying by the heat generated by the AFM electronics. The micro-scale AFM image results show that the clay-particle separations reduce linearly as the water content increases. This change in pore-size is postulated to be attributed to the reduction in the size of the diffuse double layer and more extensive hydrogen bonds between clay particles and bipolar water molecules. The AFM was not able to produce nano-scale images due to excessive adhesion between the cantilever arm and the wet clay sample.

Key Words—Clay, Conductivity, Contamination, Gasoline, Microscope, Minerals, Permeability, Porosity, Water.

INTRODUCTION

Clay liners are often used for secondary containment of underground storage tanks. The permeability of clays is linked, among other factors, to water content, which affects the microstructure and porosity of the clay. To mitigate leakage, it would be interesting to see how the microstructure of clays changes with water content, but experimental techniques typically used for measuring pore volumes require dry samples.

Various aspects of clay and its use in containment barriers have been studied. The swelling of clay reduces the permeability of the soil and the adsorption of solutes by reducing mobility (Low, 1994). The physical behavior of clay barriers close to water saturation plays an important role in nuclear waste repositories (Borgesson *et al.*, 1996). The water adsorption properties of clay play an important role in defining the clay characteristics and its behavior towards organic molecules (Yamanaka *et al.*, 1990). The quantitative study of the permeability changes in clays due to organic contaminants indicates that clay micromechanics played a vital role in clay behavior under the influence of organic contaminants (Hueckel *et al.*, 1997). Also, clay permeability is affected by pH (Keren and Singer, 1990). The conductivity of clay soils to water and organic liquids also plays a vital role in determining the clay soil behavior (Anderson *et al.*, 1985; Odom and Low, 1978).

Atomic force microscopy is a tool that can be used to map surfaces from micrometer to nanometer scales and has been employed in several previous studies. Atomic-scale imaging has been used widely in different fields to investigate the micro–nano scale of particles (Occelli *et al.*, 1994). Atomic force microscopy has been used successfully to map the surface of ultrafine clay particles in a dry state (Garnaes *et al.*, 1992; Bickmore *et al.*, 1999), and has also been used to provide topographical images of the surfaces of dry clays at the Angstrom scale (Sposito *et al.*, 1990). Studies have shown that an AFM can produce quantitative measurements of clay-particle morphology (Bickmore *et al.*, 1999) in an aqueous solution and the *in situ* dissolution of clay minerals.

The current study presents the only documented method of using an AFM to investigate the overall pore structure of wet clay.

EXPERIMENTAL METHODS

The following properties of the clay sample were provided by the clay supplier and are given here to aid in clay identification as a standard clay sample was not used. The cell parameters of the dry clay used are a = 5.17, b = 8.94, c = 9.95, β = 99.54 for a ratio of $a:b:c$ = 0.578:1:1.113, which corresponds to a montmorillonite-type clay.

For each sample, a known mass of clay was mixed with a known volume of water. The mass of clay was kept constant and the volume of water was varied. The

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Table 1. Water-content values of clay samples.

Sample no.	Volume of water (mL)	Water content by weight (%)	95% confidence limits (µm)
1	0.5	60	±0.31
2	0.75	70	±0.25
3	1.0	76	±0.19
4	1.5	82	±0.19
5	2.0	86	±0.12
6	2.5	89	±0.12

weight of the clay used was 0.3196 g. Hence, the water content in the experiments (by weight) is given in Table 1. This suspension of clay and water was stored at room temperature. The clay suspension was dried in an electric oven for ~24 h at an oven temperature of 60ºC. Ideally, the clay samples should have been studied in wet conditions, as this would be closer to field conditions, but the AFM electronics of the DI multimode system employed emits heat that dried out the samples during the imaging process. A new method was devised in which a wet sponge was secured over the AFM steel sample-mounting disc. The clay sample was loaded on the sponge and loaded on the AFM platform (Figure 1). It was observed that the sponge provided the clay with enough water (by capillary action) to prevent drying by the AFM laser. This helped the clay sample to remain wet for the entire imaging period.

The AFM used was a Digital Instruments Nanoscope 3a Multi-Mode Atomic Force Microscope and the imaging was done under constant-force mode. Nano-device, rotated-tapping mode, etched silicon probes (tips) were used during the course of the experiments, the nominal tip radius of curvature being <10 nm. The length of the cantilever beam was 125 µm. The tip height was 20 µm and the tips had a very fine finish with a cone half-angle of <25º on each side of the tip. This very narrow tip allows passage within the clay sample pore space with minimal effect on the images.

The effect of the capillary force between the fluid film and the AFM tip was ignored, and it was assumed that the AFM tip did not mechanically alter the clay texture. Though clay permeability is controlled by bulk properties of clay, due to sample preparation difficulties, it was assumed, even if some drying did occur, that the pore structure stayed essentially the same, because the clay was thinly spread on a flat surface.

RESULTS

The images obtained from the AFM are arranged in increasing order of initial water content, starting with 60% in Figure 2. The images were obtained by using the AFM to map 25 different points on the sample surface for each clay sample at various water-content values. The pore diameters were determined by two image-analysis procedures. In the first procedure, the pore was considered to be a circle and the diameter values obtained from two perpendicular axes were used to calculate the area. In the second procedure, the pores were considered to be elliptical, and the area of the ellipses was obtained from the measured diameter values.

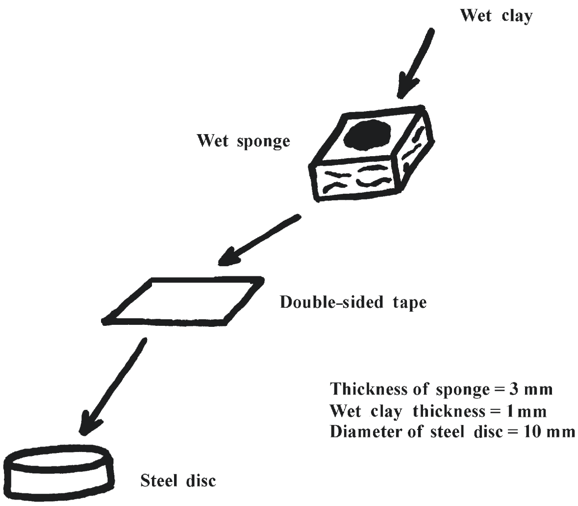


Figure 1. Use of a wet sponge in sample mounting to prevent drying during image processisn by the AFM laser.

The average pore diameters for different water contents are plotted in Figure 3 with error bars denoting the 95% confidence limits. It can be seen that there is a linear decay of pore diameter with increasing water content with 95% confidence limits of approximately 4% of the mean. The results from the circular and elliptical methods of pore-diameter determination gave similar results.

CONCLUSIONS

A new method of imaging wet clay using an AFM was introduced that used a wet sponge to keep the clay sample from drying out during the imaging process. The new method was demonstrated by studying the effect of

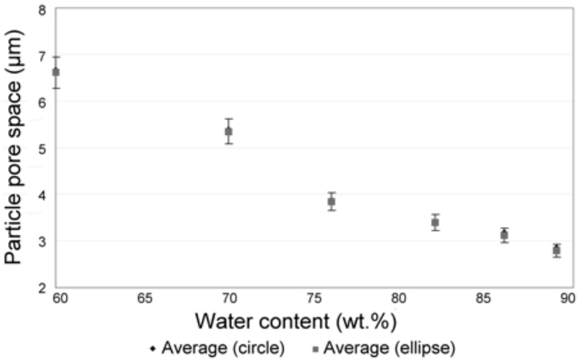
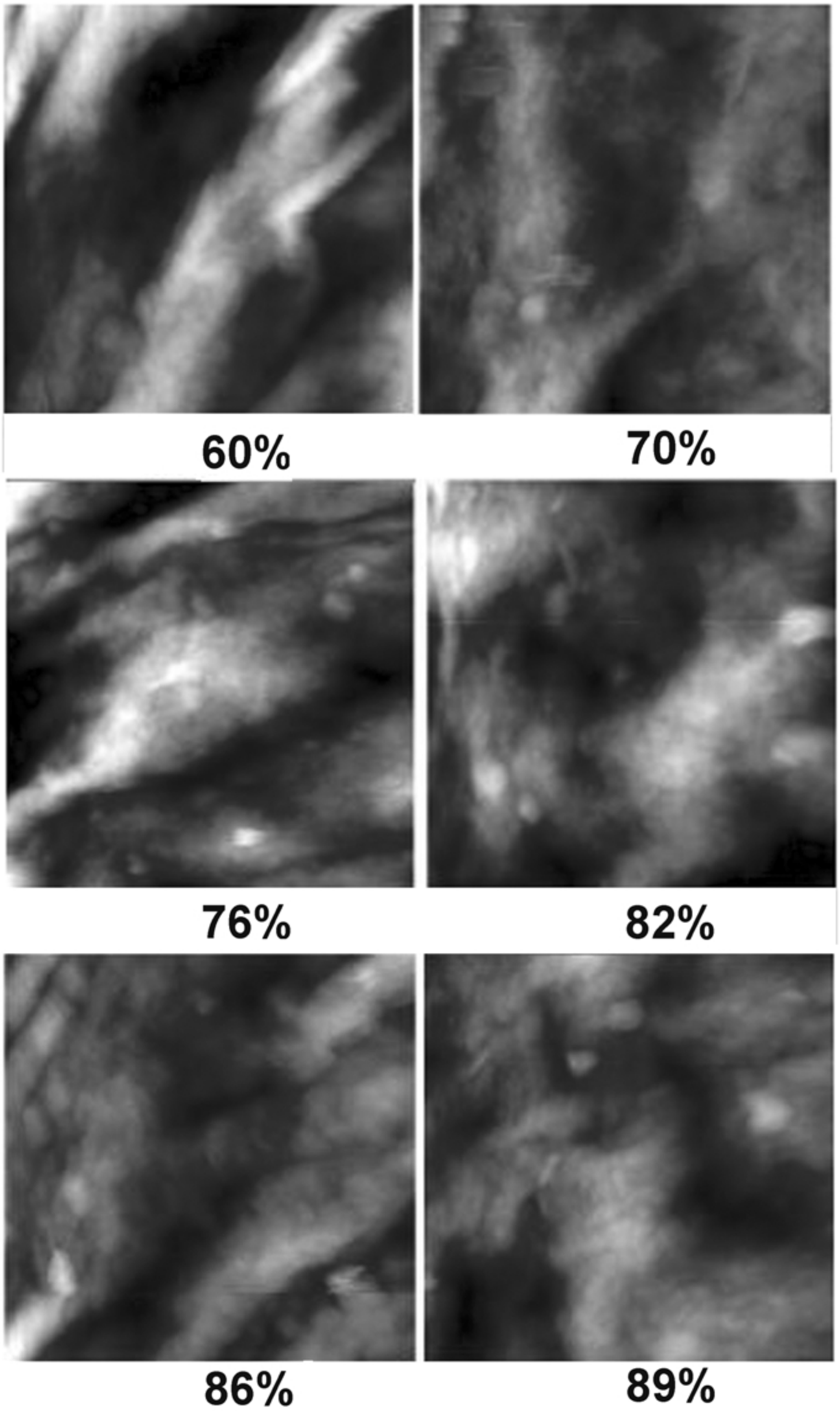


Figure 3. Water content *vs*. pore diameter from image analysis of AFM images (error bars denote 95% confidence limits).



60% 70%

76% 82%

86% 89%

Figure 2. AFM clay surface images of samples at different water contents. Each of the six images represents an area 30 μm × 30 μm.

water content on particle separations in clay. The results show that there is a decreasing trend of pore-size with increasing water content. The inversely proportional ratio of initial water content and pore-size is attributed to increased clay swelling.

REFERENCES

Anderson, D.C., Crawley, W. and Zabcik, D. (1985) Conductivity of compacted clay soils to water and organic liquids. *Waste Management and Research*, **3**, 339–349.

Bickmore, B.R., Hochella, M.F. Jr., Bosbach, D. and Charlet, L. (1999) Methods for performing atomic force microscopy imaging of clay minerals in aqueous solutions. *Clays and Clay Minerals*, **47**, 573–581.

Borgesson, L., Karnland, O. and Johannesson, L.-E. (1996) Modelling the physical behavior of clay barriers close to water saturation. *Engineering Geology*, **41**, 127–144.

Garnaes, J., Lindgreen, H., Hansen, P.L., Gould, S.A.C and Hansma, P.K. (1992) Atomic force microscopy of ultrafine clay particles. *Ultramicroscopy*, **42–44**, 1428–1432.

Hueckel, M., Kaczmarek, M. and Caramuscio, P. (1997) Theoretical assessment of fabric and permeability changes in clays affected by organic contaminants. *The Canadian Geotechinical Journal*, **34**, 588–603.

Keren, R. and Singer, M.J. (1990) Effect of pH on permeability of clay-sand mixture containing hydroxy polymers. *Soil Science Society of America Journal*, **54**, 1310–1315.

Low, P.F. (1994) Clay/water interface and its role in the environment. *Progress in Colloid and Polymer Science, v.* **95**, Surfactants and Colloids in the Environment, 98–107.

Occelli, M.L., Gould, S.A.C. and Drake, B., (1994) Atomic scale imaging of pillared rectorite catalysts with the atomic force microscope. *Microporous Materials*, **2**, 205–215.

Odom, J.W. and Low, P.F. (1978) Relation between swelling, surface area and B dimension of Na-montmorillonites. *Clays and Clay Minerals*, **26**, 345–351.

Sposito, G., Hartman, H., Manne, S., Gould, A.C. and Hansma, P.K. (1990) Molecular-scale imaging of clay mineral surfaces with the atomic force microscope. *Clays and Clay Minerals*, **38**, 337–342.

Yamanaka, S., Malla, P.B. and Komarneni, S. (1990) Water adsorption properties of alumna pillared clay. *Journal of Colloid and Interface Science*, **134**, 51–58.

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