Effect of Exchangeable Cations on Bentonite Swelling Characteristics of Geosynthetic Clay Liners

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ABSTRACT

Geosynthetic clay liners (GCLs) are thin hydraulic barriers which contain the bentonite sandwiched between geotextiles or geomembrane. Bentonite swelling is a very common phenomenon observed in GCLs. It is one of the major causes for permeability reduction in hydraulic barriers. The aim of this study is to characterize the swelling behavior of bentonite in GCLs by exchangeable cations. X-ray diffraction test and scanning electron microscopy were used to quantify the swelling characteristics of this bentonite under contact with salt solutions, as in the hydraulic barriers. The results from X-ray diffraction test showed that the presence of clay minerals was swelling montmorillonite. The swell volume of bentonite decreases with increasing valence of cations. In the case of the same valence the free swell volume of bentonite increased with decreasing concentration of permeant liquids. From another test, the scanning electron microscopy, it can be seen that the bentonite appears as corn flake like crystals for air-dried bentonite. However, specimen permeated with salt solutions, the clay has become more porous and fluffy and porous size seemed to be diminished.

1. Introduction

Geosynthetic clay liners (GCLs) are thin hydraulic barriers containing approximately 1 lb/ft² (5 kg/m²) of bentonite, sandwiched between two geotextiles or attached with an adhesive to a geomembrane. Due to surrounding environmental conditions and applied superimposed loads, conventional compacted clay liners (CCLs) develop internal cracks and shrinkage that lead to significant increase in seepage and leakage of contaminant liquid into the soil and ground water.
Bentonite used in GCLs is commonly a sodium bentonite, where sodium ions are located in the interstitial water, between clay platelets, in an adsorptive layer that results in the bentonite swelling characteristics. This swelling allows the bentonite to seal around penetrations, giving the GCL self-sealing characteristics (Bouazza, 2002).

The primary mineral in bentonites is montmorillonite (Moore and Reynolds, 1997) that is the most commonly found mineral in the dioctahedral smectite subgroup, where substitution of one Mg$^{2+}$ occurs in every sixth Al$^{3+}$ in octahedral sheets and no substitution takes place in tetrahedral sheets (Grim, 1968, Faure, 1998). Because the adsorbed layer plays in controlling the hydraulic conductivity of clay minerals and, in particular, bentonite is reported by Mesri and Olson (1971). They permeated sedimented specimens of kaolinite, illite, and montmorillonite with nonpolar liquids, salt solutions (NaCl and CaCl$_2$), and deionized water. At a given void ratio, the kaolinite, illite, and montmorillonite had identical hydraulic conductivity when permeated with nonpolar liquids. In contrast, the three minerals had very different hydraulic conductivities when permeated with the salt solutions and deionized water.

Because replacement of sodium in the exchange complex with other ions should affect the thickness of the adsorbed layer and, thus, swelling and hydraulic conductivity of the bentonite in GCLs. X-ray diffraction is a routine method in mineralogy, particularly for fine-grained material study. It is one of the primary techniques used by mineralogists and solid state chemists to examine the physicochemical composition of unknown solids. Then, this study aims to study the effect of exchangeable cations on bentonite swelling characteristics of geosynthetic clay liners by X-ray diffraction test in term of distance of clay particle (interlayer) and scanning electron microscopy. The influence of valence and concentration of solution on bentonite swelling characteristics by X-ray diffraction test and scanning electron microscopy was investigated to characterization of crystalline materials and the determination of atomic packing in the crystalline state and interatomic distances and angles.

2. Materials and methods

2.1 Materials

In this study bentonite was prepared from the high strength type of GCLs, namely: Enviromat. The GCLs, Enviromat, contained sodium bentonite placed between high strength non-woven geotextile and high-density polyethylene geomembrane. The geotextile were bonded together by needle punching. The initial air-dried thickness of the bentonite layer was approximately 3.5 mm and the initial water content of the bentonite was 12%. The total thickness
of the GCLs was about 4.0 mm. For the physical properties of the bentonite in the GCLs, liquid limit was 540 %, plastic limit was 62% and plasticity index was 472%, which were very much higher than those of general clays because its primary mineral was montmorillonite.

2.2 X-Ray Diffraction Test

The X-ray diffraction data were performed using a Bruker AXS Model D8 Discover. X-rays are generated within a sealed tube under vacuum. A current is applied that heats a filament within the tube; the higher the current the greater the number of electrons emitted from the filament. This generation of electrons is analogous to the production of electrons in a television picture tube. A high voltage, typically 15-60 kilovolts, is applied within the tube. This high voltage accelerates the electrons, which then hit a target, commonly made of copper. When these electrons hit the target, X-rays are produced. The wavelength of these X-rays is characteristic of that target. These X-rays are collimated and directed onto the sample, which is a fine powder of particle size of less than 10 microns.

2.3 Scanning Electron Microscopy

In this study, microstructure of the received bentonite was conducted by Scanning Electron Microscopy (SEM). Energy dispersive X-ray microanalysis uses detection equipment to measure the energy values of the characteristic X-rays generated within the electron microscope. An X-ray micro-analyzer system converts X-ray energy into an electronic count by using semiconductor materials that can detect the X-rays. The accumulation of these energy counts creates a spectrum, which is then plotted against relative counts of the detected X-rays and evaluated for qualitative and quantitative determination of the elements present in the specimen.

3. Results and Discussion

3.1 X-ray Diffraction Test

X-ray powder diffraction (XRD) patterns of the clay fraction were obtained using a Bruker AXS Model D8 Discover. The dispersed clay fraction separated by sedimentation under gravity was centrifuged on a glass slide in a high speed centrifuge and the XRD patterns were recorded as shown in Figure 1 and 2. Figure 1 shows the XRD patterns of air-dried bentonite specimen and bentonite permeated with DW, 0.1M NaCl and 0.1M CaCl₂. When the XRD patterns of bentonite permeated with DW (Figure 1(b)) was examined, firstly a sharp peak whose d(001) distance (approximately 7.107(2θ)) was 12.43 Å was seen. The fact that the 10.20 Å d(001) distance (7.088(2θ)) for air-dried went up to 12.43 Å proves that the DW molecule went between the bentonite layer and was bound to them. It can be concluded that when DW molecule
Figure 1: Effect of cation on microstructure swelling characteristics (a) air-dried, (b) DW, (c) 0.1 M NaCl and (d) 0.1 M CaCl₂ specimen.
Figure 2: Effect of concentration on microstructure swelling characteristics (a) DW, (b) 0.025M, (c) 0.1M and (d) 1.0M CaCl₂ specimen.
was bound between the bentonite layers, it created an inner layer space of 2.23 Å. On the other hand, in Figure 1(c) and (d) it can be seen that d(001) distance for bentonite permeated with 0.1M NaCl went up to 12.27 Å (7.200(2 \( \theta \))) and 11.26 Å (5.787(2 \( \theta \))) for bentonite permeated with 0.1M CaCl2. Then Na\(^+\) and Ca\(^{2+}\) cations created and inner double layer of bentonite 2.07 Å and 1.06 Å, respectively. Since the diffuse double layer of divalent cations (Ca\(^{2+}\)) in thinnest compare with monovalent cation (Na\(^+\)). In addition, in the XRD patterns of air-dried bentonite

**Figure 3:** Valence dependence of the \( d \)-value for X-ray diffraction test

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**Figure 4:** Concentration dependence of the \( d \)-value for X-ray diffraction test
specimen in Figure 1(a), the peak with 4.48 Å distance (19.770(2)), 3.13 Å distance (28.446(2)), 3.34 Å distance (26.622(2)) and the one with a 1.50 Å distance (61.940(2)) belong to the major montmorillonite component. Also, a quartz non-clay component with 26.62(2) was seen in the same XRD pattern.

Figure 2 shows the XRD pattern of the bentonite permeated with DW, CaCl₂ solutions at 0.025M, 0.1M and 1.0M concentrations. There is a considerable increase in the d(001) spacing of the montmorillonite for values of CaCl₂ solutions concentration under 1.0 M and the swelling increased dramatically from 11.21 Å (5.804(20)) for 1.0 M to 11.26 Å (5.787(20)) for 0.1M CaCl₂ and 11.82 Å (5.958(20)) for 0.025 M CaCl₂, respectively. It shows that double layer of montmorillonite decreased with the increasing of concentration of solution. Since when the concentration of cations in the solution increases, water moves out of the interlayer and causes the reduction in swell. In addition, valence and concentration dependence of the d-value for X-ray diffraction test are plotted in Figure 3 and Figure 4. In these figure, the d-value of bentonite decreased with increasing valence and concentration of solution.

3.2 Scanning Electron Microscopy

In this study, scanning electron microscopy (SEM) was used to proof the change in morphological features of air-dried bentonite in GCLs and after permeated with DW, NaCl and CaCl₂ solutions (Figure 5). Surface morphological analyses were made in a SEM (JSM-5800LV), working at 15 kV of electron accelerating voltage and with a beam current of about 1 nA at the specimen level. Sample were gold-coated with a layer about 10 nm thick by using a vacuum of 0.15 Pa (10-5 Torr) metal-coating process.

The surface morphology of air-dried bentonite in Figure 5(a) is different from that after permeated with DW, NaCl and CaCl₂ solutions in Figure 5(b)-(d). The air-dried bentonite appears as corn flake like crystals with fluffy appearance revealing its extremely fine platy structure. This is consistent with the reported SEM micrographs for bentonite (Nguetnkam et al., 2005 and Reinholdt et al., 2001). However, after permeated with DW as shown in Figure 5(b), clay has become more porous and fluffy. This porous and fluffy appearance probably occurs due to the change in the surface charge of the particle as a result of permeated process and the reduction in certain amorphous phase originally associated with the air-dried bentonite.

SEM picture for specimen permeated with DW, 0.1M NaCl, 0.025M CaCl₂, 0.1M CaCl₂ and 1.0M CaCl₂ were represented in Figure 6(a)-(d). It can be seen that the porous size seemed to be
diminished from bentonite specimen permeated with DW specimen in Figure 6(a) due to the large specific surface of montmorillonite adsorb a large number of hydrated cations during hydration that can comprise a significant fraction of pore space, and are essentially immobile. However, the porous and fluffy decreased with increase in concentration of CaCl2 solution as shown in Figure 6(b)-(d). Similar with free swell results of montmorillonite, at similar concentration, swell volume was larger with monovalent cation solutions than with divalent and trivalent cation solution (Anekpong and Weeraya, 2010).

**Figure 5**: SME micrographs of (a) air-dried specimen (b) distilled water (c) 0.1M NaCl solution (d) 0.1M CaCl2 solution (1,500x).
Figure 6: SME micrographs of (a) distilled water (b) 0.025 M CaCl₂ solution (c) 0.1M CaCl₂ solution and (d) 1.0M CaCl₂ solution (1,500x).

4. Conclusion

The results from X-ray diffraction test showed that the presence of clay minerals was swelling montmorillonite. The swell volume of bentonite decreases with increasing valence of cations. In the case of the same valence, the free swell volume of bentonite increased with decreasing concentration of permeant liquids. Since the diffuse double layer of trivalent cations in thinnest compare with monovalent and divalent cation. From the scanning electron microscopy, it can be seen that the bentonite appears as corn flake like crystals for air-dried bentonite. However, specimen permeated with salt solutions, the clay has become more porous and fluffy.
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6. References


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