Molecular Interactions Impact Properties of Na-Montmorillonite Clay

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ABSTRACT

In this paper, we present the results of our study on effect of polarity of fluid on the permeability and consolidation properties of Na-montmorillonite clay. Compacted clay samples were placed in a newly designed and fabricated device called “porous rigid wall and flexible wall permeameter” that allows for accurate measurement of permeability of swelling clays and for evaluation of consolidation properties of the clay sample. The fluids used in our study ranged from non-polar fluids to highly polar fluids. The results from this study show enormous impact of fluid polarity on permeability and consolidation properties of Na-montmorillonite. Further, spectroscopic studies, X-ray diffraction and electron microscopy studies on undisturbed samples provide an insight into mechanisms affecting permeability and consolidation properties of swelling clays. Molecular modeling of Na-montmorillonite with water and other fluids provide a quantitative understanding of the molecular interactions influencing the behavior of swelling clays.

1. INTRODUCTION

Geosynthetic clay liners (GCL) are being extensively used as barrier systems for landfills. The critical component of the GCL is swelling clay, typically bentonite (a clay that is predominantly montmorillonite), sandwiched between geotextiles. These swelling clays (also called as expansive clays) when hydrated swell as a result of interaction with water. The swelling mechanism results in drastic reduction in permeability of the clay, thus forming an effective barrier against water. Barrier systems and in turn the swelling clays could be subject to interaction with a variety of fluids and the effectiveness of such systems will depend upon permeability and other engineering characteristics of these clays while interacting with the fluids. In this paper, we present the results of our study on effect of polarity of fluid on the permeability and consolidation properties of Na-montmorillonite clay.

2. MATERIALS

The expansive clay used in our study is Na-montmorillonite (Svy-2) obtained from the clay minerals repository at the University of Missouri, Columbia, MO. The cationic exchange capacity of the clay is about 76.4 mequiv/100g, and has the chemical formula NaSi_{16} (A_{16}FeMg) _{2}O_{20}(OH)_{4} (van Olphen and Fritpiat, 1979). The clay is finely ground and passed through No. 325 sieve (45 µ mesh), and is dried at 50 °C for 24 hours prior to each sample preparation. The fluids used in study consist of 90-100% purity Formamide, 99.9% purity acetone 99.7% purity toluene and 99.9% purity trichloroethylene and were obtained from Mallinckrodt Baker, Inc. NJ, 99.9% purity chloroform is obtained from EMD Chemicals Inc. NJ and 99.9% purity methanol is obtained from Alfa Aesar, MA. De-ionized water prepared in our laboratory is used.

3. EXPERIMENTAL INVESTIGATIONS

Evolution of Microstructure during Swelling with Water

A controlled uniaxial swelling cell (CUS) is designed to study the evolution of microstructure of swelling clays.
during swelling using scanning electron microscopy. Details about these studies can be found in (Katti and Shanmugasundaram, 2001) and (Katti and Katti, 2006). The results in figure 1 show that with increased swelling, the clay particle sizes decrease because of separation at the interlayer due to interlayer swelling.

**Fourier Transform Infrared Spectroscopy Studies**
Experimental investigation of interactions between the Na-montmorillonite clay and fluids with a wide range of dielectric constants is carried out to investigate the role of these interactions on swelling, swelling pressure, fluid flow and compressibility characteristics of the swelling clay. Organic fluids with varying dielectric constants, formamide (110), water (80), methanol (33), acetone (20), chloroform (4.8), TCE (3.4) and toluene (2.4). The values in the parenthesis refer to the dielectric constant of the fluid. Formamide and water are high polar fluids, methanol and acetone are medium polar fluids and chloroform, TCE and toluene are low polar or non polar fluids. Fourier transform infrared (FTIR) spectroscopy experiments and x-ray diffraction experiments on clay slurries with various fluids are conducted. FTIR spectroscopy is a nondestructive technique to study molecular interactions in a material. The technique involves subjecting the material to infrared radiation which results in vibration of the various bonds in the molecules of the material. The resulting infrared spectrum provides information on the nature of bonds and shift in bond positions are indicative of influence of new or additional interactions. Detailed information about this study is presented in our previous work (Amarasinghe et al., 2009) and in a paper by the authors at this conference. FTIR spectroscopy was also used to experimentally calculate the rate of flow of water molecules in the clay interlayer(Amarasinghe et al., 2008). FTIR study relating silica-water interactions to swelling and swelling pressure is reported earlier (Katti and Katti, 2006). The results from these studies show that fluids with high dielectric constants have very large interactions with clays and low dielectric constant fluids have low or no molecular interactions with clays as shown in figure 2.

**A New Permeameter for Swelling Clays**
A new permeability device named as ‘porous rigid wall flexible wall permeameter’ allows for conducting flexible wall permeability tests on swelling clays without the sample or clay microstructure getting distorted by lateral swelling. A photograph of the device is shown in figure 3. This device also allows for removing undisturbed samples after the test, measurement of swelling pressure and the evaluation of compression and consolidation properties.

**Permeability of Na-Montmorillonite with Various Fluids**
Dry Na-montmorillonite samples were compacted in the new permeameter to identical densities and dimensions. Each sample is then saturated with fluid with which the permeability is to be determined. Standard test procedure typical for flexible wall permeability testing of clays is followed. In figure 4, a plot of the coefficient of permeability versus dielectric constant obtained from this device is presented. Permeability of the clay is strongly influenced by dielectric constant of the fluid. Low dielectric constant
fluids exhibit almost a million times higher coefficient of permeability values as compared to water.

**Consolidation of Na-Montmorillonite Saturated with Various Fluids**

The Na-montmorillonite samples saturated in the permeameter with various fluids are allowed to consolidate under a range of confining stresses to evaluate compressibility and consolidation characteristics. A plot of void ratio versus effective stress for samples saturated with various fluids is presented in figure 5. For a given effective stress, clay intercalated with a fluid of low dielectric constant, shows higher compression and the behavior is more like that of cohesionless soils. Weak molecular interactions in the clay-low-dielectric constant fluid system, do not generate swelling forces that would attempt to maintain the soil structure under external stresses.

![Image](image1.png)

**Fig. 5:** A Plot of Void Ratio Versus Effective Stress for Na-Montmorillonite Sample with High (water), Medium(methanol) and Low (toluene) Polarity Fluids.

**Microstructure of Na-Montmorillonite Saturated with Various Fluids**

Undisturbed samples of Na-montmorillonite clay saturated with various fluids were obtained from the new permeameter and the microstructure was observed using a scanning electron microscope. The images are shown in Figure 6. The microstructure of clay with low dielectric constant fluid is similar to that of the dry sample showing large particle sizes and large void spaces.

![Image](image2.png)

**Fig. 6:** SEM Images Showing Microstructure of Na-Montmorillonite Samples Saturated with High and Low Polarity Fluids.

In the case of clay with high dielectric constant fluid, the microstructure is drastically different with significantly smaller particle sizes resulting from particle breakdown and void spaces filled as a result of strong molecular interactions in the interlayer that profound effect on microstructure and permeability of the clay.

Most swelling and exfoliation occurs with high dielectric constant fluids and little or no swelling occurs with low dielectric constant fluids. Further, swelling pressure under no-volume-change condition, is observed to increase with increasing dielectric constant of the fluid.

4. **MODELING**

**Discrete Element Modeling**

For the first time a new discrete element methodology was developed to incorporate particle breakdown to evaluate the effect of particle subdivision and its influence on swelling and swelling pressure (Katti et al., 2009). It was observed that with increased particle subdivision the magnitude of swelling as well as swelling pressure increased. Observation of evolution of microstructure (figure 7) as a result of subdivision indicates that the exfoliated clay sheets fill in the large initial voids as well as provide larger surface for interactions thus reducing the permeability.

![Image](image3.png)

**Fig. 7:** DEM Snapshots Show Exfoliated Clay Sheets Filling the Large Initial Void Spaces. (Katti et al., 2009).

**Molecular Modeling**

First steered molecular dynamics studies were conducted by our group to quantitatively evaluate the mechanical properties of the clay and interlayer at the nanoscale (figure 8) (Katti et al., 2005a; Katti et al., 2009; Katti et al., 2005b, 2007; Schmidt et al., 2005). CHARMM force field parameters necessary for conducting steered molecular dynamics simulations are evaluated. An innovative technique is developed to transform parameters from one force field to another force field. Mechanical properties of clay sheets and the interlayer with increasing hydration are found.

In order to understand the mechanism of interlayer swelling in Na-montmorillonite and to evaluate energetic triggers that could lead to breakdown of particle at the interlayer, molecular dynamics simulations are conducted. Water layers are introduced in the interlayer, one layer at a time and the d-spacing, and interaction energies between
the clay sheets, Na-ions and clay sheets and water and clay sheets are evaluated. The evolution of interaction energies during swelling provides an insight into the mechanism of interlayer swelling in Na-montmorillonite.

Fig. 8: Molecular Model of Na-Montmorillonite Interlayer with two Monolayers of Water Molecules. Forces are Applied to Individual Oxygen Atoms on the Clay surface. (Schmidt et al., 2005)

Summary and CONCLUSIONS

Na-montmorillonite clay obtained from clay repository of America is used in the study. Compacted clay samples are placed in a newly designed and fabricated device called “porous rigid wall and flexible wall permeameter” that allows for accurate measurement of permeability of swelling clays and for evaluation of consolidation properties of the clay sample. The fluids used in our study ranged from non-polar fluids to highly polar fluids. The results from this study show enormous impact of fluid polarity on permeability and consolidation properties of Na-montmorillonite. Further, spectroscopic studies, x-ray diffraction and electron microscopy studies on undisturbed samples provide an insight into mechanisms affecting permeability and consolidation properties of swelling clays. Molecular modeling of Na-montmorillonite with water and other fluids provide a quantitative understanding of the molecular interactions influencing the behavior of swelling clays.

ACKNOWLEDGEMENTS

Support from National Science Foundation Grant #0556020, 0114622-Dr. Richard Fragaszy, program director and 0320657(MRI) and 0315513(IMR). The work of our graduate students Mr. Vijaykumar Shanmugasundaram, Mr. Steven Schmidt, Dr. Mohamed Matar, Dr. Priyanthi Amarasinghe and Mr. Shashindra Pradhan is acknowledged.

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