

**DOKUZ EYLÜL UNIVERSITY**  
**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**DETERMINING THE HYDRAULIC  
CONDUCTIVITY AND SWELLING BEHAVIORS  
OF ATTAPULGITE ENHANCED  
GEOSYNTHETIC CLAY LINERS WITH SALT  
SOLUTIONS**

by  
**Meriç ÖZTÜRK ŞAHİNCİ**

**May, 2018**  
**İZMİR**

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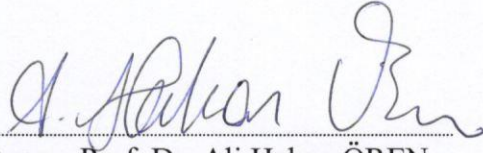
**A Thesis Submitted to the  
Graduate School of Natural and Applied Sciences of Dokuz Eylül University  
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Science in Civil Engineering, Geotechnics Program**

**by  
Meriç ÖZTÜRK ŞAHİNCİ**

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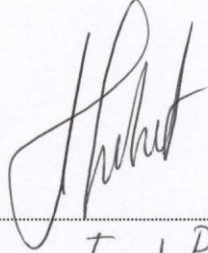
## M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**DETERMINING THE HYDRAULIC CONDUCTIVITY AND SWELLING BEHAVIORS OF ATTAPULGITE ENHANCED GEOSYNTHETIC CLAY LINERS WITH SALT SOLUTIONS**” completed by **MERİÇ ÖZTÜRK ŞAHİNCİ** under supervision of **ASSOC. PROF. DR. A. HAKAN ÖREN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.



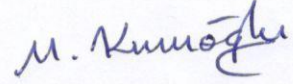
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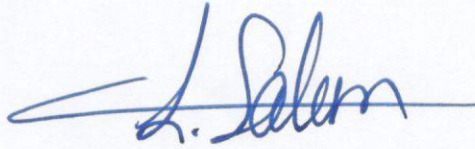
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Meriç ÖZTÜRK ŞAHİNCİ

# **DETERMINING THE HYDRAULIC CONDUCTIVITY AND SWELLING BEHAVIORS OF ATTAPULGITE ENHANCED GEOSYNTHETIC CLAY LINERS WITH SALT SOLUTIONS**

## **ABSTRACT**

This study covers the basic characteristics, swelling indices and hydraulic conductivities of geosynthetic clay liners (GCLs) which were produced with attapulgite-polymer bentonite mixtures (0, 30, 50, and 70 percent of attapulgite) under a research project. It is observed that as the amount of attapulgite in the GCL increased, the liquid limit, plasticity index, fine-clay content, and cation exchange capacity of GCLs decreased. Swell indices in deionized water (DIW) decreased from 21 mL/2g (Polymer Bentonite-PB) to 6 mL/2g (attapulgite-A), whereas it slightly reduced in salt solutions (10 mL/2g to 6 mL/2g).

In the hydraulic conductivity tests, DIW, 100 mM KCl, 50, 100 and 500 mM CaCl<sub>2</sub>, 50 mM MgCl<sub>2</sub> and 50 mM CuCl<sub>2</sub> solutions were used as the permeant. The tests with DIW, the hydraulic conductivities of non-prehydrated GCLs up to 50 percent attapulgite content slightly increased from  $5.8 \times 10^{-11}$  m/s (PB GCL) to  $1.2 \times 10^{-10}$  m/s (50%PB+50%A) and those of prehydrated GCLs decreased from  $3.2 \times 10^{-11}$  m/s to  $2.0 \times 10^{-11}$  m/s. However, when attapulgite content in GCL increased to 70 percent, then hydraulic conductivity remarkably increased to  $8.7 \times 10^{-7}$  and  $1.3 \times 10^{-8}$  m/s for non-prehydrated and prehydrated GCLs, respectively (i.e. 30%PB+70%A). Accordingly, as the cell pressure increased gradually from 35 to 280 kPa, the hydraulic conductivities gradually decreased. Regardless of solution type and concentration, the hydraulic conductivities obtained with salt solutions were found to be 3-4 orders of magnitude greater than those obtained with DIW. The only exception is the tests conducted with 50 mM CuCl<sub>2</sub> solutions. With this solution, the hydraulic conductivities were low ( $10^{-11}$  -  $10^{-12}$  m/s). All permeability and swell indices were evaluated together and found to be partially compatible with the relationship previously given in the literature. Although the final water content of GCLs increased with the amount of attapulgite, no relationship was established with

hydraulic conductivity. Similarly, there is no correlation between the final water contents and the hydraulic conductivities.

**Keywords:** Attapulgite, physicochemical properties, geosynthetic clay liner, hydraulic conductivity, prehydration, polymer bentonite, swell index, salt solutions



**ATAPULJİTLE GELİŞTİRİLMİŞ GEOSENTETİK KİL ÖRTÜLERİN  
HİDROLİK İLETKENLİK VE ŞİŞME DAVRANIŞLARININ TUZ  
ÇÖZELTİLERİ İLE BELİRLENMESİ  
ÖZ**

Bu çalışma, bir araştırma projesi kapsamında üretilen ve ağırlıkça belirli oranlarda atapuljit-polimer bentonit karışımları (yüzde 0, 30, 50 ve 70 atapuljit) içeren geosentetik kil örtülerin (GKÖ) temel karakteristik özelliklerini, şişme indislerini ve hidrolik iletkenlik deney sonuçlarını kapsamaktadır. GKÖ içeriğindeki atapuljit miktarı arttırıldıkça likit limit, plastisite indisi, ince dane-kil yüzdesi, katyon değişim kapasitesinin azaldığı gözlemlenmiştir. GKÖ içerisindeki atapuljit miktarına bağlı olarak şişme indisleri DIS'da 21 mL/2g'dan (Polimer Bentonit-PB) 6 mL/2g'a (atapuljit) azalırken tuz çözeltilerinde şişme indisleri eser miktarda azalmıştır (10 mL/2g'dan 6 mL/2g'a).

Hidrolik iletkenlik deneylerinde süzdürme sıvısı olarak DIS, 100 mM KCl, 50, 100 ve 500 mM CaCl<sub>2</sub>, 50 mM MgCl<sub>2</sub> ve 50 mM CuCl<sub>2</sub> çözeltileri kullanılmıştır. DIS ile yapılan deneylerde, yüzde 50 atapuljit içeriğine kadar önıslatmasız GKÖ'lerin hidrolik iletkenlikleri  $5.8 \times 10^{-11}$  m/s'den (PB-GKÖ)  $1.2 \times 10^{-10}$  m/s'ye (%50PB+%50A), ön ıslatmalı GKÖ'lerde  $2.0 \times 10^{-11}$  m/s'den  $3.2 \times 10^{-11}$  m/s'ye kadar azalmıştır. Fakat GKÖ içerisinde atapuljit yüzde 70'e çıktığında, hidrolik iletkenlikler belirgin biçimde artarak ön ıslatmasız ve ön ıslatmalı GKÖ'ler için sırasıyla  $8.7 \times 10^{-7}$  and  $1.3 \times 10^{-8}$  m/s'ye düşmüştür. Buna göre hücre basıncı 35 kPa'dan 280 kPa'a kadar kademeli arttırıldıkça hidrolik iletkenlikler de kademeli olarak azalmıştır. Tuz çözeltileri ile yapılan deneylerden, çözelti tipinden ve konsantrasyonundan bağımsız olarak, elde edilen hidrolik iletkenlikler suyla belirlenenlerden 3-4 mertebe daha yüksek bulunmuştur. Buna tek istisna 50 mM CuCl<sub>2</sub> çözeltileriyle yapılan deneylerdir. Bu çözelti ile hidrolik iletkenlikler düşük seyretmiştir ( $10^{-11}$  –  $10^{-12}$  m/s). Tüm permabilite ve şişme indisleri birlikte değerlendirilmiş ve daha önce literatürde verilmiş olan ilişkiyle kısmen uyumlu olduğu görülmüştür. GKÖ su içeriklerinin atapuljit miktarıyla arttığı görülmüş olsa

da hidrolik iletkenlikle herhangi bir iliřki kurulamamıřtır. Benzer řekilde final su ierikleriyle hidrolik iletkenlikler arasında da bir iliřki belirlenememiřtir.

**Anahtar Kelimeler:** Atapuljit, fizikokimyasal zellikler, geosentetik kil rt, hidrolik iletkenlik, n ıslatma, polimer bentonit, serbest řiřme, tuz zeltileri



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# CHAPTER ONE

## INTRODUCTION

### 1.1 Background

Turkey is one of the developing countries in world. Nevertheless, storing waste in regular landfills in a way not to harm the environment had been neglected until the end of the 1990s in Turkey. Until that time, the wastes had been randomly stored on clayey soils. However, by the year 2000, a certain awareness of waste storage and management issues began to emerge.

Because of their low hydraulic conductivity ( $<10^{-9}$  m/s), compacted clay liners (CCLs) have been used as barrier material in landfills for a long time. These barriers prevent flowing of leachate to the groundwater. However, considering the size of the landfill area, it is quite difficult to perform homogeneous compaction at every point (accessing the same dry unit weight and water content). Furthermore, it is known that CCLs are adversely affected by the freeze-thaw and wet-dry cycles and cause severe cracks on the barrier, especially when used as covers (Wu & Daniel, 1992; Benson & Othman, 1993; Benson, Chamberlain, Erickson & Wang, 1995; Benson, Abichou, Olson & Bosscher, 1995; Yesiller, Miller, Inci & Yaldo, 2000; Albrecht & Benson, 2001). These environmental factors undesirably increase the hydraulic conductivity of the CCLs.

With the development of technology in recent years, geosynthetic clay liners (GCLs) have begun to be used as an impermeable barrier in landfills or in mine applications. Geosynthetic clay liners are fabricated synthetic materials produced by laying thin bentonite layer ( $\sim 5\text{-}10$  mm) between woven and non-woven geotextiles (Jo, Katsumi, Benson & Edil, 2001; Ruhl & Daniel, 1997). The general appearance of a geosynthetic clay liner is shown in Figure 1.1.

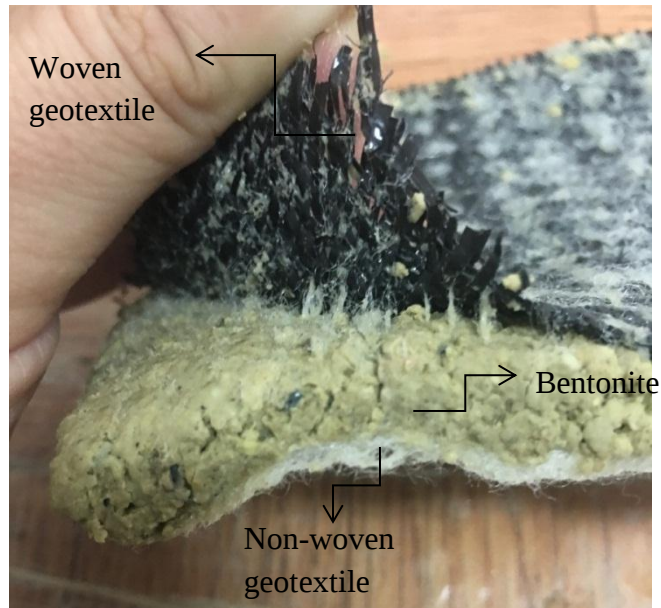


Figure 1.1 General view of the GCL (Personal archive, 2015)

The differences between the GCLs depend on the physical, chemical and mineralogical properties of the bentonite, such as montmorillonite content, particle size, type and amount of exchangeable cations available on bentonite. Apart from this, GCLs may vary depending on geotextile bonding methods, hydration conditions (i.e. prehydrated or non-prehydrated) and textiles used (woven and non-woven) (Bouazza, 2002; Shackelford, Benson, Katsumi, Edil & Lin, 2000).

GCLs have considerably lower hydraulic conductivity than CCLs ( $<10^{-11}$  m/s). In addition, the cost of GCLs is relatively low and their applicability in the field is much faster and easier (Benson, Ören & Gates, 2010; Guyonnet, Gaucher, Gaboriau, Pons, Clinard, Norotte & Didier, 2005; Jo et al., 2001; Katsumi, Ishimori, Onikata & Fukagawa, 2008; Kolstad, Benson, & Edil, 2004).

## 1.2 Brief Information About Attapulgite

Atapulgite is a non-expanding (non-swollen), negatively charged and needle shaped (fibrous) mineral that composed of long double chains of silica tetrahedra (Broderick and Daniel, 1990). Since this mineral is not vastly found on earth when

compared to kaolin or smectite, the studies conducted on attapulgite as a barrier material is scarce as well.

Broderick and Daniel (1990) reported two hydraulic conductivity data for compacted attapulgite, which were permeated with water, with an average of  $8.5 \times 10^{-10}$  m/s. The other study conducted on attapulgite has been carried out by Silva and Almanza (2009). Among other clay minerals, Silva and Almanza (2009) reported that the hydraulic conductivity of compacted attapulgite to water is  $2.0 \times 10^{-10}$  m/s.

Stern and Shackelford (1998) used attapulgite as a clay additive in sand at 10, 15, and 20% and compared the hydraulic conductivity with that of sand-bentonite mixtures that were prepared at the same percentages. Depending on the attapulgite content, the hydraulic conductivity of sand-attapulgite mixtures to water were within the range of  $2.0 \times 10^{-6}$  -  $7.0 \times 10^{-10}$  m/s. This shows that increase in the attapulgite content in sand matrix decreases the hydraulic conductivity. However, when compared to sand-bentonite mixtures, the hydraulic conductivities were still at least two orders of magnitude higher for sand-attapulgite mixtures.

Al Rawas et al. (2006) investigated some engineering properties of sand-attapulgite mixtures. They noted that the compacted attapulgite has a hydraulic conductivity of  $4.0 \times 10^{-9}$  m/s when permeated with water. When attapulgite was used as an additive in sand at 5, 10, 20, and 30%, the hydraulic conductivity to water reduced from  $1.7 \times 10^{-5}$  m/s to  $6.5 \times 10^{-9}$  m/s. The greatest and the lowest hydraulic conductivities were obtained at 5 and 30% attapulgite contents. This conclusion agrees with the findings of Stern and Shackelford (1998).

### **1.3 Scope of This Study**

The main purpose of this study is to determine swell properties and hydraulic conductivities of GCLs to deionized water and salt solutions. The bentonite portion of GCLs has been manufactured with polymer bentonite (PB) and mixture of PB and attapulgite (A) which were mixed with different amounts by weight. The number of GCL studies carried out in all over the world over the last twenty years has increased

rapidly, though; the number of studies carried out in Turkey is quite limited. This study, as far as is known, is the first study of which investigates the swell and hydraulic conductivity behaviors of GCLs, including mixture of attapulgite and polymer bentonite.

Initially, the physico-chemical properties of all GCLs were determined. Then, the changes in the consistency limits, specific gravities, fine-clay contents, exchangeable cation types and cation exchange capacities were inspected as a function of attapulgite content. Subsequently, swell indices of GCLs were determined under different pore fluids.

The influences of prehydration conditions and effective stress on the hydraulic conductivity of GCLs were examined with deionized water (DIW). Then hydraulic conductivity tests were carried out with basically 50 mM salt solutions of divalent cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cu}^{2+}$ . The influence of concentration on the hydraulic conductivity was measured as well. To do this, the concentration level increased to 100 and 500 mM just for  $\text{CaCl}_2$  solution.

## **CHAPTER TWO**

### **MATERIALS AND METHODS**

#### **2.1 Materials**

##### ***2.1.1 Geosynthetic Clay Liner and Attapulgite***

Within the scope of this study, four different geosynthetic clay liners (GCLs), manufactured by Geomas Co., have been used. These GCLs consist of polymer bentonite (PB) and the mixture of polymer bentonite and attapulgite (70%PB+30% Attapulgite (A), 50%PB+50%A and 30%PB+70%A). GCLs in roughly 4m<sup>2</sup> rolls have been delivered to Soil Mechanics Laboratory at Dokuz Eylül University (DEU). The rolls were unpacked in the laboratory and area distance of 0.4 m from the sides was drawn with a soft-tipped board marker on the GCL. As some materials might have been lost (or poured) from the edges of GCL during the delivery, sampling outside the drawn area has not been preferred. For this reason, sampling has been carried out in the area shown in Figure 2.1.

The initial weights of the GCLs cut in each roll were weighed on a scale with a sensitivity of 0.01 and their heights were measured with the help of a caliper from 4 different points. The weighed samples were dried for 24 hours at a temperature of 105 °C in an oven to determine the initial water content. The amount of bentonite (PB) and bentonite-attapulgite (PB-A) in the unit area was determined according to ASTM D5993. To calculate the mass per unit area of bentonite, the weights of the geotextile components of the GCL were subtracted from the GCL weight and the mass of the remaining material was divided into the GCL area. The initial thicknesses, weights, water contents and bentonite mass per unit area of these GCLs are summarized in Table 2.1.

According to the information obtained from the company, the attapulgite used in GCLs had been imported from Greece. However, production of a GCL containing 100% attapulgite had not been preferred by the company. Instead, the attapulgite

used in GCLs was sent to DEU Soil Mechanics Laboratory in a plastic bag. This attapulgite sample was used in the determination of specific gravity, sieve analysis and consistency limits tests. Moreover, its swell index was determined. However, no hydraulic conductivity tests were performed on attapulgite.

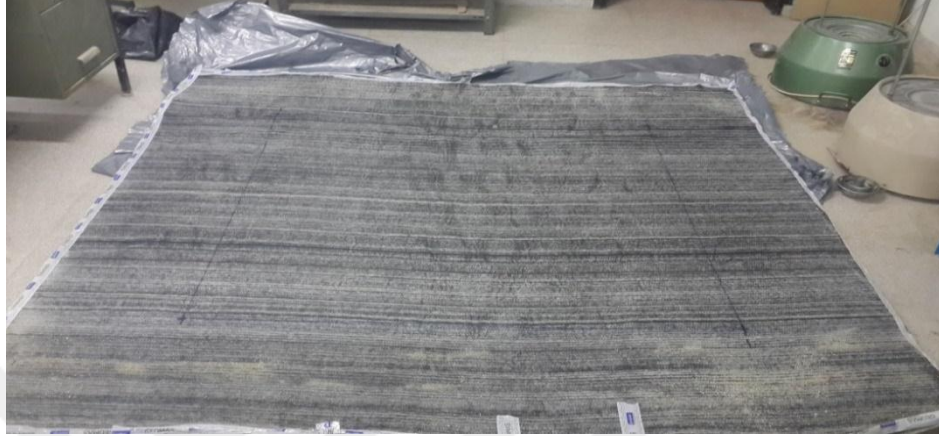


Figure 2.1 An overview of GCL roll (Personal archive, 2015)

Table 2.1 Some physical properties of bentonite (PB) and bentonite-attapulgite mixtures (PB-A)

| <b>GCL Type</b>   | <b>Mass Per Unit Area<br/>(kg/m<sup>2</sup>)</b> | <b>Initial Thickness<br/>(cm)</b> | <b>Initial Water<br/>Content<br/>(%)</b> |
|-------------------|--------------------------------------------------|-----------------------------------|------------------------------------------|
| <b>PB</b>         | 5.9                                              | 0.69                              | 9.4                                      |
| <b>70%PB+30%A</b> | 6.3                                              | 0.76                              | 9.6                                      |
| <b>50%PB+50%A</b> | 6.0                                              | 0.74                              | 9.5                                      |
| <b>30%PB+70%A</b> | 4.9                                              | 0.82                              | 9.5                                      |

### **2.1.2 Permeants**

In hydraulic conductivity experiments, deionized water (DIW) and salt solutions in different concentrations were used as the permeant. DIW was obtained from Milli-Q Gradient Water Purification System in Environmental Engineering Laboratory at DEU. The pure water was taken from the Environmental Engineering Laboratory

several times a week in 10lt canisters and it was kept at room temperature in Soil Mechanics Laboratory.

### **2.1.3 Chemicals**

In the experiments, salt solutions of different molarities have been used. The salts were Merck branded products, and the solutions were prepared with DIW. These chemical formulas of the solutions were: 50 mM  $\text{CaCl}_2$  ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ), 50 mM  $\text{MgCl}_2$  ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), 50 mM  $\text{CuCl}_2$  ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), 100 mM KCl, 100 mM and 500 mM  $\text{CaCl}_2$ .

To determine soluble/bound cations and cation exchange capacity of PB and PB-A GCLs; 1 M (potassium chloride) KCl, 1 M ammonium acetate ( $\text{NH}_4\text{OAc}$ ), isopropanol [ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ ] and nitric acid ( $\text{HNO}_3$ ) were used. In the cation exchange capacity, 1 dose of  $\text{NH}_4\text{-1K}$  was added to the reaction cell. In addition, all materials and test equipment were cleaned with a 10% nitric acid solution after the experiments.

## **2.2 Methods**

### **2.2.1 Index Properties**

To determine the natural water content, geotextile components of GCLs were peeled off and bentonite (PB) or bentonite/attapulgite (PB-A) portion was poured in a can. Then, PB and PB-A were dried at a temperature of 105 °C. The sieve and hydrometer analyses were carried out in accordance with ASTM D421 and ASTM D422, respectively. The clay contents in the materials were determined from particle size distribution curves.

The PB and PB-A were prepared in different water contents to determine consistency limits. These samples were then kept in sealed plastic bags for 24 hours in order to allow the water to penetrate homogeneously into the material pores. To

determine liquid limits, the fall cone test apparatus was used first (BS 1377-2:90, 1990). However, since the use of the Casagrande method is recommended for high plastic clays (Sridharan and Prakash, 2000), the liquid limit of PB and PB-A were also determined by the Casagrande test apparatus (ASTM D4318).

Since bentonite is a swelling clay and high affinity for water, specific gravity experiments were carried out on PB and PB-A with 30 g. The air entrapped in the bentonite was taken with the aid of a vacuum pump. This action was carried out for two full days (ASTM D854).

### **2.2.2 Swell Index**

The swell index tests of PB and PB-A were determined according to ASTM D5890. Before starting the experiment, the materials were dried in an oven at a temperature of 105 °C. During the preliminary experiments, it was seen that the container in which the product was put into had an adverse or negative effect on the swell index of PB (if metal corrosion is present in the metal container, bentonite may interact with the corrosive part and the swell index may be lower). During the drying process, porcelain vessels were preferred instead of metal ones. These specimens were then powdered and sieved through No.200 (75 µm) and 2 grams of samples were reserved from each for the experiment. Graduated cylinders with 100 ml volume were filled up to 90 ml with DIW or salt solutions and 0.1 g of the sample was poured into the cylinder for 30 seconds in free form. When each 0.1 g sample is poured, 10 minutes were allowed to the material to settle. This process was continued until the end of 2 g of the sample. Then, the cylinder was filled up to 100ml level and the mouths of the cylinders were closed with parafilm pieces and the samples were left to swell for a day. The swelling volumes in each cylinder were recorded in terms of mL/2g by observing the sharp interface between blurred water and the swollen bentonite as shown in Figure 2.2.

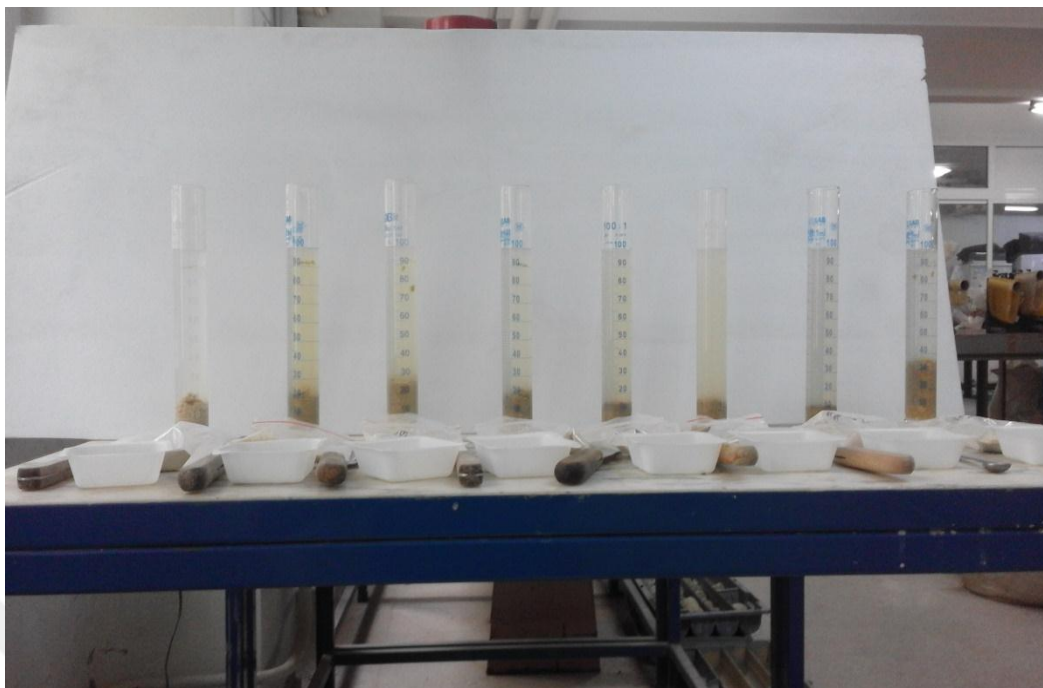


Figure 2.2 A picture from swell index test (Personal archive, 2016)

### ***2.2.3 Soluble Cations, Exchangeable Cations and Cation Exchange Capacity***

Soluble cations, bound cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) and cation exchange capacities (CECs) of PB and PB-A were determined according to ASTM D7503.

#### ***2.2.3.1 Soluble Cations***

In order to determine the soluble cations, the dried samples were sieved from No. 10 sieve and weighed to give a dry sample weight of 2 g. The weighted sample was placed in a plastic container and 100 ml of DIW was added. The plastic container was tightly closed and shaken on an end-over-end shaker at 30 rounds per minute (rpm) for 1 hour. The suspension was then filtered by placing an ashless filter paper with a pore size of  $2.5\ \mu\text{m}$  on a Buchner funnel (Figure 2.3). A low vacuum was applied during the filtering process ( $<10\ \text{kPa}$ ).

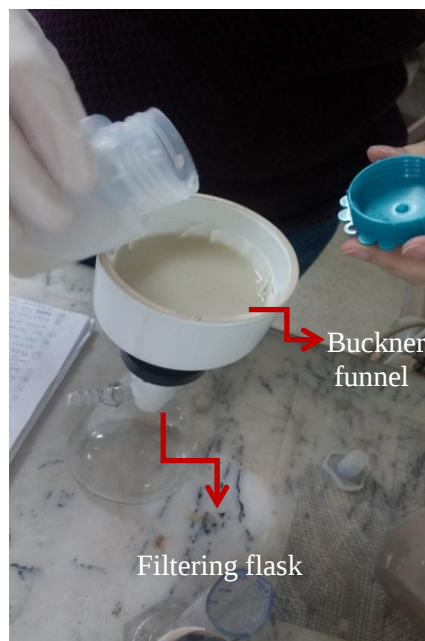


Figure 2.3 Filtering of bentonite (PB) and bentonite/attapulgitite (PB-A) through ashless filter paper (Personal archive, 2016)

The filtered liquid (filtrate) was taken up in a 100-ml volumetric flask which priorly had been washed with 10% nitric acid solution. Then, 1 ml of nitric acid was added to this liquid to prevent the degradation of the filtered liquid. The volumetric flask was filled with DIW up to 100 ml level and this sample was stored in the refrigerator. The specimens were then sent to the Environmental Engineering Laboratory to be tested for the determination of exchangeable cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) in the Inductively Coupled Plasma (ICP-OES) test instrument. Soluble cations of PB and PB-A were determined after the measurements.

#### 2.2.3.2 Exchangeable Cations

To determine the bound cations in the PB and PB-A, 10 g air dried material sieved from No.10 sieve was used. These samples were placed in a plastic container and 40 ml of 1M ammonium acetate was added. The plastic container was then put on the end-over-end shaker and shaken at 30 rpm for 5 minutes (Figure 2.4). The mixture was kept for 24 hours and after 24 hours it was again shaken at 30 rpm for 15 minutes.



Figure 2.4 Samples on an end-over-end shaker (Personal archive, 2016)

The Buchner funnel and 500 mL volume of Erlenmeyer were washed with 1M ammonium acetate solution. A filter paper with 2.5  $\mu\text{m}$  pore size was placed on a Buchner funnel. The PB and PB-A suspension was poured onto the filter paper without splashing. Particles remaining on the Buchner funnel and on the plastic container were washed towards the Buchner funnel with ammonium acetate solution to prevent material loss. A small suction pressure was applied to the filtrate which would flow into the Erlenmeyer (<10 kPa). Material in Buchner funnel was filtered by washing 4 times with 30 ml of 1M ammonium acetate solution. The filtrate was taken up in a 250-ml volumetric flask and the flask was filled with ammonium acetate up to 250 ml. Finally, 1 ml of nitric acid was dropped on the filtrate and the sample was stored in the refrigerator. Subsequently, the collected samples were sent to the Environmental Engineering Laboratory for the determination of the cation concentrations.

#### 2.2.3.3 Cation Exchange Capacity (CEC)

Ammonium acetate-washed materials were also used to determine the cation exchange capacity (CEC). Erlenmeyer was washed with 10% nitric acid solution and then it was washed with isopropanol. The Buchner funnel, which was washed with

1M ammonium acetate, was placed on top of the Erlenmeyer flask and the suction pressure was applied (<10 kPa). The materials in the filtration bottle were washed 3 times with 40 ml of isopropanol. By this process, residual ammonium acetate was removed from the material. The Erlenmeyer was then discarded and washed with DIW and the Buchner funnel was placed on the Erlenmeyer flask again. The material on the Buchner funnel was washed with 50 ml of 1 M potassium chloride solution 4 times. Low suction pressure was applied during the washing process. The volumetric flask was washed with 1 M potassium chloride and the filtrate collected in the flask was transferred into a volumetric flask. The volumetric flask was filled with water up to 250 ml level.

To determine the CEC, 1 ml of potassium chloride was withdrawn with a micropipette out of the volumetric flask and a dose of NH<sub>4</sub>-1K pill was added to it (Figure 2.5). The pill was stirred in the reaction cell until it was completely dissolved and after this process discoloration was observed. The nitrogen concentration was determined with a spectrophotometer after the sample was stored for 15 minutes in this way (Figure 2.6).

The cation exchange capacity was calculated as follows:

$$\frac{\text{CEC}}{\text{N}} = \frac{\text{mg/L}}{\text{cmol/kg}} \quad (2.1)$$

Here, the CEC corresponds to cation exchange capacity (cmol/kg) and N corresponds to nitrogen concentration (mg/L). The results of cation exchange capacity were evaluated in the following chapters.



Figure 2.5 Preparation of samples for CEC: (a) Adding 0.1 ml KCl extract and (b) one dose of reagent in a reaction cell (Personal archive, 2016)



Figure 2.6 Spectrophotometry measurement on colored extract: a) before and b) after analyzing (Personal archive, 2016)

#### 2.2.4 Hydraulic Conductivity

For hydraulic conductivity experiments, a circle was drawn on the GCL with the help of a 10-cm diameter ring, and this circle was partially wetted with deionized water. This process prevents the loss of bentonite from the GCL with swelling. Then, the GCL was carefully cut with the help of a sharp-edged razor knife and the sample was removed (Figure 2.7). Four different points of the sample were marked for

diameter and thickness measurements. They were measured with calipers and GCLs were then weighed. In order to prevent the loss of bentonite from the cut area on GCL roll, the removed part of the sample was taped as shown in Figure 2.7.



Figure 2.7 GCL sample cut from the GCL roll (Personal archive, 2015)

Non-woven geotextiles were used instead of porous stone during the hydraulic conductivity tests. The GCL sample was placed between two heavy non-woven geotextiles and then placed in a flexible wall permeameter cells. Circumference of the sample was covered with bentonite removed from the GCL to prevent sidewall leakage. After covering, a latex membrane was placed around the sample. O-rings were mounted on the top and bottom pedestals. The permeameter was filled with water and prepared for hydraulic conductivity (ASTM D6766). Tests were performed under 35 kPa cell pressure and mean effective stress of 26 kPa. The applied hydraulic gradient varied between 64 and 158 depending on the sample thickness. Hydraulic conductivity tests were initiated by allowing flow direction from top to bottom. After application of the cell pressure in the hydraulic conductivity tests, the air in the tubings and between the geotextile fibers were removed by flushing. The GCL samples were hydrated with the permeants for 24h before the flow was started. To do this, the inlet valve was left open so that the liquid could be contacted with the GCL. However, the outlet valve was kept closed. This situation has been expressed as

"prehydrated condition" during the thesis. After the 24h elapsed, the outlet valve was open and hydraulic conductivity test was initiated for the flow to take place. In contrast, if permeation is started immediately after the placement of the GCL on permeameter (without waiting for 24h), then this condition was denoted as the "non-prehydrated" and GCL was named as "non-prehydrated GCL".

### ***2.2.5 pH and Electrical Conductivity Measurements***

During the hydraulic conductivity tests, samples were taken from inflow and outflow ports of permeameters at certain time intervals (or pore volumes of flow). The samples were filled in 50 ml plastic tubes and kept in the fridge for the purpose of not to enable any changes on the chemical contents. The samples were then subjected to pH and electrical conductivity (EC) measurements at 25 °C using ACCUMET XL50 instrument. The probes were calibrated before the measurements started. Three buffer solutions (pH = 4, pH = 7 and pH = 10) were used to calibrate the pH probe and two buffer solutions (0.1M KCl and 0.01M KCl) were used to calibrate the probe for EC. The  $pH_{out}/pH_{in}$  ve  $EC_{out}/EC_{in}$  ratios were checked to see if the chemical equilibrium condition was maintained during the hydraulic conductivity test. In order to terminate the hydraulic conductivity test, the required equilibrium condition ( $pH_{out}/pH_{in}$  ve  $EC_{out}/EC_{in}$ ) was defined as  $1.0 \pm 0.1$  in ASTM D 7100 and in ASTM D 6766. The same condition was observed in this study, as well.

### CHAPTER THREE

#### PHYSICO-CHEMICAL AND MINERALOGICAL PROPERTIES OF BENTONITES

##### 3.1 Index Properties of Bentonite and Bentonite-Attapulgite Mixture

Specific gravity, consistency limits (liquid limit- $w_L$ , plastic limit- $w_P$  and plasticity index- $I_P$ ) and sieve analyses of GCLs are summarized in Table 3.1.

Table 3.1 Index properties of bentonite

| GCL               | $G_s$ | Fine<br>Content<br>(%) | Clay<br>Content<br>(%) | $w_L$<br>(%)<br>Fall Cone | $w_L$<br>(%)<br>Casagrande | $w_P$<br>(%) | $I_P$<br>(%) |
|-------------------|-------|------------------------|------------------------|---------------------------|----------------------------|--------------|--------------|
| <b>PB</b>         | 2.77  | 94                     | 77                     | 325                       | 385                        | 58           | 327          |
| <b>70%PB+30%A</b> | 2.68  | 71                     | 55                     | 232                       | 295                        | 69           | 226          |
| <b>50%PB+50%A</b> | 2.63  | 71                     | 52                     | 218                       | 253                        | 78           | 175          |
| <b>30%PB+70%A</b> | 2.65  | 55                     | 39                     | 178                       | 189                        | 82           | 107          |
| <b>100%A</b>      | 2.59  | 73                     | 43                     | 136                       | 157                        | 79           | 78           |

The specific gravity of PB GCL was 2.77 in the experiments. As shown in Figure 3.1, as the attapulgite content in GCL increased, the specific gravity of GCL decreased to 2.63.

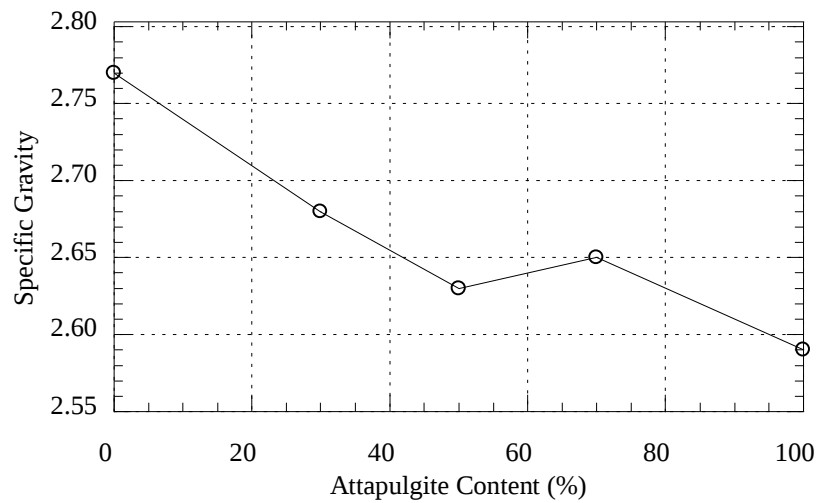


Figure 3.1 Relationship between attapulgite content and specific gravity of GCLs

The particle size distribution curves obtained from the sieve analysis on GCLs are given in Figure 3.2a-b. According to this, the amount of fine material passing under the No.200 sieve (silt+clay percentage) was 94% for PB GCL, 71% for both 70%PB+30%A and 50%PB+50%A GCLs, and 55% for 30%PB+70%A GCL (Figure 3.2a). Clay contents of bentonites were determined by hydrometer analysis and quantities smaller than 0.002 mm were determined at maximum for PB GCL (77%) and at least for 30%PB+70%A GCL (39%). The percentage of fine and clay contents decreased as the amount of attapulgite in GCL increased. This linear decreasing relationship is shown in Figure 3.2b. It is seen here that the size of attapulgite particles are greater than the the size of PB particles and thus, it can be concluded that attapulgite increases the overall particle size in the GCL.

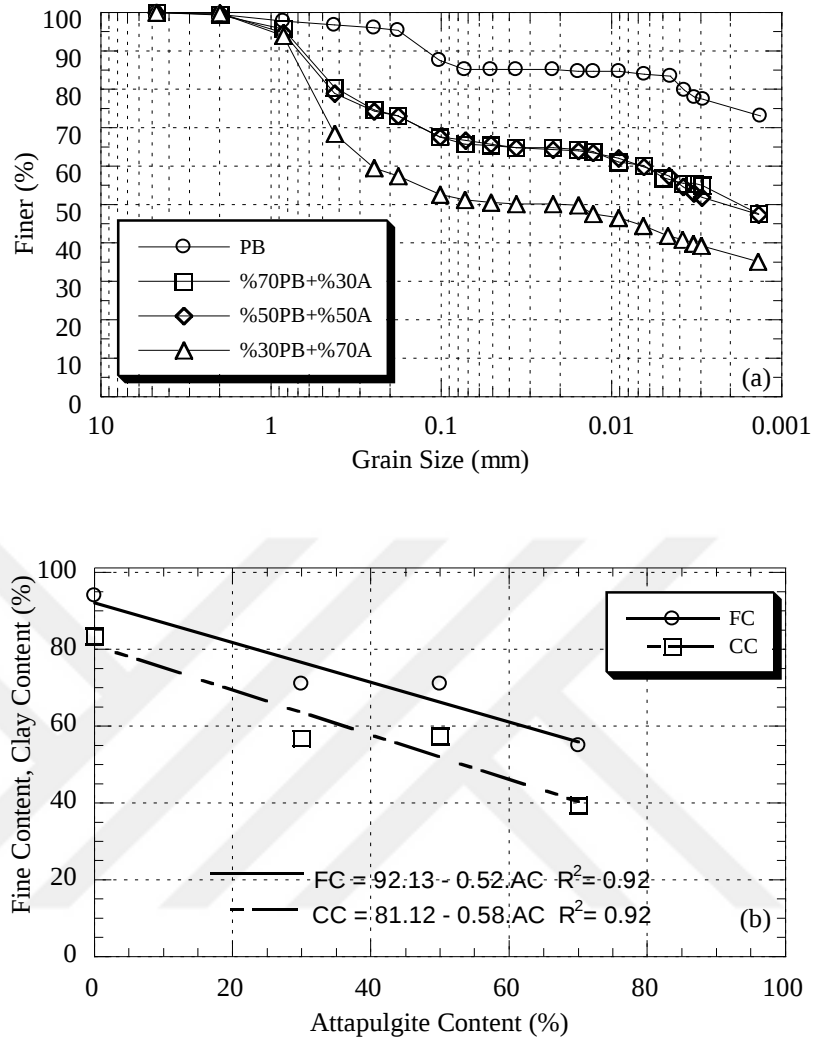


Figure 3.2 a) Grain size distribution curves of GCLs and b) relationships between attapulgite content and fine content/clay content of GCLs

Sridharan & Prakash, (2000) emphasized that the liquid limit determined by the Casagrande method for high plastic clays better reflects the general characteristics of bentonites. However, the liquid limit determined from fall cone method reduces the operator dependent errors to a minimum. For this reason, the liquid limits of bentonites were determined by both methods and plotted in Figure 3.3 with a 1:1 line. As can be seen from Figure 3.3 and Table 3.1, the liquid limit values were found higher with the Casagrande method. This result is consistent with the literature.

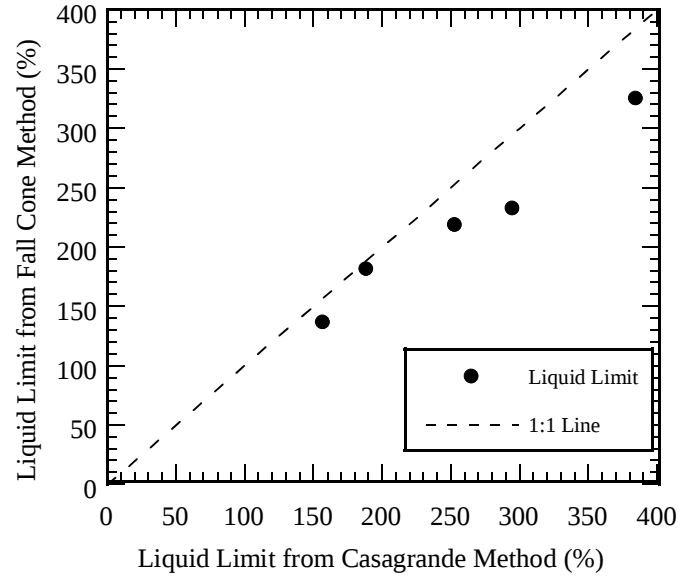


Figure 3.3 Comparison of the liquid limits of GCLs obtained from fall cone and Casagrande methods

The liquid limits and plasticity indices obtained using Casagrande method are given in Figure 3.4 depending on the attapulgite content. Within this context, it is seen that as the attapulgite content increased, liquid limit and the plasticity index decreased linearly. In other words, while the liquid limit value of PB GCL was 385%, this value decreased to 189% for 30%PB+70%A GCL due to increment of attapulgite content in GCL. Besides, as presented in Table 3.1, the plastic limit values increased as the attapulgite content increased (58%, 69%, 78% ve 82%).

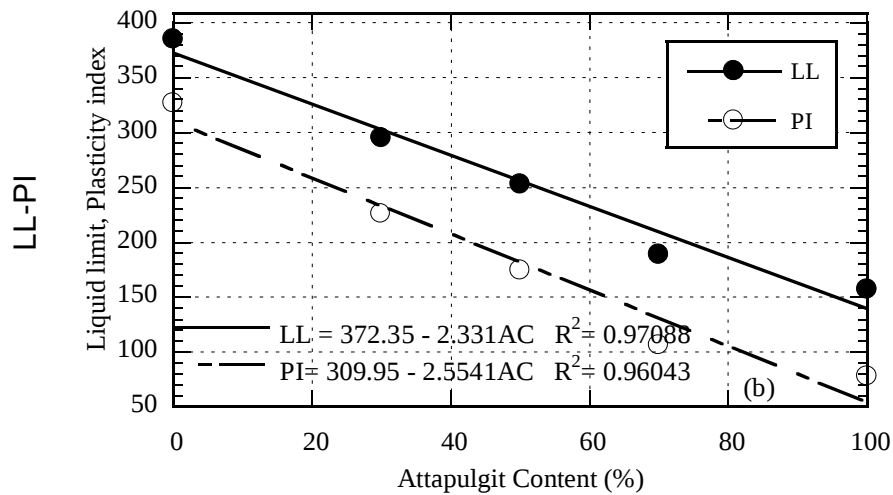


Figure 3.4 Relationships between attapulgite content and consistency limits of GCLs

### 3.2 Chemical Properties of Bentonite

As a result of ICP-OES analysis, the concentrations of soluble cations and bound cations were determined and are shown in Table 3.2 together with the CECs. Concentrations of each exchangeable soluble and bound cations are shown in Figure 3.5, Figure 3.6 and Figure 3.7, as a function of the attapulgite content, respectively.

PB GCL contains significant amounts of sodium (soluble: 57 cmol/kg ve bound: 62 cmol/kg). However, by increasing attapulgite content in the GCL, the soluble and bound sodium concentrations obviously reduced (Figure 3.5a ve Figure 3.6a). Note that almost no sodium was detected in Attapulgitte (100%A) (soluble: 0.4 cmol/kg ve bound: 0.7 cmol/kg).

The other monovalent potassium has relatively low concentration values as compared to other exchangeable cation species (0.4~3.5 cmol/kg). While potassium for soluble cations decreased with attapulgite (Figure 3.5b), there was no such reduction observed for bound cations. However, this difference between soluble and bound cations can be accepted as “not important” in practice.

Concentrations of divalent cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) can be evaluated separately in terms of soluble and bound cations. Although the general trends of soluble cations seem to be decreasing with attapulgite content (Figure 3.5c and Figure 3.5d), concentrations at 30% and 50% attapulgite contents increased when compared to PB GCL. While the soluble  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of PB GCL were 12.3 and 21.2 cmol/kg, respectively, these values increased to 17.6 and 38 cmol/kg at 30% attapulgite content and to 21.8 and 46.3 cmol/kg at 50% attapulgite content, respectively (Table 3.2). It is interesting to note that higher soluble calcium and magnesium concentrations were obtained at intermediate attapulgite mixtures, when compared to the soluble divalent concentrations for attapulgite and PB GCLs.

The general trends of bound  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations tend to increase with attapulgite (Figure 3.6c and Figure 3.5d). The most important reason for this is that

the bound  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of attapulgite were significantly greater than the soluble  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations (31.1 cmol/kg versus 7.9 cmol/kg for  $\text{Ca}^{2+}$  and 25.0 cmol/kg versus 10.3 cmol/kg for  $\text{Mg}^{2+}$ ) (Table 3.2). Therefore, the bound  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of GCL with attapulgite admixture were detected between PB GCL and A, and thus linear relationships were obtained for these cations. From this, it can be revealed that the divalent cations can limitedly be extracted from the attapulgite during the soluble cations analysis in which DIW is used. However, these cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) can be broken off from the clay body by bound cation experiments using chemical solutions. This is an important finding.



Table 3.2 Soluble cations (SC), bound cations (BC) and cation exchange capacity (CEC) of GCLs

| GCL Type          | Soluble Cations (cmol/kg) |                |                  |                  |       | Bound Cations (cmol/kg) |                |                  |                  |       | CEC<br>(cmol/kg) |
|-------------------|---------------------------|----------------|------------------|------------------|-------|-------------------------|----------------|------------------|------------------|-------|------------------|
|                   | Na <sup>+</sup>           | K <sup>+</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Total | Na <sup>+</sup>         | K <sup>+</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Total |                  |
| <b>PB</b>         | 57.1                      | 1.4            | 12.3             | 21.2             | 91.9  | 62.1                    | 1.3            | 16.1             | 6.7              | 86.3  | 81.4             |
| <b>70%PB+30%A</b> | 43.2                      | 1.2            | 17.6             | 38.0             | 100.1 | 44.8                    | 1.0            | 20.9             | 11.9             | 78.5  | 63.9             |
| <b>50%PB+50%A</b> | 38.9                      | 1.1            | 21.8             | 46.3             | 107.9 | 37.6                    | 1.1            | 21.1             | 14.2             | 74.0  | 56.4             |
| <b>30%PB+70%A</b> | 21.0                      | 0.4            | 11.6             | 25.7             | 58.8  | 19.9                    | 3.3            | 41.3             | 25.3             | 89.9  | 48.9             |
| <b>100%A</b>      | 0.4                       | 0.6            | 7.9              | 10.3             | 19.3  | 0.7                     | 1.2            | 31.1             | 25.0             | 58.0  | 45.4             |

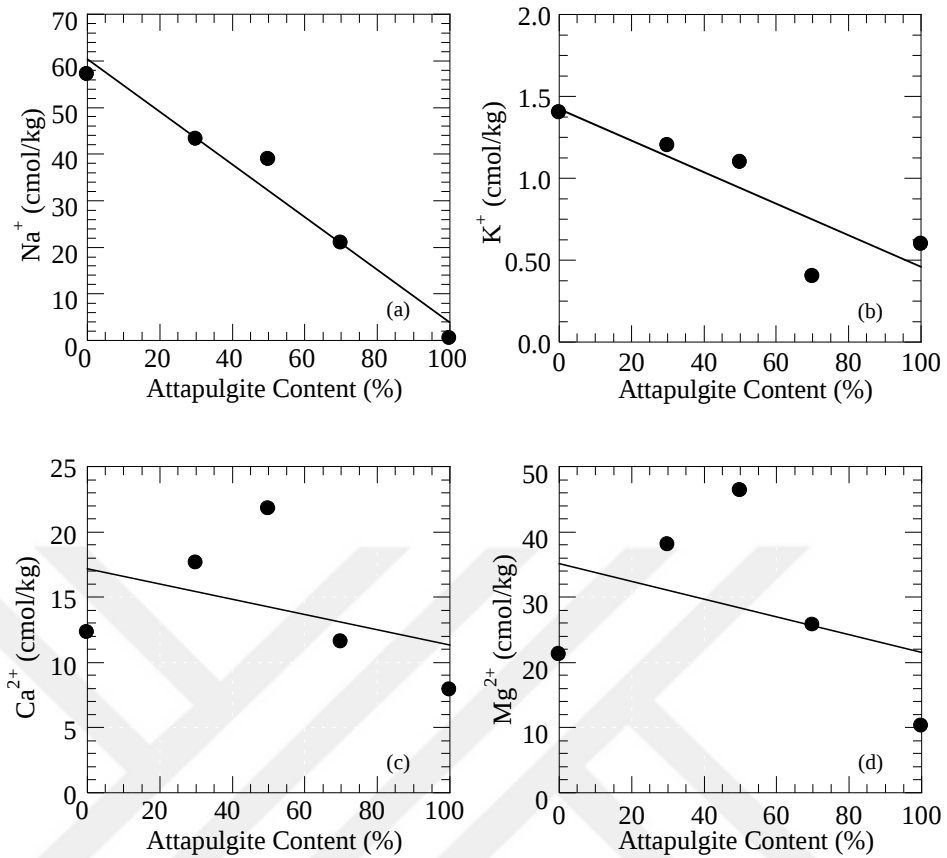


Figure 3.5 Soluble cations of GCLs as a function of attapulgite content: a) Na<sup>+</sup>, b) K<sup>+</sup>, c) Ca<sup>2+</sup> and d) Mg<sup>2+</sup>

It is generally expected that soluble cation concentrations would be less than the bound cation concentrations. This is due to the fact that the soluble cation analyses were performed with 2 g dry samples and the DIW, whereas bound cations experiments were conducted with 10 g dry samples and using various chemicals. There is no doubt that it is easier to chemically remove the exchangeable cations from the clay body than with water. Except Mg<sup>2+</sup>, the soluble and bound cation concentrations for exchangeable cations were very close to each other in this study (Figure 3.7a-d). For magnesium, however, soluble cations were generally higher than bound cations. It is not known why this situation was originated from. Therefore, the results obtained herein should be supported with further analyses.

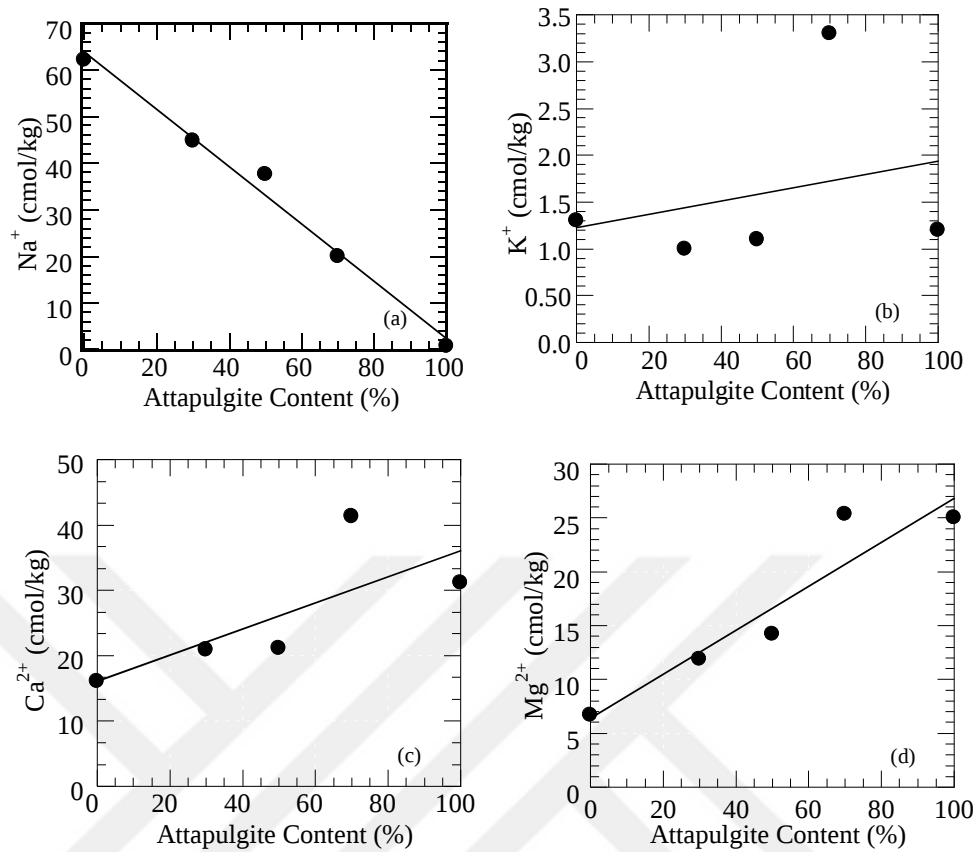


Figure 3.6 Bound cations of GCLs as a function of attapulgite content: a) Na<sup>+</sup>, b) K<sup>+</sup>, c) Ca<sup>2+</sup> and d) Mg<sup>2+</sup>

In particular, it is expected that the sum of the bound cations' concentrations (as well as the sum of the soluble cations' concentrations) will be equal to or close to the cation exchange capacity (CEC) of the GCLs. In these independent analyses, CECs were obtained after bound cations (by using 10 g materials and chemicals). This situation is examined in Figure 3.8a-d. Figure 3.8a shows that CECs decreased linearly with increasing attapulgite content in GCL. On the other hand, the concentrations of total soluble and bound cations also follow a linear trend, but there are points that scattered from linearity (Figure 3.8b-c). But it can be seen that the tendency of the bound cations is closer to that of the attitude of the CEC. This is more evident in Figure 3.8d, which compares the results of all three analyses. The differences between the analyses possibly due to PB which was polymer modified. For PB-GCL all three concentrations are in the range of 81.4-91.9 cmol/kg. However, as attapulgite was added into the GCL, the difference between all three

cation concentrations became evident. The concentration of total soluble cations in the intermediate attapulgite contents (30, 50 and 70%) was about twice that of CEC (maximum 107.9-56.4 cmol/kg); but at 100%A it fell below the CEC (19.3 versus 45.4 cmol/kg). In general, total soluble concentrations increased until 50% attapulgite content and then decreased. In contrast, total bound concentrations were closer to those of the CECs (Figure 3.8d).

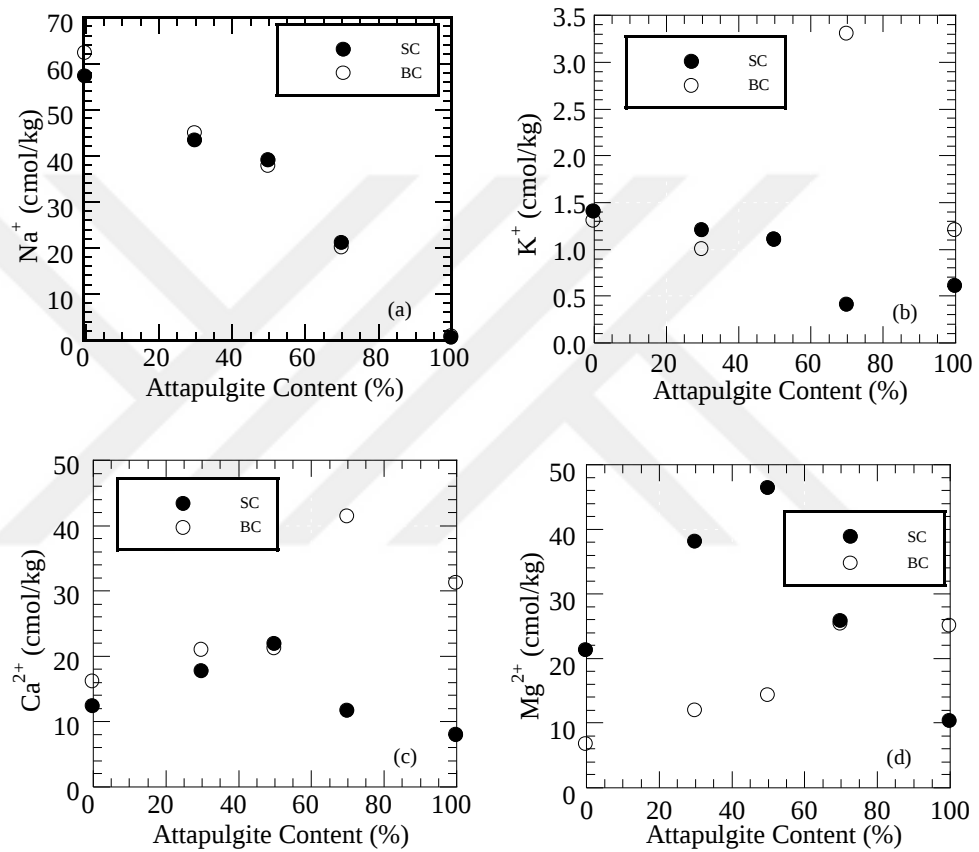


Figure 3.7 Comparison of soluble and bound cations as a function of attapulgite content: a) Na<sup>+</sup>, b) K<sup>+</sup>, c) Ca<sup>2+</sup> and d) Mg<sup>2+</sup>

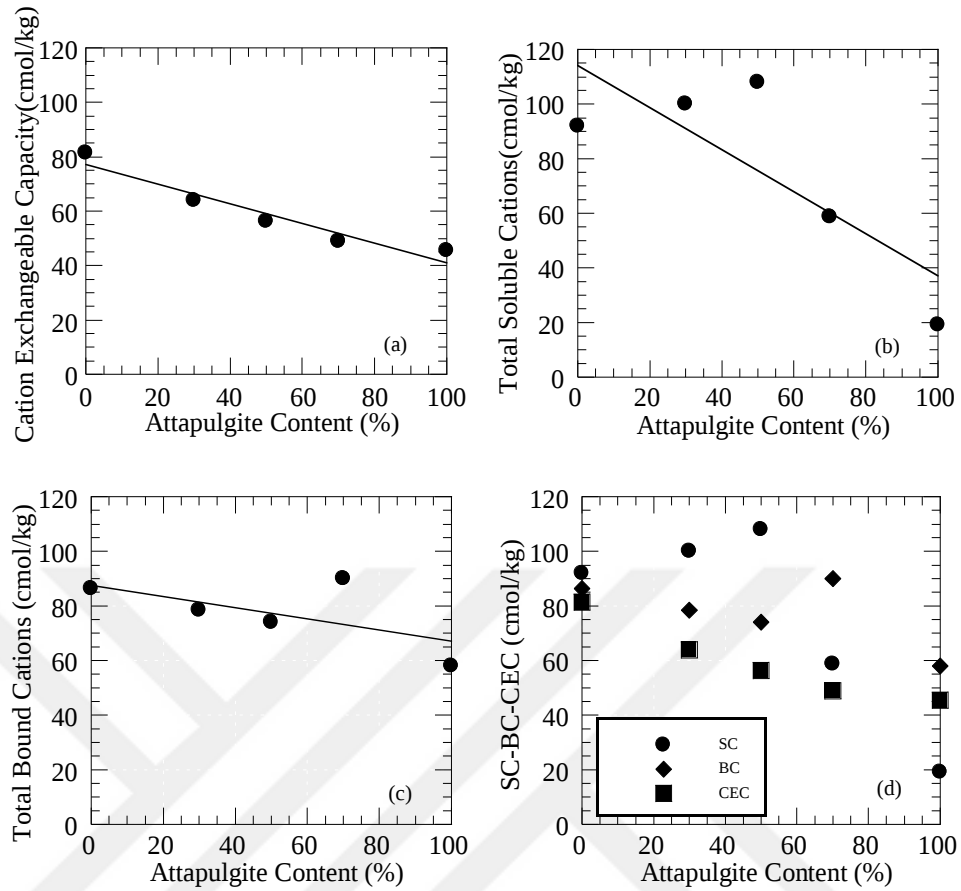


Figure 3.8 Change of concentrations as a function of attapulgite content: a) Cation exchange capacity (CEC), b) soluble cations (total of  $\text{Na}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), c) bound cations (total of  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and d) comparison of CEC, SC and BC within each other

Concentrations of soluble and bound cations are also discussed in terms of mole fractions. Actually, it is not exactly right to examine it in this way, because mole fractions are widely used to express the cation exchange on a single GCL. In this study, the mole fractions of GCLs containing different amounts of attapulgite were calculated. In Figure 3.9, the soluble concentration of each cation is divided by the total soluble cations concentration and CEC and in Figure 3.10, it is divided by the total bound cations concentration and CEC. This is a kind of normalization process. For example, in Figure 3.9a the mole fractions of soluble sodium in PB-GCL are 0.62 (62%) and 0.70 (70%) which are obtained by dividing the soluble sodium concentration of 57.1 cmol/kg to the total soluble cations concentration of 91.9 cmol/kg (closed symbol) and to CEC of 81.4 cmol/kg, respectively (open symbols).

The same calculation was made in Figure 3.11a by taking into account of bound sodium concentrations and total bound concentrations ( $62.1 / 86.3 = 0.72$ ).

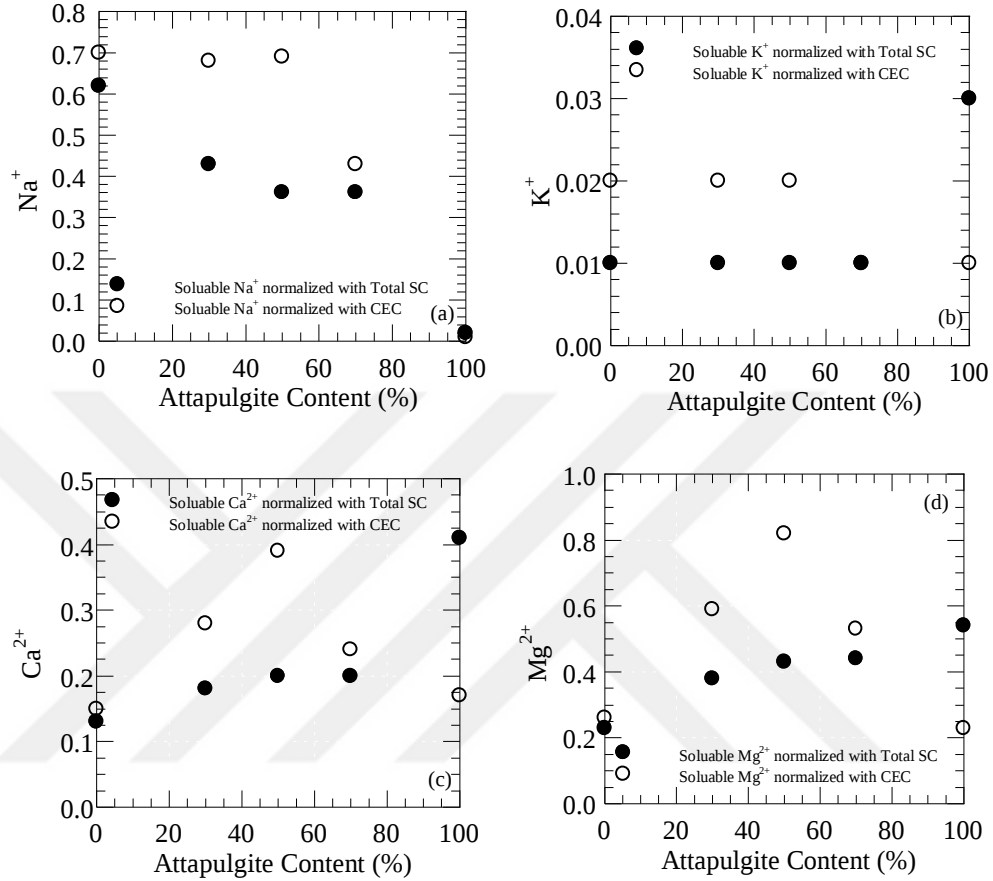


Figure 3.9 Expression of cation concentrations in terms of mole fractions and results were shown as a function of attapulgite content (mole fractions were obtained by dividing each cation concentration to total soluble cation concentrations or to CEC): a) Na<sup>+</sup>, b) K<sup>+</sup>, c) Ca<sup>2+</sup> and d) Mg<sup>2+</sup>

The relationships of mole fractions of bound cations and the CEC with attapulgite content are smoother and have a near uniform distribution (Figure 10a-d) when compared to the relationships shown in Figure 3.9a-d and taking into account the mole fractions of soluble cations and CEC with attapulgite content.

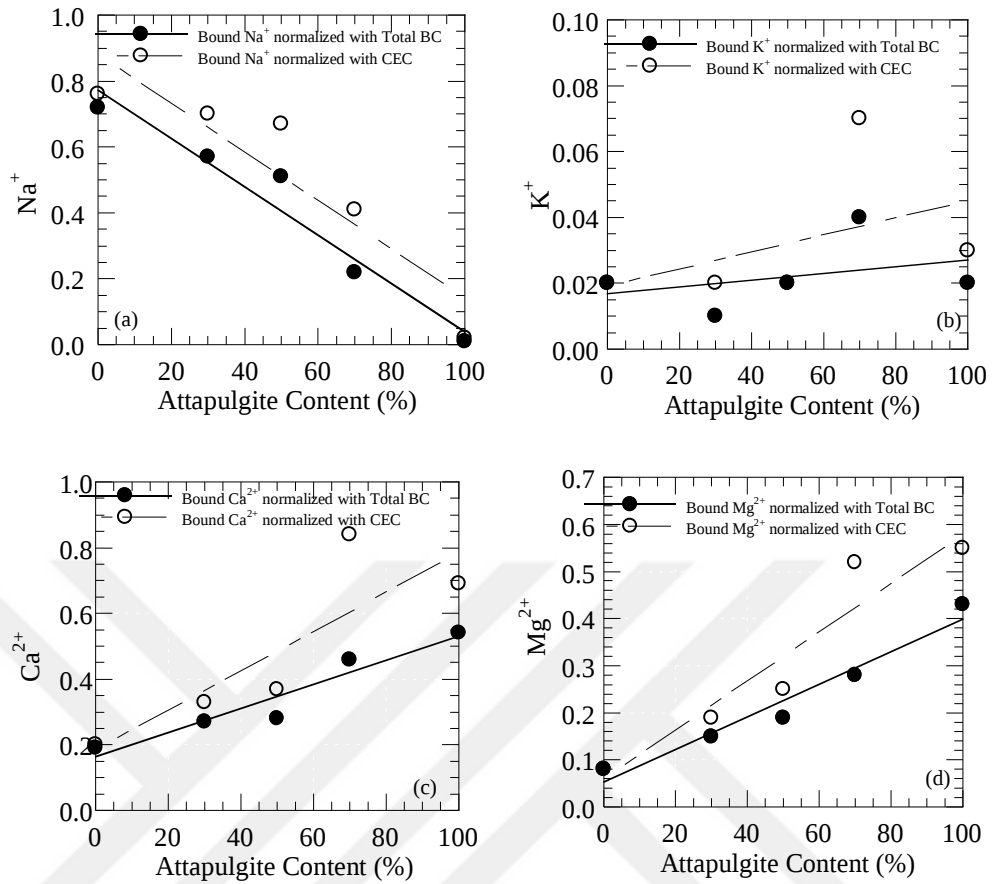


Figure 3.10 Expression of cation concentrations in terms of mole fractions and results were shown as a function of attapulgite content (mole fractions were obtained by dividing each cation concentration to total bound cation concentrations or to CEC): a) Na<sup>+</sup>, b) K<sup>+</sup>, c) Ca<sup>2+</sup> and d) Mg<sup>2+</sup>

On the other hand, mole fractions normalized by total soluble cations, total bound cations and by CEC gave also a proportional change of the amount of cations in GCL by the addition of attapulgite (Figure 3.9a-d ve Figure 3.10a-d). Accordingly, while the sodium content was about 0.70 in PB-GCL, it decreased linearly below 0.1 by increasing the attapulgite content. The other monovalent cation, potassium, is relatively low compared to other cations. For this reason, although the change seems to be increasing with the addition of attapulgite, it did not actually change ( $<0.05$ ). Mole fractions of divalent calcium and magnesium (Ca<sup>2+</sup> and Mg<sup>2+</sup>) linearly increased with the attapulgite content. Thus, it should be expected that the sodium concentration will decrease, while divalent cation concentrations will increase when attapulgite is added in GCL. This may have a significant influence on the hydraulic conductivity of GCL.

## **CHAPTER FOUR**

### **SWELL INDEX OF GEOSYNTHETIC CLAY LINERS WITH DEIONIZED WATER AND SALT SOLUTIONS**

#### **4.1 Background**

Bentonite is high plasticity clay that can swell a few times more than its dry volume when it contacts with water (Jo et al., 2001; Kolstad et al., 2004). The low hydraulic conductivity of bentonite is related to the thickness of the adsorbed water layer surrounding the clay particles. This layer is immobile and the pore spaces available between the particles for mobile water are quite limited. However, bentonite swelling (or adsorbed water thickness) is influenced by pore fluid chemistry. When the thickness of the adsorbed water layer surrounding the particles decreases, the pore spaces between the particles grow and the hydraulic conductivity increases as the flow is faster (Sridharan, 1991). To demonstrate this effect, hydraulic conductivity tests have been conducted with DIW and inorganic salt solutions and the differences have been reported in the literature. Several studies have been carried out to investigate the effects of solution concentration, cation valence and pH on the hydraulic conductivity of GCL, as well as experiments with salt solutions containing monovalent, divalent or both, up to this time (Petrov, Rowe & Quigley, 1997, Shackelford et al., 2000; Kolstad et al., 2004; Jo, Benson, Shackelford, Lee & Edil, 2005, Katsumi, Ishimori, Ogawa, Yoshikawa, Hanamoto & Fukagawa, 2007; Katsumi et al., 2008, Benson et al., 2010; Ören & Akar, 2016).

In these studies, it was found that the increase of cation concentration and solution concentration caused the increase of hydraulic conductivity of GCLs. For example,  $\text{Na}^+$  in Na-bentonite can easily be replaced with  $\text{Ca}^{2+}$  found in the pore liquid (Jo et al., 2001, 2005; Kolstad et al., 2004). This causes the swelling value to decrease and the hydraulic conductivity to increase because divalent cations suppress the water layer thickness around bentonite. In addition, in various studies, bentonite swell index is directly related to hydraulic conductivity of GCL (Shackelford et al., 2000; Jo et al., 2001; Ashmawy, El-Hajji, Sotelo & Muhammad, 2002; Kolstad et al., 2004;

Lee, Shackelford, Beson, Jo & Edil, 2005; Katsumi et al., 2008; Benson et al., 2010). In other words, the greater the swell index of bentonite, the lower is the hydraulic conductivity of GCL (Petrov et al., 1997; Shackelford et al., 2000; Jo et al., 2001; Kolstad et al., 2004; Lee & Shackelford, 2005; Katsumi et al., 2007, 2008). Thus, the swell index of bentonite (PB) and bentonite/attapulgite GCLs were initially handled herein.

#### 4.2 Swell Index of GCLs in DIW and its correlations with bentonite properties

In this study, swell index tests were started with DIW. As seen in Table 4.1, swell indices were 21, 18, 15, 10 and 6 mL/2g, for PB, 70%PB+30%A, 50%PB+50%A, 30%PB+70%A and attapulgite (A), respectively. It is seen that as the attapulgite content increases, the swell index decreases. The reason for this decrease was attributed to the fact that the thickness of the adsorbed water layer of the attapulgite mineral is less than that of polymer bentonite. When attapulgite was being abundant, the swell index of GCLs dramatically decreased.

Table 4.1 Swell indices of GCLs in different solutions

| <b>GCL TYPE</b>   | <b>DIW</b> | <b>50mM CaCl<sub>2</sub></b> | <b>50mM MgCl<sub>2</sub></b> | <b>50mM CuCl<sub>2</sub></b> |
|-------------------|------------|------------------------------|------------------------------|------------------------------|
| <b>PB</b>         | 21         | 10                           | 7                            | 10                           |
| <b>70%PB+30%A</b> | 18         | 9                            | 7                            | 9                            |
| <b>50%PB+50%A</b> | 15         | 8                            | 8                            | 8                            |
| <b>30%PB+70%A</b> | 10         | 7                            | 8                            | 7                            |
| <b>100%A</b>      | 6          | 6                            | 6                            | 6                            |

The relationship between swell index and consistency limits are also evaluated and shown in Figure 4.1. Basically, the swell index of GCLs increased as the liquid limit of bentonite increased, or the plastic limit decreased. For example, the swell index of polymer bentonite (PB), which had the highest liquid limit (385%) and the lowest plastic limit (58%), had also the highest swell index value (21 mL/2g). Further increase in the attapulgite content led to decrease the swell index of 70%PB+30%A GCL to 18 mL/2g. For this GCL, the liquid limit decreased to 295% and plastic limit

increased to 69%. Finally, swell index of attapulgite mineral was determined as 6 mL/2g and liquid and plastic limits determined as 157% and 79%, respectively.

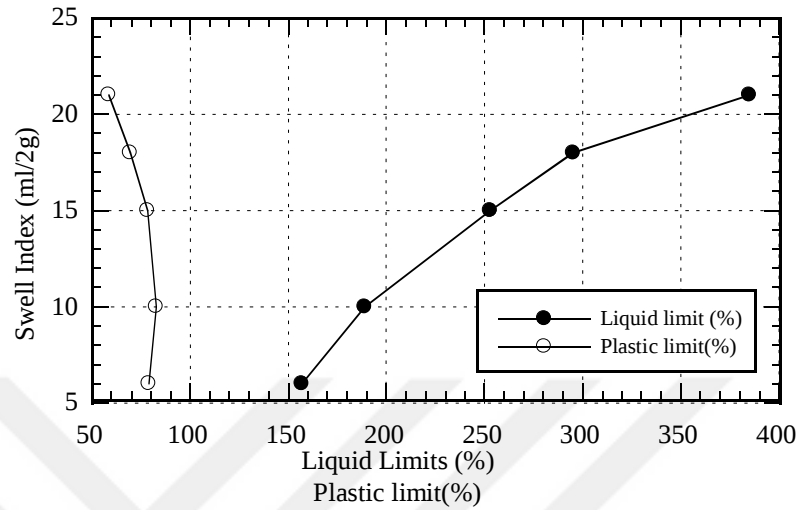


Figure 4.1 Relationships between consistency limits and swell indices of GCLs

The swell index values of GCLs are also related to the fine content and clay contents of GCLs (Figure 4.2). As mentioned earlier, increasing the amount of attapulgite in GCL reduces the fine content and clay content. Because of this, the swell index increased when the fine and clay contents of GCL increased (Figure 4.2).

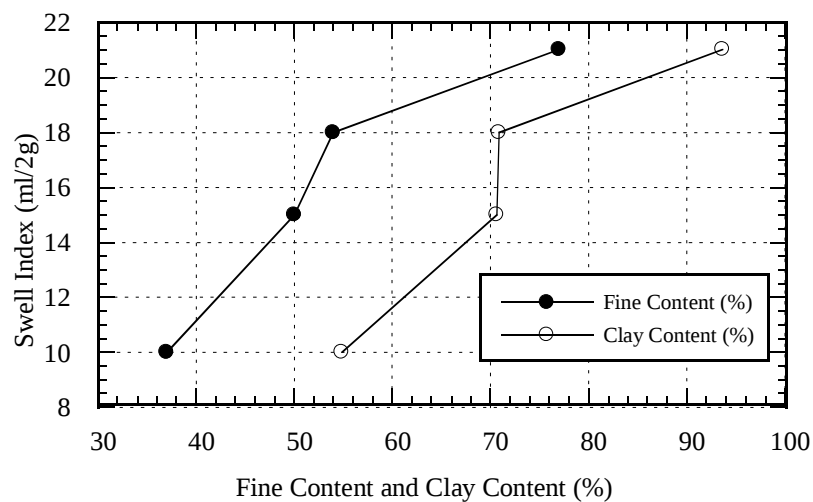


Figure 4.2 Relationships between fine content/clay content and swell indices of GCLs

There is also an increasing tendency between swell index and cation exchange capacity, depending on the amount of attapulgite in the GCL (Figure 4.3). It is not surprise to see an increase in the swell index when CEC was increased. Because, CEC was ranged between 45 and 82 cmol/kg depending in the attapulgite content.

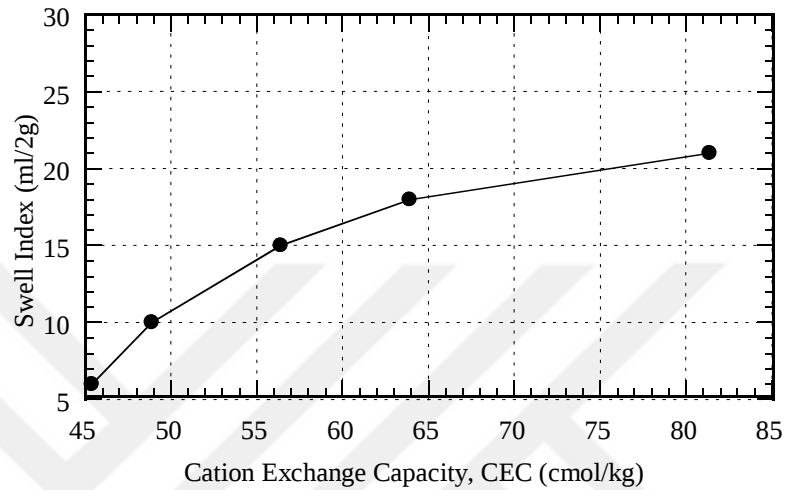


Figure 4.3 Relationship between cation exchange capacity (CEC) and swell indices of GCLs

#### 4.3 Swell Index of GCLs in Salt Solutions

The swell index tests were also performed in different salt solutions. Experiments were first carried out with 50 mM  $\text{CaCl}_2$  and it was noted that swell indices were significantly reduced when compared to those obtained with DIW (Table 4.1). The swell indices reduced to 10 mL/2g for PB GCL, 9 mL/2g for 70%PB+30%A GCL, 8 mL/2g for 50%PB+50%A GCL, 7 mL/2g for 30%PB+70%A GCL, however, it did not change in the attapulgite itself (6 mL/2g). These tests were carried out in other salt solutions prepared at the same concentration level. Hence, the effect of the molecular difference on the swell index was observed. In the case of 50 mM  $\text{MgCl}_2$  solution, swell index values were 7, 7, 8, 8, and 6 mL/2g for PB-GCL, 70%PB+30%A GCL, 50%PB+50%A GCL, 30%PB+70%A GCL and attapulgite, respectively (Table 4.1). In addition, swell indices were determined in 50 mM  $\text{CuCl}_2$  solution and similar results were obtained: 10 mL/2g for PB GCL, 9 mL/2g for

70%PB+30%A GCL, 8 mL/2g for 50%PB+50%A GCL, 7 mL/2g for 30%PB+70%A GCL, and 6 mL/2g for attapulgite mineral (Table 4.1).

A graphical representation of the swell indices with divalent salt solutions is shown in Figure 4.4, including swell index of GCLs in 100mM  $\text{CuCl}_2$  solution. Accordingly, the molecular difference in the divalent salt solution affected the swell indices of GCLs at about the same degree. The difference between the swell indices obtained in DIW and salt solutions was obviously seen in PB GCL. In this GCL, the swell index in salt solutions reduced to half of its value in DIW (it decreased from 21 mL/2g to 7-10 mL/2g). The difference between the swell indices (DIW and salt solutions) decreased as the attapulgite content increased in GCL and eventually it became equal in attapulgite. Depending on the attapulgite content, the remarkable changes in the swell indices were obtained when DIW was used as the pore fluid. The range of reduction in the swell index was 15 mL/2g (or from 21 to 6 mL/2g). However, this change is less important when salt solution was used. Because the range was only 4 mL/2g (or from 10 mL/2g to 6 mL/2g). Thus, the influence of attapulgite on the swell index can only be seen when DIW is used as the test liquid.

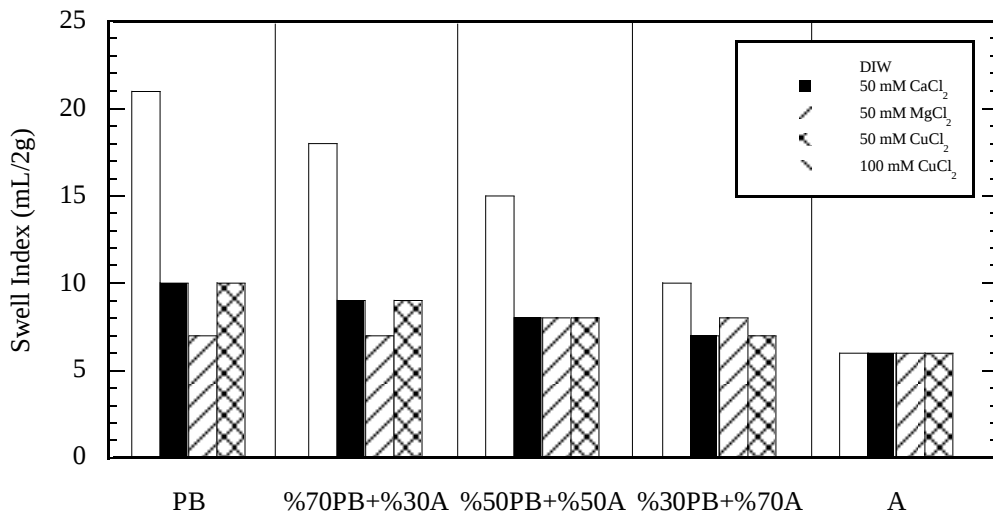


Figure 4.4 Swell indices of GCLs in different pore fluids

## **CHAPTER FIVE**

### **HYDRAULIC CONDUCTIVITIES OF GEOSYNTHETIC CLAY LINERS TO DEIONIZED WATER**

#### **5.1 Background**

The type of permeant used in the hydraulic conductivity tests and prehydration conditions have significant effects. When bentonite is in contact with DIW, it swells in GCL and hydraulic conductivity reduces. The hydraulic conductivity of GCLs manufactured with such bentonites (i.e. high swelling ability) is very low when permeated with DIW ( $\leq 2 \times 10^{-11}$  m/s). In literature, it is reported that the hydraulic conductivity of GCLs to tap water is similar to DIW (Ruhl & Daniel, 1997; Egloffstein, 2001; Shan & Lai, 2002; Katsumi et al., 2007; Ören & Demirkıran, 2015).

Prehydration allows bentonite to swell by contacting the GCL with deionized water or tap water (the inlet valve of the permeameter cell is open, the outlet valve is closed) for a while before the flow is started. It is known that the hydraulic conductivities of prehydrated GCLs are several orders of magnitude lower than the hydraulic conductivities of non-prehydrated GCLs (Lee et al., 2005).

#### **5.2 Hydraulic Conductivity of non-prehydrated GCLs with DIW**

Experiments conducted on GCLs with DIW were first given for the non-prehydrated condition. In this case, GCLs were directly subjected to flow with DIW without waiting for 24h. The hydraulic conductivity behaviors of GCLs obtained along the test durations are shown in Figures 5.1a-g as a function of pore volumes of flow (PVF). The average of the last four readings was taken as the final hydraulic conductivity of the GCLs (Table 5.1). To determine the physical equilibrium state during the tests, the  $Q_{out}/Q_{in}$  values are also shown on the secondary axis of the same figures. The dashed lines in the graph represent boundary conditions for  $Q_{out}/Q_{in}$  values ( $1.0 \pm 0.25$ ).

Table 5.1 Final hydraulic conductivity results of experiments with DIW

| GCL Type          | Non prehydrated |        |                       |                       | Prehydrated for 24h |                       |
|-------------------|-----------------|--------|-----------------------|-----------------------|---------------------|-----------------------|
|                   | Test            |        | Hydraulic             |                       | Test                | Hydraulic             |
|                   | Duration        |        | Conductivity          |                       | Duration            | Conductivity          |
|                   | (days)          |        | (m/s)                 |                       | (days)              | (m/s)                 |
|                   | Test 1          | Test 2 | Test 1                | Test 2                | Test 1              | Test 1                |
| <b>PB</b>         | 60              | -      | $5.8 \times 10^{-11}$ | -                     | 351                 | $2.0 \times 10^{-11}$ |
| <b>70%PB+30%A</b> | 117             | 60     | $7.9 \times 10^{-11}$ | $1.0 \times 10^{-6}$  | 153                 | $3.7 \times 10^{-11}$ |
| <b>50%PB+50%A</b> | 277             | 174    | $1.2 \times 10^{-10}$ | $6.7 \times 10^{-11}$ | 155                 | $3.2 \times 10^{-11}$ |
| <b>30%PB+70%A</b> | 29              | 28     | $9.5 \times 10^{-7}$  | $8.7 \times 10^{-7}$  | 152                 | $1.3 \times 10^{-8}$  |

As can be seen in Figure 5.1a, the hydraulic conductivity of PB GCL was  $3.3 \times 10^{-10}$  m/s where DIW was used as the permeant. The hydraulic conductivity of PB GCL followed a fluctuating course along the test duration and it was determined as (~8 PVF)  $5.8 \times 10^{-11}$  m/s at the end of the test.

Two samples were prepared for each attapulgite mixed polymer GCLs to determine the reproducibility of hydraulic conductivity tests. In the first test conducted on 70%PB+30%A GCL, the hydraulic conductivity value was  $5.9 \times 10^{-7}$  m/s and the GCL hydraulic conductivity continued to fluctuate and decrease until 32 PVF. The hydraulic conductivity value then stabilized at approximately  $5.7 \times 10^{-11}$  m/s (Figure 5.1b). Figure 5.1c shows the hydraulic conductivity behavior of second test conducted on 70%PB+30%A GCL. The initial hydraulic conductivity of GCL was found to be  $2.6 \times 10^{-10}$  m/s. However, this value then increased, and the final hydraulic conductivity reached  $1.0 \times 10^{-6}$  m/s at approximately 49 PVF (Figure 5.1c). There are approximately 5 orders of magnitude differences between the hydraulic conductivity values obtained from two tests. This difference was not normally expected. This is because the presence of 70% polymer bentonite in the GCL is more than enough to block the flow channels that may exist between the attapulgite particles. Therefore, it is believed that this difference may be due to the fact that the

polymer bentonite and attapulgite are not homogeneously distributed within the GCL at the prepared ratios.

Out of the attapulgite mixtures, the initial hydraulic conductivity values of 50%PB+50%A GCLs were  $1.7 \times 10^{-10}$  m/s for the first test sample and  $1.2 \times 10^{-6}$  m/s for the second test sample (Figure 5.1d-e). In the first test, the hydraulic conductivity of GCL reached  $1.2 \times 10^{-10}$  m/s at about 10 PVF and it reached equilibrium (Figure 5.1d). In the second test, however, it decreased significantly at 15 PVF and finally hydraulic conductivity reached to  $6.7 \times 10^{-11}$  m/s (Figure 5.1e). Low hydraulic conductivities were also expected for the GCL containing 50% polymer bentonite. However, it is quite difficult to prepare and spread these mixtures in homogeneous and desired proportions in plane (or two-dimensional) materials such as GCL. At the same time, bentonite/attapulgites can move in the GCL during rolling and transporting which may result in segregation of attapulgite in GCL. In the second test, this may be the reason why the hydraulic conductivity was initially high and finally low. It is highly probable that the polymer bentonite swells and clogs the flow channels with the permeation.

The hydraulic conductivity value for the first test sample of 30%PB+70%A GCL was measured relatively higher ( $6.8 \times 10^{-8}$  m/s). This value decreased until about 7 PVF and then gradually increased (Figure 5.1f). The hydraulic conductivity finally reached to  $9.5 \times 10^{-7}$  m/s and the test was terminated. It is important to note that polymer bentonite attempted to swell and hence, reduce the hydraulic conductivity to  $2.0 \times 10^{-10}$  m/s at 7 PVF (Figure 5.1f). This shows the role of polymer bentonite in GCL. However, since bentonite content was 30%, the hydraulic conductivity tended to increase after 7 PVF. This increase in the hydraulic conductivity may be possibly due to loss of bentonite during hydraulic conductivity test. Bentonite particles may be swept away between attapulgite particles by the seepage forces acting on the GCL, resulting larger pores between the particles. Thus, the hydraulic conductivity increased about four orders of magnitude at the end of the test. In the second test of this GCL, however, the hydraulic conductivity was stable throughout the test duration and was 2.7 times greater than the first sample ( $2.6 \times 10^{-6}$  m/s) (Figure 5.1g),

indicating limited role of polymer bentonite on reducing the hydraulic conductivity. As a result, it is obvious that the final hydraulic conductivities of 30%PB+70%A GCLs were higher than the others because of high attapulgite content (70%) in GCL.

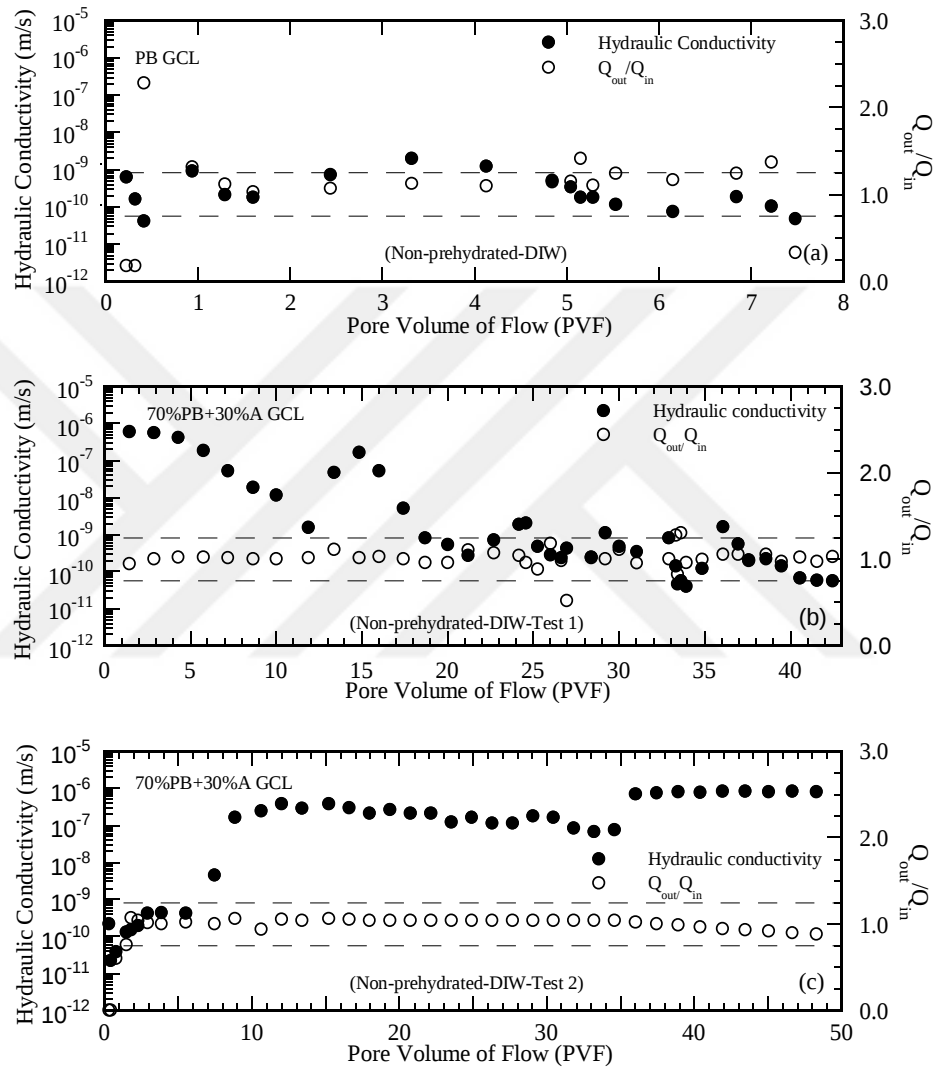


Figure 5.1 Hydraulic conductivity of GCLs to DIW: a) PB, b) 70%PB+30%A (Test-1), c) 70%PB+30%A (Test-2), d) 50%PB+50%A (Test-1), e) 50%PB+50%A (Test-2), f) 30%PB+70%A (Test-1) and g) 30%PB+70%A (Test-2)

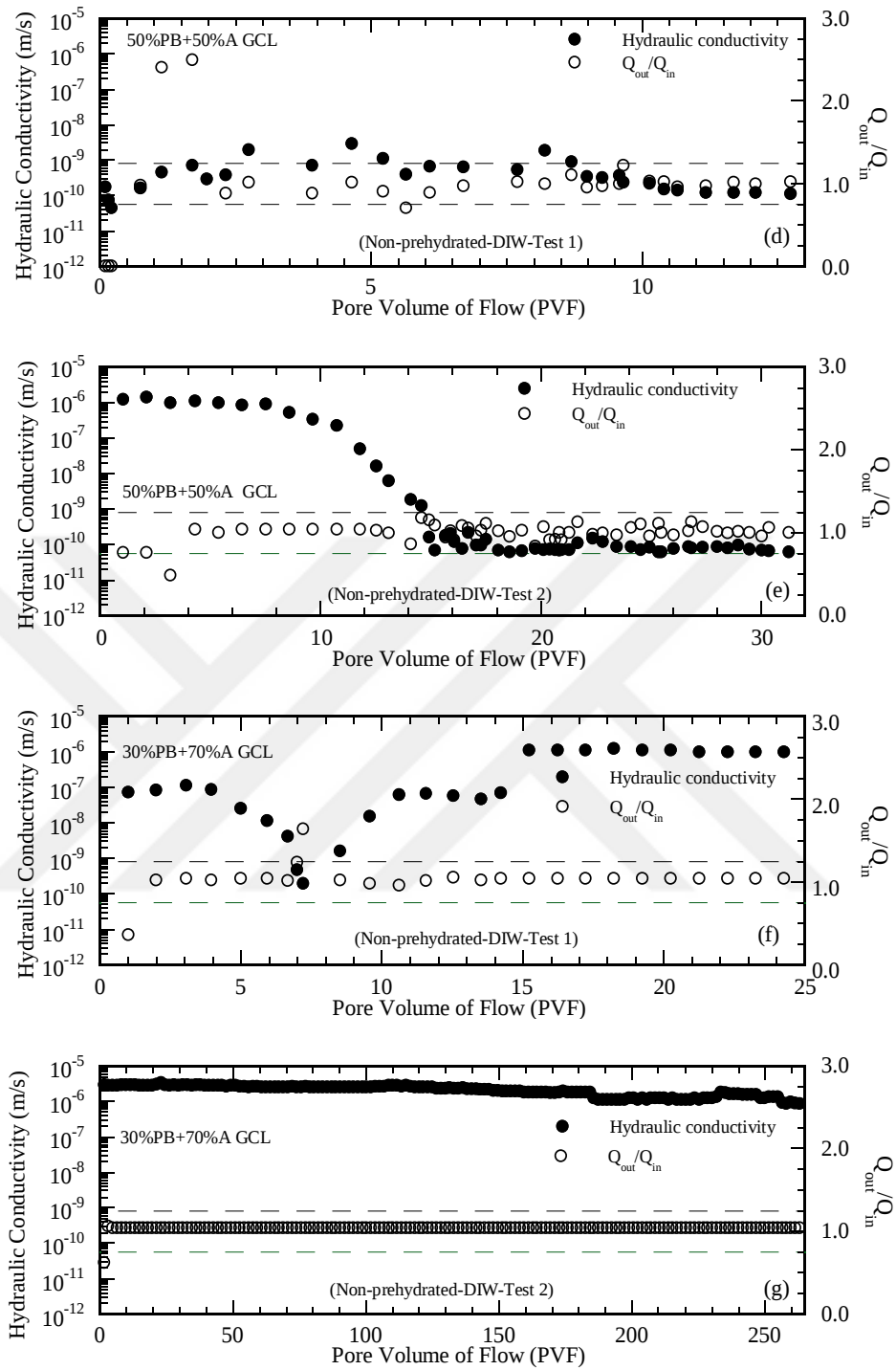


Figure 5.1 Continue

### 5.3 Influence of Prehydration Condition on the Hydraulic Conductivity of GCLs

To investigate the effect of prehydration on hydraulic conductivity, GCL specimens were prehydrated for 24 hours with DIW. The initial hydraulic conductivity of prehydrated PB GCL was  $4.2 \times 10^{-12}$  m/s. This value was  $3.3 \times 10^{-10}$  m/s for non-prehydrated PB GCL (Figure 5.1a and 5.2a). Prehydrated PB GCL had 100 times lower initial hydraulic conductivity than the non-prehydrated PB GCL. But when the final hydraulic conductivities were compared, the prehydrated GCL was found to be 3.0 times lower than the non-prehydrated GCL ( $2.0 \times 10^{-11}$  m/s) (Table 5.1). Blocking the flow paths with the swollen bentonites after prehydration led to such a reduction in the hydraulic conductivity.

Among attapulgite mixed GCLs, initial hydraulic conductivity of prehydrated 70%PB+30%A was  $2.5 \times 10^{-11}$  m/s. The flow stabilized at 5 PVF ( $\sim 4.0 \times 10^{-11}$  m/s) and this test was continued until 14 PVF (Figure 5.2b). For the other bentonite/attapulgite GCL (i.e. 50%PB+50%A), the initial hydraulic conductivity of  $7.5 \times 10^{-8}$  m/s increased to  $5.8 \times 10^{-11}$  m/s at 10 PVF. Then, hydraulic conductivity decreased slightly until the end of the test ( $3.2 \times 10^{-11}$  m/s) (Figure 5.2c). Although there was an increasing trend in the hydraulic conductivity of GCLs up to 50% attapulgite content, the hydraulic conductivities ranged between  $2.0 \times 10^{-11}$  and  $4.0 \times 10^{-11}$  m/s. However, when attapulgite content was increased to 70% (30%PB+70%A GCL), the final hydraulic conductivity was measured as  $1.3 \times 10^{-8}$  m/s at 45 PVF (Figure 5.2d). This shows that the amount of attapulgite mixed with polymer bentonite is important, while evaluating the hydraulic conductivity to DIW.

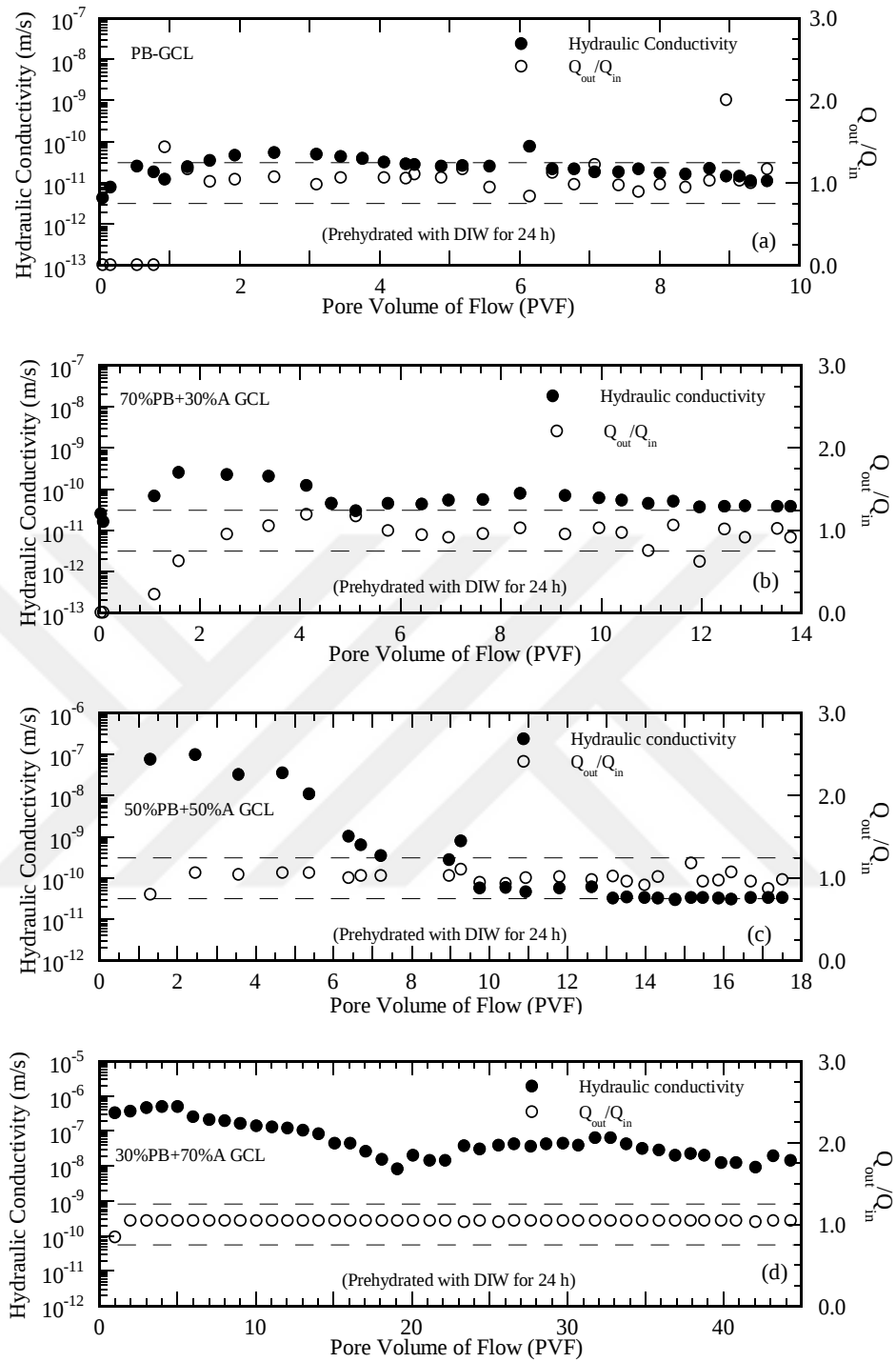


Figure 5.2 Influence of prehydration on the hydraulic conductivity of GCLs when permeated with DIW: a) PB, b) 70%PB+30%A, c) 50%PB+50%A and d) 30%PB+70%A

The comparisons of the final hydraulic conductivities of prehydrated and non-prehydrated GCLs are shown in Figure 5.3. It is clear that the hydraulic conductivities of prehydrated GCLs are somewhat lower than non-prehydrated

GCLs. These differences are about 3-fold for PB GCL and about 3.5-fold for 70%PB+30%A and 50%PB+50%A. At 30%PB+70%A GCL, which is the other attapulgite mixture, this difference is about 70-fold. As can be seen from these results, the differences between the hydraulic conductivities of prehydrated and non prehydrated GCLs gradually increased as the amount of attapulgite in GCL increased. This is proportional to the decrease of bentonite content or increase of attapulgite content in the GCL. Bentonite has significant swelling ability when compared to attapulgite. As the amount of bentonite in the mixture decreases, it becomes more difficult for GCL to swell and clog the flow paths. However, prehydrated 30%PB+70%A bentonite, which had been left in GCL for 24 hours, swelled during this hydration period to clog flow paths in a certain amount, causing a 70-fold decrease in the hydraulic conductivity compared to non-prehydration GCLs.

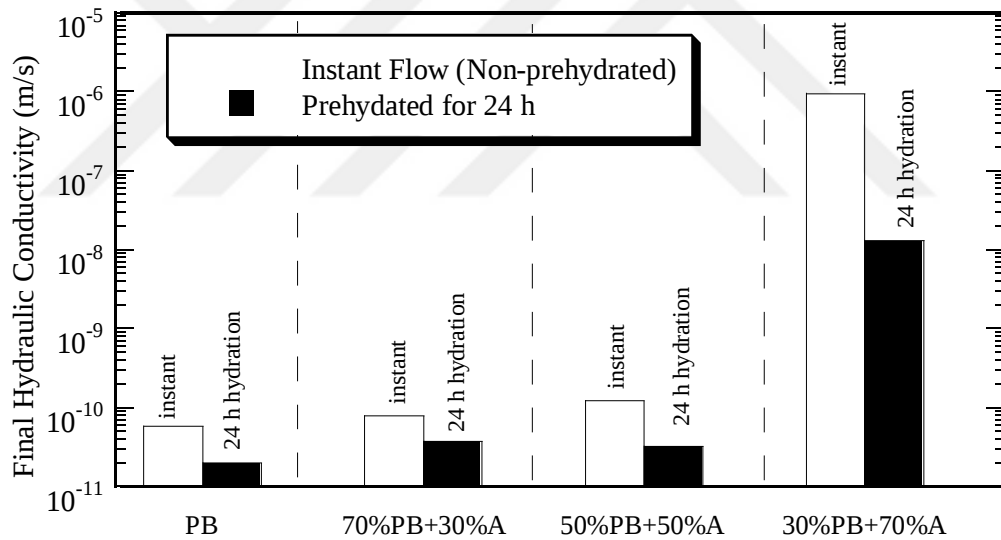


Figure 5.3 Comparison of the final hydraulic conductivities of non-prehydrated and prehydrated GCLs permeated with DIW

#### 5.4 Influence of Effective Stress on the Hydraulic Conductivity of non-prehydrated GCLs

To investigate the effect of cell pressure on the hydraulic conductivity, the cell pressures of some of the experiments conducted with DIW were gradually increased

(70 kPa, 140 kPa and 280 kPa). The hydraulic conductivities obtained by increasing the effective stress are shown in Table 5.2 and Figure 5.4.



Table 5.2 Summary of the hydraulic conductivity of GCLs under different effective stresses

| GCL Type          | Effective Stress (kPa) |                              |                      |                              |                      |                              |                      |                              |
|-------------------|------------------------|------------------------------|----------------------|------------------------------|----------------------|------------------------------|----------------------|------------------------------|
|                   | 35                     |                              | 70                   |                              | 140                  |                              | 280                  |                              |
|                   | Test Duration (days)   | Hydraulic Conductivity (m/s) | Test Duration (days) | Hydraulic Conductivity (m/s) | Test Duration (days) | Hydraulic Conductivity (m/s) | Test Duration (days) | Hydraulic Conductivity (m/s) |
| <b>PB</b>         | 60                     | $5.8 \times 10^{-11}$        | 42                   | $2.5 \times 10^{-11}$        | 44                   | $6.2 \times 10^{-11}$        | 122                  | $1.8 \times 10^{-12}$        |
| <b>70%PB+30%A</b> | 117                    | $7.9 \times 10^{-11}$        | 41                   | $3.5 \times 10^{-11}$        | 44                   | $1.8 \times 10^{-12}$        | 122                  | $8.6 \times 10^{-12}$        |
| <b>50%PB+50%A</b> | 277                    | $1.2 \times 10^{-10}$        | 43                   | $7.1 \times 10^{-11}$        | 44                   | $5.0 \times 10^{-11}$        | 122                  | $2.9 \times 10^{-12}$        |
| <b>30%PB+70%A</b> | 29                     | $9.5 \times 10^{-7}$         | -                    | -                            | -                    | -                            | -                    | -                            |

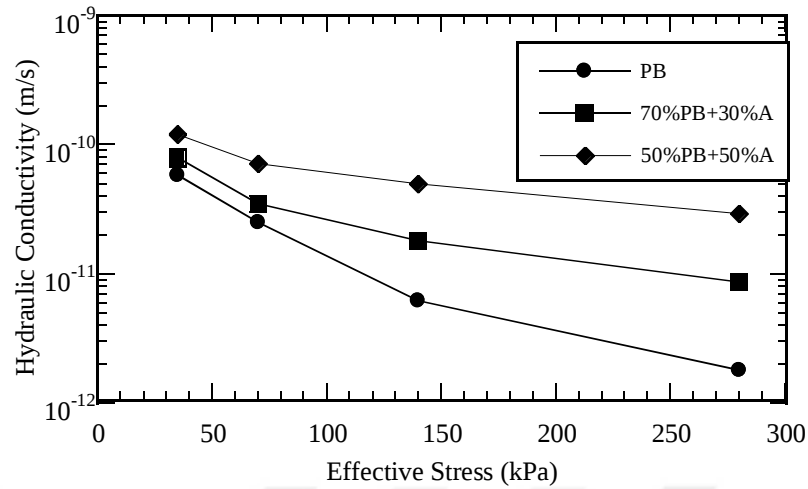


Figure 5.4 Influence of effective stress on the hydraulic conductivity of GCLs

After cell pressure was increased to 70 kPa, final hydraulic conductivity values for PB GCL, 70%PB+30%A GCL and 50%PB+50%A GCLs were  $2.5 \times 10^{-11}$  m/s,  $3.5 \times 10^{-11}$  m/s, and  $7.1 \times 10^{-11}$  m/s, respectively. After about one month, this pressure was increased from 70 kPa to 140 kPa. Then the hydraulic conductivity decreased to  $6.2 \times 10^{-12}$  m/s,  $1.8 \times 10^{-11}$  m/s, and  $5.0 \times 10^{-11}$  m/s, respectively (Figure 5.4). However, when the cell pressure was increased to 280 kPa, hydraulic conductivity values decreased to  $1.8 \times 10^{-12}$  m/s for PB, to  $8.6 \times 10^{-12}$  m/s, for 70%PB+30%A and to  $2.9 \times 10^{-11}$  m/s for 50%PB+50%A GCLs (Figure 5.4). Increasing the cell pressure led to decrease the pore spaces between the bentonite particles and consequently decreased the hydraulic conductivity of GCLs (Petrov & Rowe, 1997).

### 5.5 The Relationship between the Hydraulic Conductivities of Geosynthetic Clay Liners and Physico-Chemical Properties of Bentonite

The number of studies in which shows the relationship between the liquid limits of bentonites and the hydraulic conductivities of GCLs are very scarce in the literature. In these studies, generally the effects of aggressive salt solutions on liquid limit and hydraulic conductivity have been investigated. By increasing the concentration of the solutions prepared by the salt solutions, the liquid limits of the

bentonites decrease and the hydraulic conductivities of the GCLs increase (Gleason, Daniel, Eykholt, 1997; Lee et al., 2005).

The results of hydraulic conductivity tests conducted on three kinds of prehydrated GCLs and permeated with DIW were evaluated together with the liquid limits and plasticity indices of bentonites (Figure 5.5). While the liquid limit and plasticity index decrease to 253% and 175%, respectively, by increasing the attapulgite content to 50% in GCL, the change in the hydraulic conductivity is negligible. However, when the attapulgite content in GCL is increased to 70%, liquid limit and the plasticity index decreases significantly (to 189% and 106%, respectively), whereas hydraulic conductivity increases several orders of magnitude. This result also in agreement with the other findings of this study.

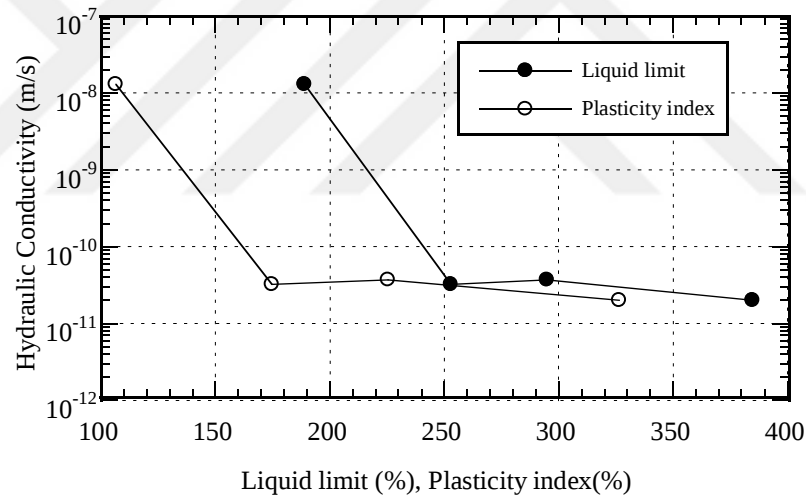


Figure 5.5 Change in hydraulic conductivity of GCLs with respect to consistency limits of bentonites

Figure 5.6 shows the relationship between the hydraulic conductivity of GCLs and the amount of fine and clay contents in bentonites. Similarly, the hydraulic conductivity negligibly increases, but still low, as the fine content decreases from 94% to 71% and clay content decreases from 77% to 54%. This range corresponds to the increase of attapulgite content to 50% in GCL as well. However, further increase in the attapulgite content (70%) lead to reduce fine and clay contents to 55% and

37%, respectively, whereas increase the hydraulic conductivity dramatically from  $3.2 \times 10^{-11}$  m/s to  $1.3 \times 10^{-8}$  m/s.

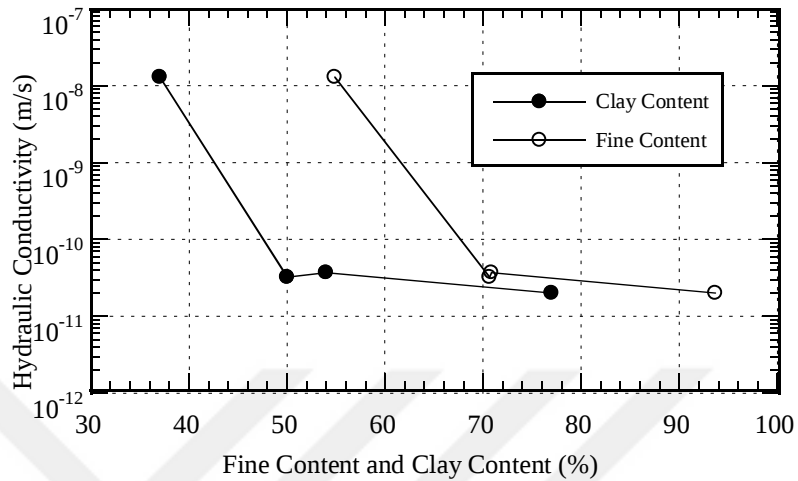


Figure 5.6 Hydraulic conductivity of GCLs as a function of fine content and clay content

Similar relationship obtained between hydraulic conductivity and CECs of bentonites (Figure 5.7). No significant change in hydraulic conductivity was observed until the attapulgite content was 50% or CEC of 56 cmol/kg. However, when CEC decreases to 49 cmol/kg, which corresponds to 70% attapulgite content, the hydraulic conductivity increased rapidly as shown in Figure 5.7.

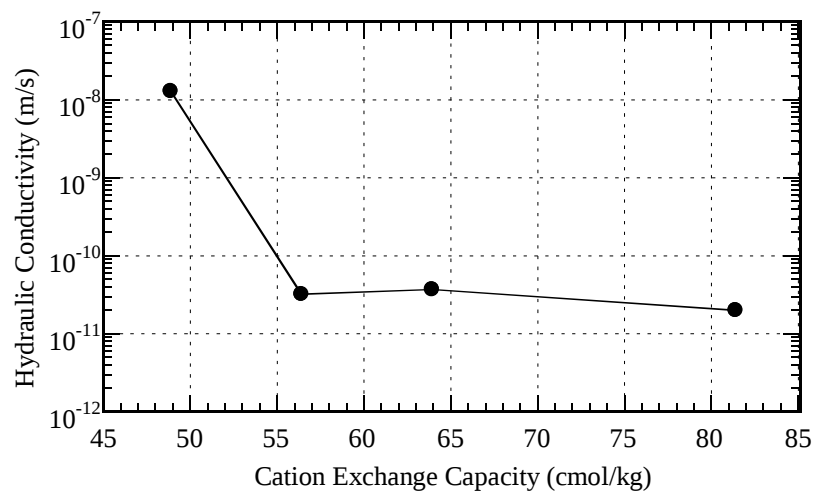


Figure 5.7 Hydraulic conductivity of GCL versus Cation Exchange Capacity of bentonite

In general, there is no significant change in the hydraulic conductivity of GCLs up to 50% attapulgite content when the permeant was DIW. However, the hydraulic conductivity increased several orders of magnitude by increasing the attapulgite content to 70%. However, it is noteworthy that when the hydraulic conductivities were related to the physicochemical properties of bentonites (consistency limits, fine grain and clay contents, and CEC), no linear trends were observed.



## **CHAPTER SIX**

### **HYDRAULIC CONDUCTIVITY OF GEOSYNTHETIC CLAY LINERS TO SALT SOLUTIONS**

#### **6.1 Background**

Numerous studies have been carried out to determine the effects of various chemical solutions on the hydraulic performance of GCLs, most of which use inorganic salts or organic chemical solutions. Chemical solutions are used to represent harmful liquids in landfills or mine tailings. The results of the studies show that the hydraulic conductivity increases with increasing concentration in the leachate (Ruhl & Daniel, 1997; Didier and Comeaga, 1997; Petrov & Rowe, 1997; Shackelford et al., 2000; Jo et al., 2001, 2005; Egloffstein, 2001; Vasko, Jo, Edil & Katsumi, 2001; Shan & Lai, 2002; Kolstad et al., 2004; Guyonnet et al., 2005; Lee et al., 2005; Lee & Shackelford, 2005; Katsumi et al., 2007, 2008). Bentonite in GCL is sensitive to chemical interactions with the leachate. It is observed that the cation exchange, which significantly changes the chemical properties of bentonite, affects the hydraulic conductivity behavior (Gleason et al. 1997; Ruhl & Daniel 1997; Shackelford et al. 2000; Jo et al. 2001, 2004; Vasko et al. 2001; Kolstad et al. 2004). Recent research shows that, under some conditions, the combined effects of cation exchange and physical dehydration can significantly increase the hydraulic conductivity of GCLs (Lin & Benson 2000).

Divalent cations are dominant in landfill leachates and in mine tailings (Shan & Lai, 2002; Benson et al., 2010; Bradshaw & Benson, 2013). Because of the difficulties in storage conditions of these liquids, however, it is preferable to use salt solutions in most of the soil mechanics laboratories which will show similar effects. It has been found that these divalent salts are easily replaced with monovalent cations present in bentonite and increase the hydraulic conductivity of GCL (Petrov et al., 1997; Ruhl & Daniel, 1997; Shan & Lai, 2002; Jo et al., 2001; Kolstad et al., 2004; Katsumi et al., 2008; Benson et al., 2010).

The effects of the concentration of chemical salt solutions on swelling and hydraulic conductivity of non-prehydrated GCLs have also been investigated so far. Swell index and hydraulic conductivity tests were carried out in different concentrations (0.01M - 1.00M) and different salt solutions (NaCl, KCl, LiCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, ZnCl<sub>2</sub>, CuCl<sub>2</sub> and LaCl<sub>3</sub>). It has been found that higher hydraulic conductivity and lower swell index values are obtained when the concentration and cation valence of the leachate increases. Moreover, it turns out that there is a strong relationship between the swell index and the hydraulic conductivity of GCLs (Jo et al., 2001).

Ashmawy et al. (2002) compared the hydraulic conductivity performance of seven types of GCLs three of which were polymer treated. They permeated GCLs with landfill leachates taken from three different waste storage sites. In these tests, it was observed that the hydraulic conductivity of GCLs was influenced by prehydration conditions and chemical compositions. It was also found that the concentration of divalent cations, such as Ca<sup>2+</sup> and Mg<sup>2+</sup>, are the most important cation types affecting the hydraulic conductivity of bentonite and these divalent cations increase the hydraulic conductivity due to the cation exchange mechanism that take place between leachate and bentonite.

In this study, hydraulic conductivity tests were carried out on three kinds of polymer and attapulgite mixture GCLs (50%PB+50%A, 30% PB+70%A, 100%PB GCLs) with different salt solutions at different concentrations. These experiments were first started with a monovalent KCl solution and followed by experiments with divalent CaCl<sub>2</sub>, MgCl<sub>2</sub> and CuCl<sub>2</sub>.

## **6.2 Hydraulic Conductivity of non-prehydrated GCLs with Monovalent Cations**

The effect of attapulgite-polymer mixed GCLs with monovalent salt solutions on the hydraulic conductivity has been investigated in this chapter. The 100 mM concentration was selected as the permeant which can be accepted at moderate leachate and may cause changes in hydraulic conductivity within a reasonable time.

Therefore, in the hydraulic conductivity tests, 100 mM KCl solution was first preferred in the non-prehydrated condition.

Hydraulic conductivity tests were performed on two GCLs (70%PB+30%A and 50%PB+50%A). As can be seen in Figure 6.1a, although the initial hydraulic conductivity value of 70%PB+30%A GCL was  $8.6 \times 10^{-7}$  m/s, this value decreased two-fold at the end of the test and was determined as  $3.8 \times 10^{-7}$  m/s. For 50%PB+50%A GCL, where the attapulgite content was increased to 50%, the hydraulic conductivity value decreased from  $7.0 \times 10^{-7}$  m/s to  $6.8 \times 10^{-8}$  m/s at 18 PVF which corresponds to ten-fold decrease.

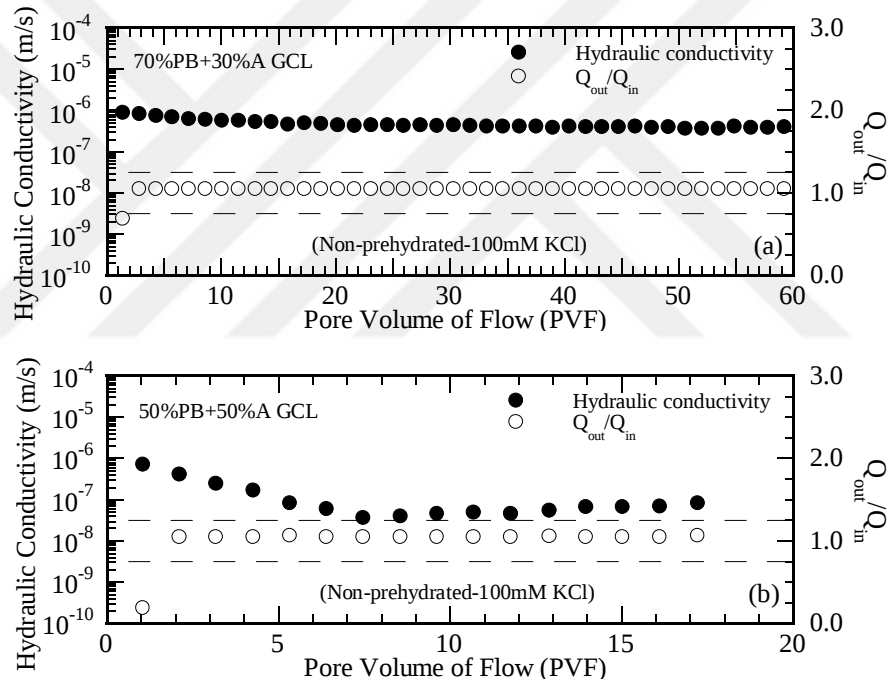


Figure 6.1 Hydraulic conductivity of geosynthetic clay liners permeated with 100 mM KCl solution: a) 70%PB+30%A and b) 50%PB+50%A

### **6.3 Hydraulic Conductivity of non-prehydrated and prehydrated GCLs with Divalent Cations**

#### **6.3.1 Hydraulic Conductivity with $\text{CaCl}_2$ solutions**

##### *6.3.1.1 Effect of Concentration on Hydraulic Conductivity*

The effect of the  $\text{CaCl}_2$  solution on the hydraulic conductivities of GCLs has been examined in this section. GCLs were subjected to hydraulic conductivity tests with different concentrations of salt solutions. The 50 mM concentration can be accepted as neither weak nor strong salt solution. In addition, 100 mM  $\text{CaCl}_2$  and 500 mM  $\text{CaCl}_2$  solutions were also preferred in the hydraulic conductivity tests. Hydraulic conductivity tests were conducted on non-prehydrated and prehydrated GCLs. The hydraulic conductivity tests were initiated on non-prehydrated GCLs using 50 mM  $\text{CaCl}_2$  solution (no prehydration phase applied, flow initiated directly or without waiting for 24h). As can be seen in Figure 6.2a, higher hydraulic conductivity value was obtained with PB GCL throughout the test duration. While the hydraulic conductivity value at the beginning was  $7.0 \times 10^{-7}$  m/s, this value showed a constant trend up to 33 PVF and the final hydraulic conductivity was  $5.0 \times 10^{-7}$  m/s. Similarly, the hydraulic conductivity of 70%PB+30%A GCL was initially  $3.5 \times 10^{-6}$  m/s, but its hydraulic conductivity decreased at about 105 PVF and then remained stable until the end of the test (Figure 6.2b). The hydraulic conductivity behavior of the other attapulgite GCL (50%PB+50%A) was somewhat different from other GCLs. While the hydraulic conductivity value at the beginning of the test was  $6.5 \times 10^{-7}$  m/s, this value tended to decrease until 24 PVF and then increased a little (Figure 6.2c).

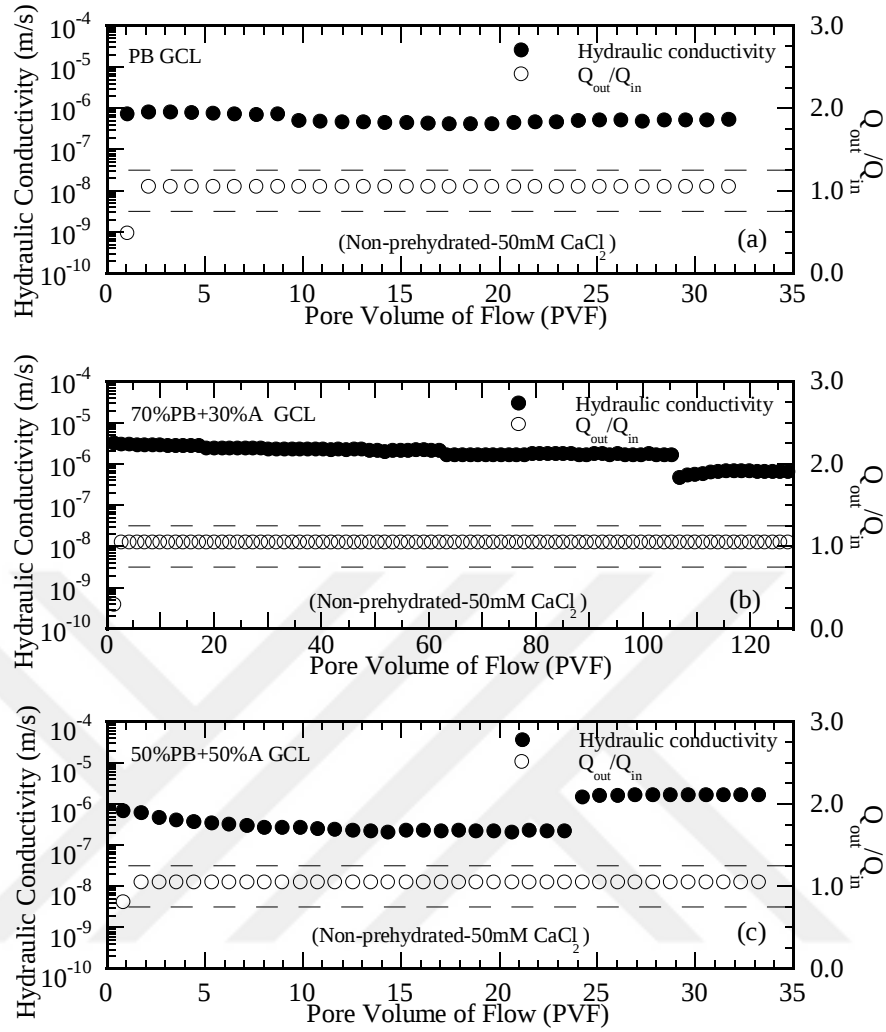


Figure 6.2 Hydraulic conductivity of non-prehydrated geosynthetic clay liners permeated with 50 mM  $\text{CaCl}_2$  solution: a) PB, b) 70%PB+30%A and c) 50%PB+50%A

The hydraulic conductivity of prehydrated GCLs with the same solution is shown in Figures 6.3a-c (here prehydration refers to the prehydration phase of GCLs before flow initiated using the permeant solution, which is  $\text{CaCl}_2$  herein, for 24h). The hydraulic conductivity behavior of PB GCL is different from the behavior obtained with non-prehydrated GCL. The hydraulic conductivity of the PB GCL with an initial hydraulic conductivity of  $1.0 \times 10^{-11}$  m/s increased over time with the replacement of the cations between the bentonite and the permeant. The hydraulic conductivity of the PB GCL reached  $1.4 \times 10^{-9}$  m/s and was about 10 times higher than its initial value at 8 PVF. This hydraulic conductivity value gradually increased up to 50 PVF and the test was terminated when the hydraulic conductivity reached to  $1.1 \times 10^{-7}$  m/s (Figure 6.3a). Prehydrated 70%PB+30%A GCL's hydraulic

conductivity follows a trend similar to non-prehydrated GCL (Figure 6.3b). But the hydraulic conductivity value of prehydrated 70%PB+30%A GCL was 10 times lower than that of non-prehydrated ( $1.7 \times 10^{-7}$  m/s). A different behavior was observed for the prehydrated 50%PB+50%A GCL when compared to the non-prehydrated GCL (Figure 6.3c). The hydraulic conductivity of 50%PB+50%A GCL was initially  $2.5 \times 10^{-7}$  m/s, however, it decreased to  $5.5 \times 10^{-9}$  m/s at 70 PVF. From 70 PVF to the end of the test (i.e. 80 PVF), the hydraulic conductivity increased to  $1.5 \times 10^{-8}$  m/s.

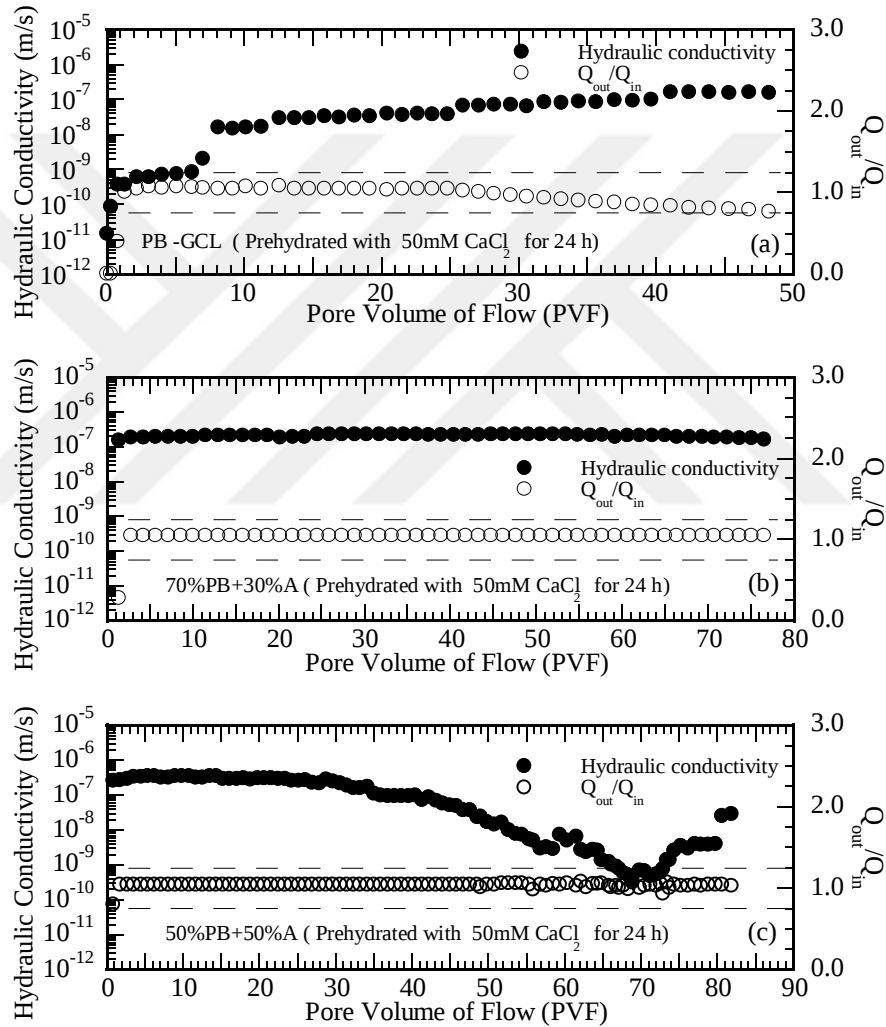


Figure 6.3 Hydraulic conductivities of prehydrated geosynthetic clay liners permeated with 50mM  $CaCl_2$  solution: a) PB, b) 70%PB+30%A and c) 50%PB+50%A

Hydraulic conductivity tests permeated with 100 mM  $CaCl_2$  solution were carried out with prehydrated condition on PB GCL and non-prehydrated condition on 70%PB+30%A and 50%PB+50%A GCLs. For the prehydrated PB GCL, the

hydraulic conductivity was  $6.8 \times 10^{-8}$  m/s at the beginning, but it tended to increase with the loss of bentonite swelling due to the high concentration of  $\text{CaCl}_2$ . This increase continued approximately to 30 PVF (Figure 6.4a). Afterwards, the hydraulic conductivity value stabilized and the test was terminated ( $1.9 \times 10^{-7}$  m/s). The hydraulic conductivity behaviors of 70%PB+30%A and 50%PB+50%A GCLs were similar. The final hydraulic conductivities of non-prehydrated 70%PB+30%A and 50%PB+50%A GCLs were measured as  $1.7 \times 10^{-6}$  m/s ve  $2.0 \times 10^{-6}$  m/s, respectively (Figure 6.4b-c). These non-prehydrated values are about 10 times higher than prehydrated PB GCL. Since the final hydraulic conductivity of prehydrated PB GCL is found to be approximately 50 times greater than allowable hydraulic conductivity value for barriers ( $1.0 \times 10^{-9}$  m/s), it was not preferred to carry out the hydraulic conductivity tests on prehydrated 70%PB+30%A and 50%PB+50%A GCLs. Because, as previously explained, attapulgitte had a tendency to increase the hydraulic conductivity of GCLs.

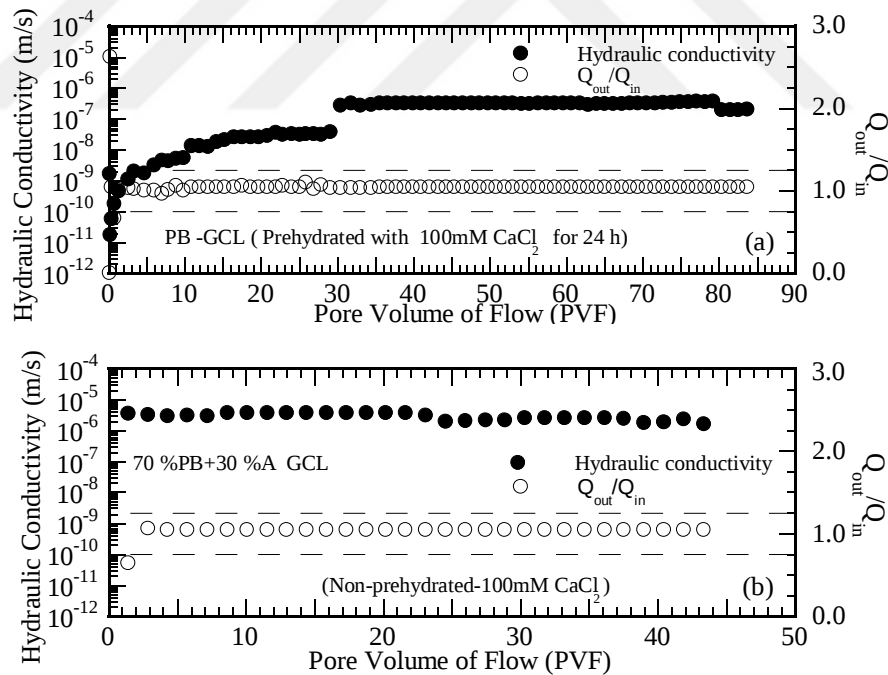


Figure 6.4 Hydraulic conductivities of geosynthetic clay liners permeated with 100 mM  $\text{CaCl}_2$  Solution: a) prehydrated PB, b) non-prehydrated 70%PB+30%A and c) non-prehydrated 50%PB+50%A

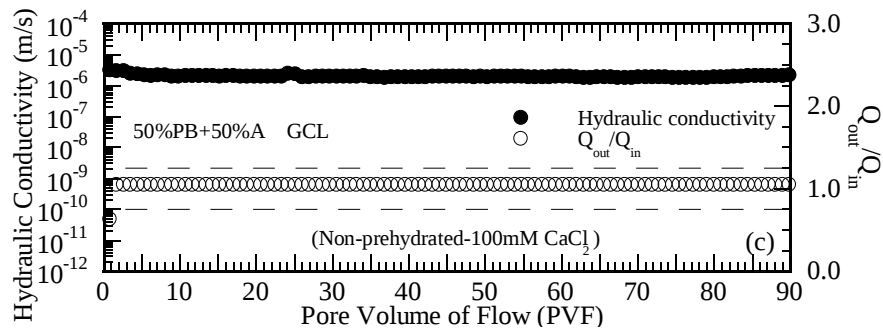


Figure 6.4 Continue

Hydraulic conductivity tests were also conducted with 500 mM  $\text{CaCl}_2$ , which can be accepted as an aggressive salt solution, to determine the concentration effect of the  $\text{CaCl}_2$  solution on the hydraulic conductivity of GCLs. Hydraulic conductivity of PB GCL was determined with prehydrated and non-prehydrated conditions. However, 50%PB+50%A GCL was tested only one time under non-prehydrated condition. The final hydraulic conductivity of prehydrated and non-prehydrated PB GCL was  $4.3 \times 10^{-7}$  m/s and  $1.0 \times 10^{-7}$  m/s, respectively (Figure 6.5a-b). The hydraulic conductivity of non-prehydrated 50%PB+50%A GCL was greater than PB GCL ( $1.7 \times 10^{-6}$  m/s) (Figure 6.5c). Since 500 mM is a high level concentration, prehydrating the GCL did not reduce the hydraulic conductivity.

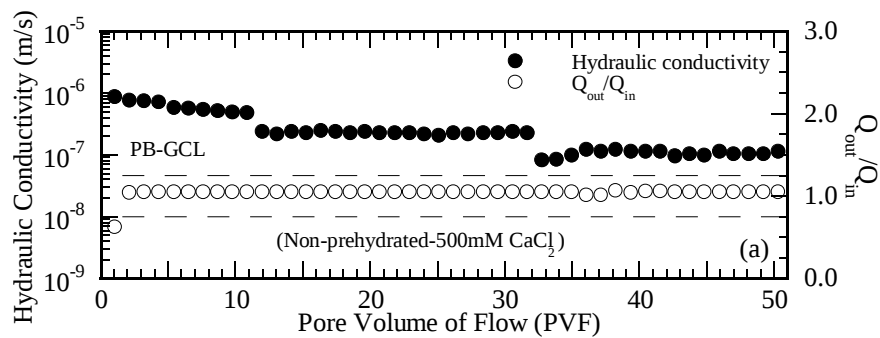


Figure 6.5 Hydraulic conductivities of geosynthetic clay liners permeated with 500 mM  $\text{CaCl}_2$  solution: a) non-prehydrated PB, b) prehydrated PB and c) non-prehydrated 50%PB+50%A

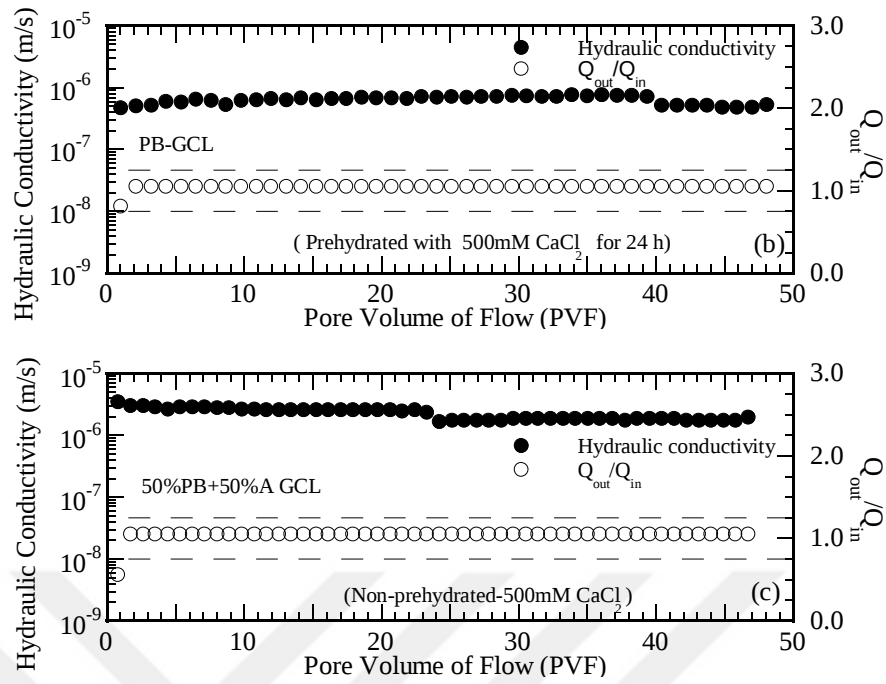


Figure 6.5 Continue

The effect of CaCl<sub>2</sub> concentration on the final hydraulic conductivity is shown in Figure 6.6. It is expected that increase in the concentration results in a sudden increase in the hydraulic conductivity of GCLs at 50 mM. Regardless of prehydration condition, hydraulic conductivity negligibly changed beyond this concentration level. The thickness of the adsorbed water layer surrounding the bentonite particles decreases as the concentration increases. This situation causes the increase of pore spaces between bentonite particles, resulting more flow channels for the mobilized water. Thus, the hydraulic conductivity increases (Jo et al., 2004, 2001; Katsumi et al., 2008).

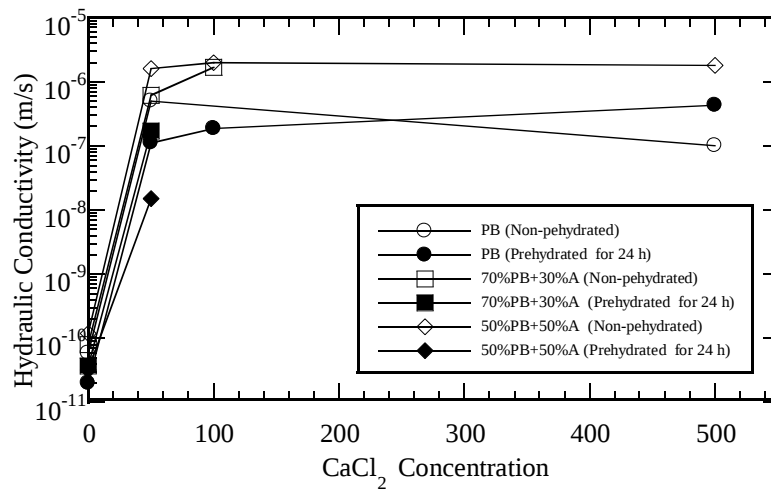


Figure 6.6 Effect of  $\text{CaCl}_2$  concentration on the hydraulic conductivity of GCLs

#### 6.3.1.2 pH and Electrical Conductivity Measurement

In the hydraulic conductivity tests, the liquids taken from the inflow and outflow valves were transferred to plastic tubes and the electrical conductivity (EC) and pH of the samples were measured (Figure 6.7).

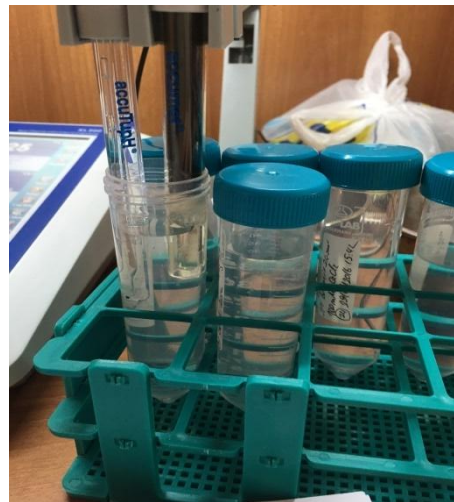


Figure 6.7 A picture taken during pH and EC measurement (Personal archive, 2015)

Since there were many samples tested so far, only some of them (50 and 100 mM) will be given herein to support the hydraulic conductivity results. The results of pH

and EC measurements of the inflow and outflow samples of prehydrated PB GCL permeated with the 50 mM  $\text{CaCl}_2$  solution are shown in Figure 6.8a. Initial  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  of PB GCL was 1.5, however, it came closer to 1.0 until the end of the hydraulic conductivity test. Similarly,  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$  ratio was 1.1 at the beginning of the experiment and it reached finally to 1.0.

For the other GCL, 70%PB+30%A GCL, the  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  o decreased to 1.1, whereas  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$  reached approximately 1.0 at the end of the test. The  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  and  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$  for 50%PB+50%A GCL had similar trend as with 70%PB+30%A GCL (Figure 6.8c). That is, the final  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  decreased to 1.1 and the final  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$  ratio was 1.0. The  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  of the samples with 100 mM  $\text{CaCl}_2$  solution was initially 1.5 and this ratio decreased to 1.4 at the end of the hydraulic conductivity test. Unlike  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$ ,  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$  ratio was initially 0.7 and it finally increased to 1.0 (Figure 6.8d).

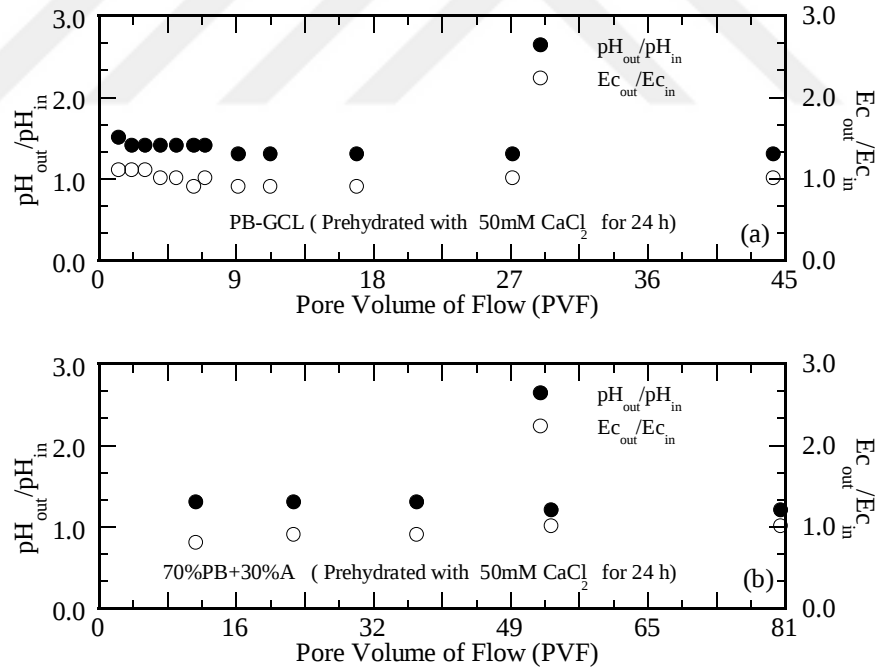


Figure 6.8 Outflow to inflow ratio of pH and electrical conductivity, when 50 mM  $\text{CaCl}_2$  was used as the permeant for: a) PB, b) 70%PB+30%A, c) 50%PB+50%A GCLs and d) when 100 mM  $\text{CaCl}_2$  was used as the permeant for PB GCL

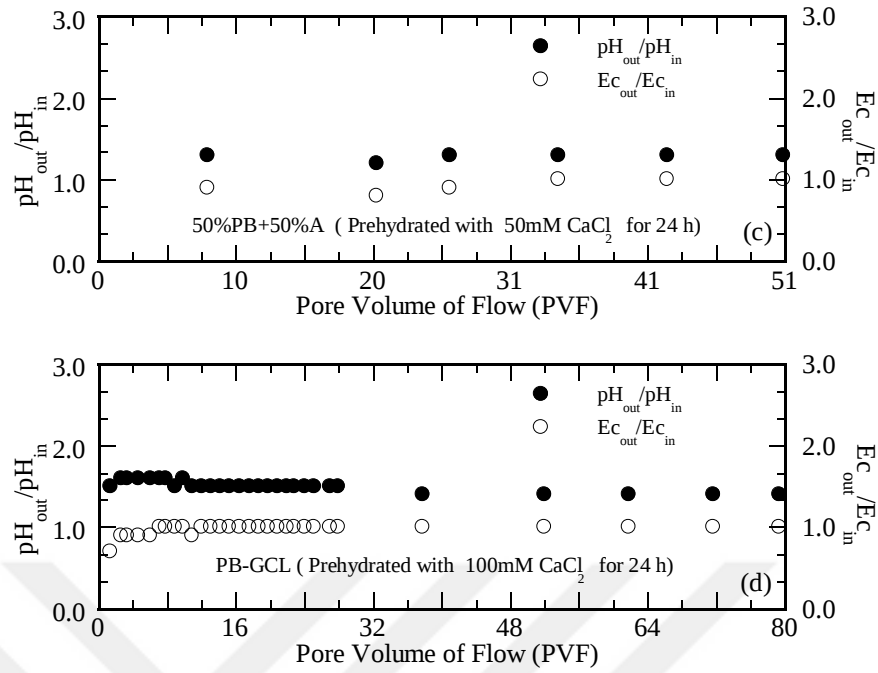


Figure 6.8 Continue

### 6.3.2 Hydraulic Conductivity of prehydrated GCLs with 50mM MgCl<sub>2</sub> Solution

The hydraulic conductivities of prehydrated GCLs using 50 mM MgCl<sub>2</sub> solution as the permeant are shown in Figure 6.9a-c. As can be seen from Figure 6.9a, the hydraulic conductivity of PB GCL was  $9.3 \times 10^{-10}$  m/s from the beginning of the test up to 4 PVF. At 5 PVF, however, a sudden drop was observed in the hydraulic conductivity ( $1.1 \times 10^{-10}$  m/s). Subsequently, the hydraulic conductivity value started to increase and reached to  $8.6 \times 10^{-8}$  m/s at 23 PVF. Then, the test was ceased. The hydraulic conductivity of 70%PB+30%A and 50%PB+50%A GCL were almost the same (Figure 6.9b-c). For these GCLs, the hydraulic conductivities changed little since the beginning of the experiment and finally measured as  $7.5 \times 10^{-7}$  m/s for 70%PB+30%A GCL and  $2.7 \times 10^{-7}$  m/s for 50%PB+50%A GCL.

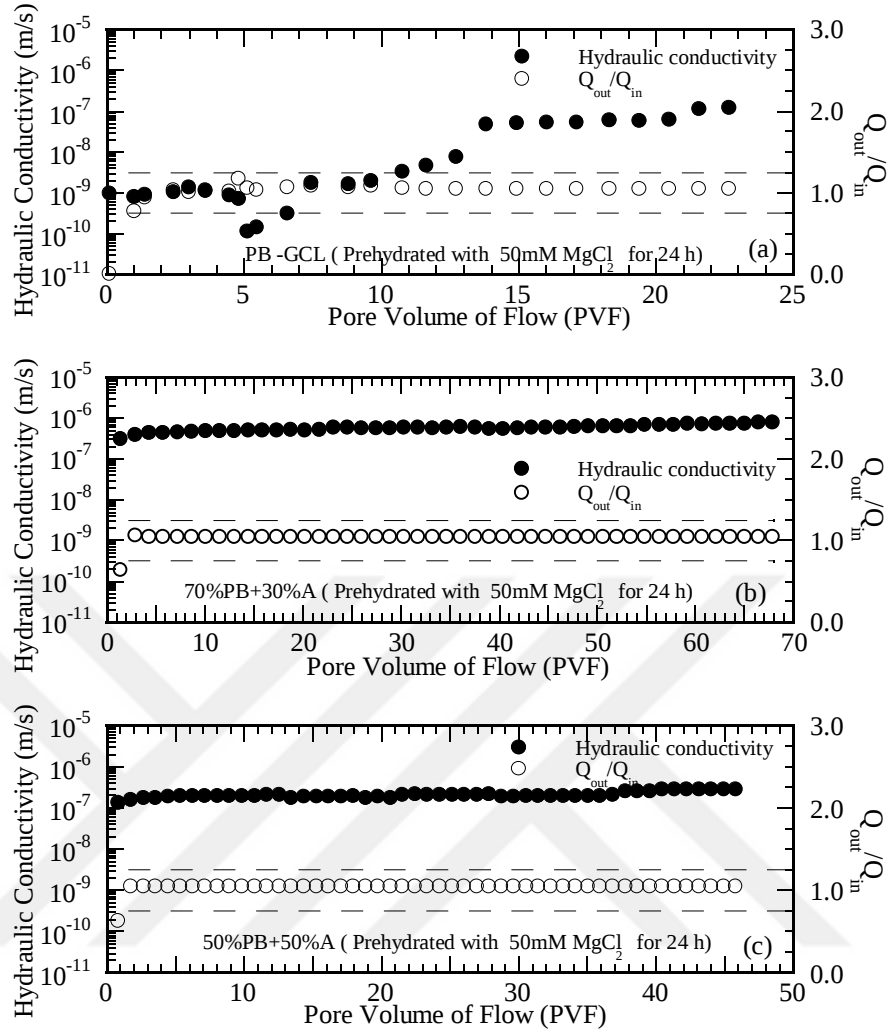


Figure 6.5 Hydraulic conductivities of prehydrated geosynthetic clay liners permeated with 50 mM  $MgCl_2$  solution: a) PB, b) 70%PB+30%A and c) 50%PB+50%A

### 6.3.2.1 pH and Electrical Conductivity Measurement

The pH and EC measurements of samples taken during the hydraulic conductivity of prehydrated PB GCL using magnesium chloride solution are shown in Figure 6.10.  $pH_{out}/pH_{in}$  ratio was 1.5 at the beginning, however, it was 1.2 at the end of the experiment. In contrast,  $EC_{out}/EC_{in}$  ratio was initially 1.1, then it reached chemical stability at the end (i.e. 1.0).

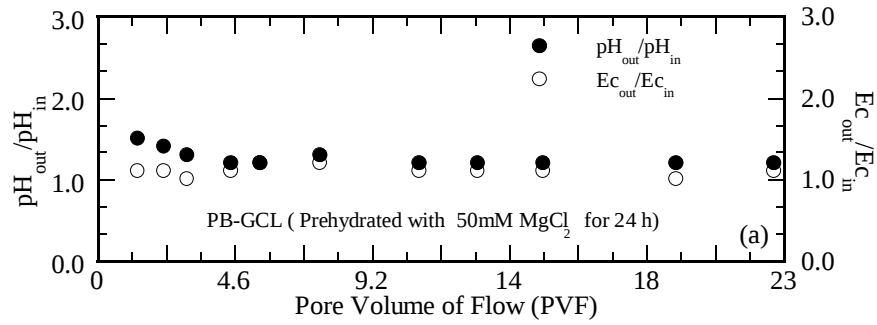


Figure 6.6 Outflow to inflow ratio of pH and electrical conductivity, when 50 mM  $\text{CaCl}_2$  was used as the permeant for PB GCL

### 6.3.3 Hydraulic Conductivity with 50mM $\text{CuCl}_2$ Solution

Similar experiments were carried out also with a heavy metal solution (50 mM  $\text{CuCl}_2$ ). These experiments were conducted on prehydrated GCLs. The hydraulic conductivity of PB GCL was initially  $8.0 \times 10^{-11}$  m/s which gradually decreased to  $1.5 \times 10^{-11}$  m/s until 1 PVF. Then, the hydraulic conductivity tended to increase between 1.5 PVF and 2.5 PVF about one order of magnitude (Figure 6.11a). From this point to the end of the test (i.e. 3.5 PVF), the amount of flow remarkably reduced and finally, flow stopped due to clogging of the influent tubing with copper precipitates. When the sample was opened, it appeared that the entrance of the flexible wall permeameter cell reacted with copper and became congested (Figure 6.11b-c).

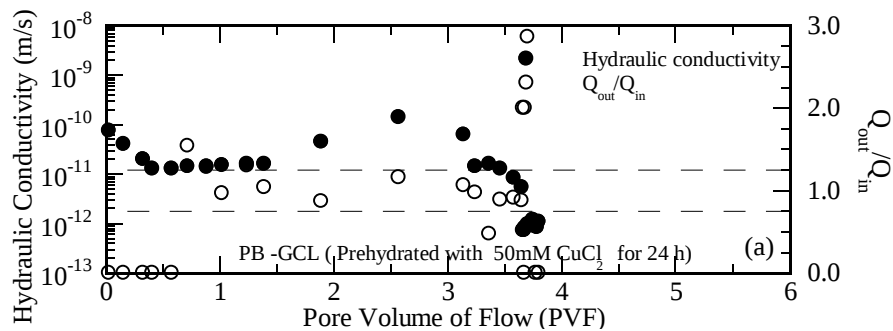


Figure 6.7 a) Hydraulic conductivity of PB-GCL permeated with 50 mM  $\text{CuCl}_2$  solution and copper induced clogs on: b) influent valve and c) tubing connected to the top pedestal of the permeameter and d) precipitated copper ions on the geosynthetic clay cover



Figure 6.8 Continue (Personal archive, 2016)

A similar case was observed in 70%PB+30%A GCL as well. This congestion was due to the fact that the inlet valve is metal and the valve reacts with the 50 mM  $\text{CuCl}_2$  solution. Hydraulic conductivity value was  $3.4 \times 10^{-10}$  m/s at the beginning, and this value decreased a little at 2 PVF and was balanced at  $7.3 \times 10^{-11}$  m/s. Thereafter, as shown in PB GCL, a sudden reduction in the hydraulic conductivity was observed because of clogging of the influent tubing and thus, the hydraulic conductivity test was terminated (Figure 6.12a-b).

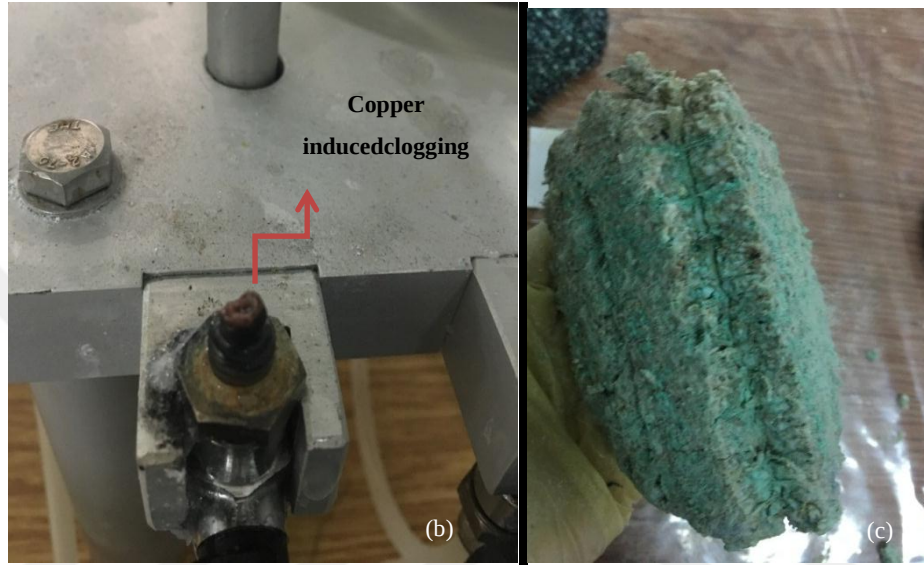
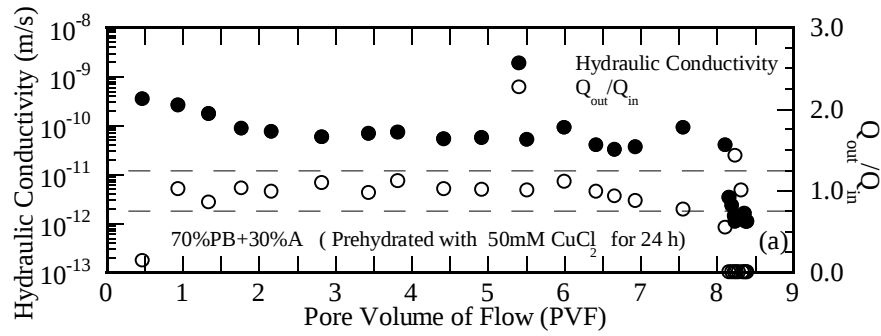


Figure 6.92 a) Hydraulic conductivity of 70%PB+30%A GCL permeated with 50 mM  $CuCl_2$  solution and b) copper induced clogs on influent valve and c) precipitated copper ions on the geosynthetic clay cover (Personal archive, 2016)

The behavior of another sample, 50%PB+50%A GCL, with the 50 mM  $CuCl_2$  solution was different from the other two GCLs. The hydraulic conductivity of this GCL was found to be higher than that of the other GCLs, and the obstruction observed at the entrance of the flexible wall permeameter cell was not observed this time (Figure 6.13). Hydraulic conductivity of 50%PB+50%A GCL was initially  $2.8 \times 10^{-8}$  m/s, it followed a fluctuative course until 10 PVF. Then, it was balanced, and the test was terminated ( $3.7 \times 10^{-9}$  m/s).

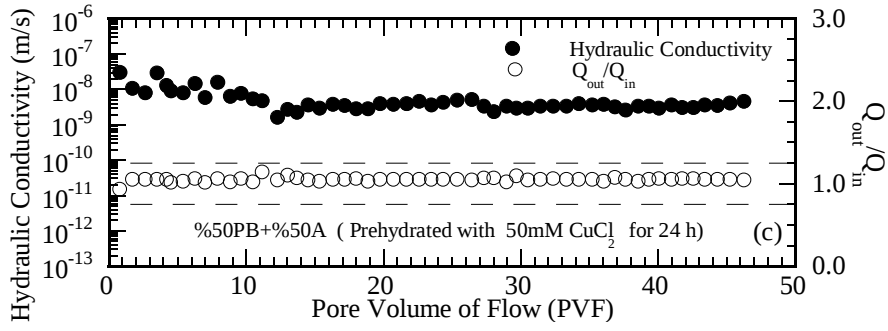


Figure 6.10 Hydraulic conductivity of 50%PB+50%A GCL permeated with 50 mM  $\text{CuCl}_2$  solution

### 6.3.3.1 pH and Electrical Conductivity Measurement

Figure 6.14a-c show the  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  and  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$  of the samples taken from the hydraulic conductivity tests of GCLs carried out with 50 mM  $\text{CuCl}_2$ . The  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  and  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$  ratios were 2.0 and 1.6 for PB GCL and 1.7 and 1.1 for 70%PB+30%A GCL. Since  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  and  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$  should have been  $1.0 \pm 0.1$  to terminate the experiments, these values show that hydraulic conductivity tests did not reach chemical equilibrium before termination. However, because of clogging of the influent tubings with copper species, the hydraulic conductivity tests had to be ceased.

$\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  and  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$  ratios of 50%PB+50%A GCL can also be seen in Figure 6.13c. At the beginning of the hydraulic conductivity test,  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  was 1.2 and it was 1.1 when the test was terminated. Similarly,  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$  ratio was 1.1 at the beginning, whereas it decreased to 0.9 at the end. In terms of  $\text{pH}_{\text{out}}/\text{pH}_{\text{in}}$  ve  $\text{EC}_{\text{out}}/\text{EC}_{\text{in}}$ , chemical stability was satisfied just for the 50%PB+50%A GCL.

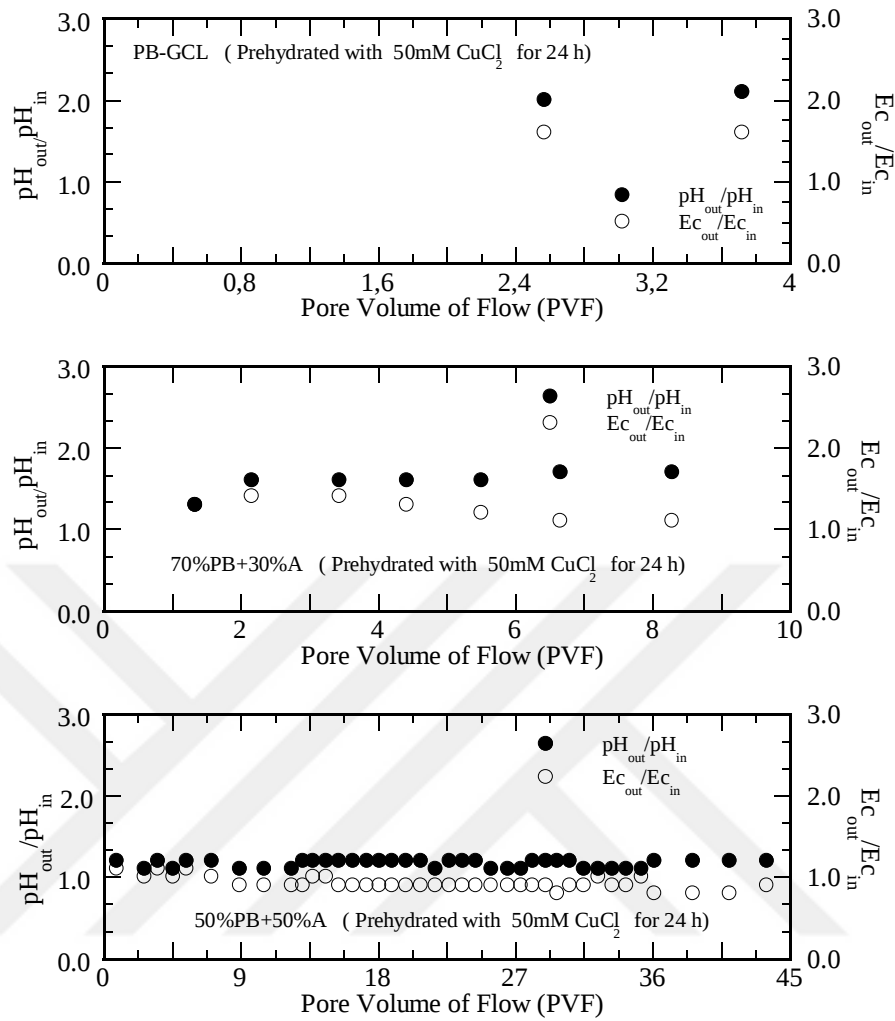


Figure 6.11 Outflow to inflow ratio of pH and electrical conductivity, when 50 mM  $CuCl_2$  was used as the permeant for a) PB, b) 70%PB+30%A and c) 50%PB+50%A GCLs

### 6.3.3.2 Chemical Analyses Conducted on Influent and Effluents

The effluent concentrations of the GCLs obtained throughout the hydraulic conductivity tests are shown in Figure 6.14a-c. The effluent concentrations were detected just for  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Cu^{2+}$ . The effluent concentrations are first given for PB GCL in Figure 6.15a. It is clear that  $Na^+$  concentration was significantly greater than the other exchangeable cations where it was 5559 mg/L at 1.4 PVF and 3994 mg/L at 3.7 PVF. In contrast,  $Ca^{2+}$  concentration was 29.3 mg/L at 1.4 PVF and decreased to 43.2 mg/L at 3.7 PVF. Similarly, the  $K^+$  concentration was 20.9 mg/L at 1.4 PVF and 19.7 mg/L at 3.7 PVF. In the  $Mg^{2+}$  concentration, it was only 90.3 mg/L at 3.7 PVF. The  $Cu^{2+}$  concentration in the effluent can be neglected, because it was

3.4 mg/L at 1.4 PVF and 0.5 mg/L at 3.7 PVF. This shows that the basic mechanism governing the hydraulic conductivity of PB GCL is the replacement of sodium with copper. However, almost all copper was adsorbed on the bentonite, negligible amount of copper was detected in the effluent.

Similar conclusion can be drawn for 70%PB+%30A GCL as well. The  $\text{Na}^+$  concentration decreased from 1959 mg/L to 251.3 mg/L throughout the test period. In contrast, the release of other exchangeable cations increased along the test duration. For example, it increased from 10.5 mg/L to 12.6 mg/L for  $\text{K}^+$ , from 62.4 mg/L to 133.2 mg/L for  $\text{Ca}^{2+}$ , from 36.3 mg/L to 90.1 mg/L for  $\text{Mg}^{2+}$ . However, the  $\text{Cu}^{2+}$  concentration decreased from 89.1 mg/L at 1.3 PVF to 1.4 mg/L at 8.3 PVF.

The effluent concentrations of 50%PB+50%A GCL is shown in Figure 6.15c. The  $\text{Na}^+$  concentration was again significantly high in the effluent with respect to other exchangeable cations. It was initially 1059 mg/L and then decreased to 8.7 mg/L at 42 PVF. Although negligible amount of  $\text{K}^+$  was detected, the  $\text{Ca}^{2+}$  concentration was 304.1 mg/L, whereas  $\text{Mg}^{2+}$  was 95.5 mg/L when the test was terminated. In addition, the  $\text{Cu}^{2+}$  concentration in the effluent was 341.0 mg/L at the end of the hydraulic conductivity test which was the highest among PB and 70%PB+%30A GCLs.

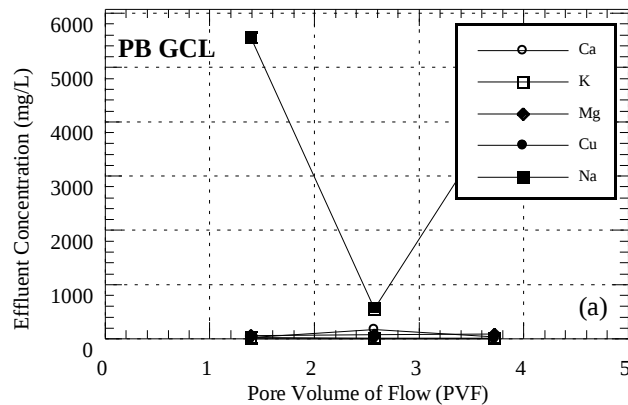


Figure 6.15 Effluent concentrations of exchangeable cations and copper a function of pore volumes of flow: a) PB, b) 70%PB+%30A and c) 50%PB+50%A

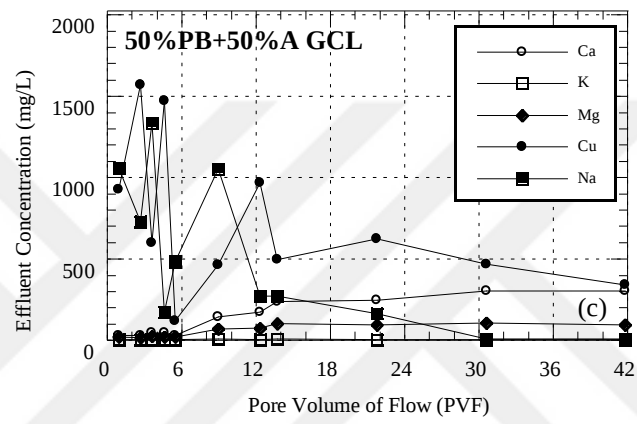
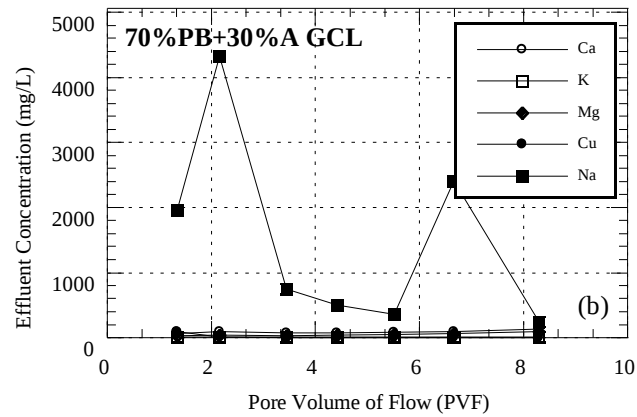


Figure 6.15 Continue

### 6.3.3.3 Brand New GCL and Post Test Changes on GCLs after $\text{CuCl}_2$ Permeation

The bentonites of a brand new GCL and post test GCL (after hydraulic conductivity tests with copper) were removed by cutting the fibers of the needle punctured geotextiles. Then, the exchangeable cation concentrations of bentonites (i.e. PB, 70%PB+30%A and 50%PB+50%A) were detected as a function of soluble and bound cations (Figure 6.16a-c).

As can be seen in Figure 6.15a-c, bentonite in brand new GCLs did not contain  $\text{Cu}^{2+}$ ; however, when it was permeated with  $\text{CuCl}_2$  solution, the  $\text{Cu}^{2+}$  amount in the GCL increased. This suggests that bentonite takes up  $\text{Cu}^{2+}$  from the solution and releases Na, K, Ca and Mg to the solution.

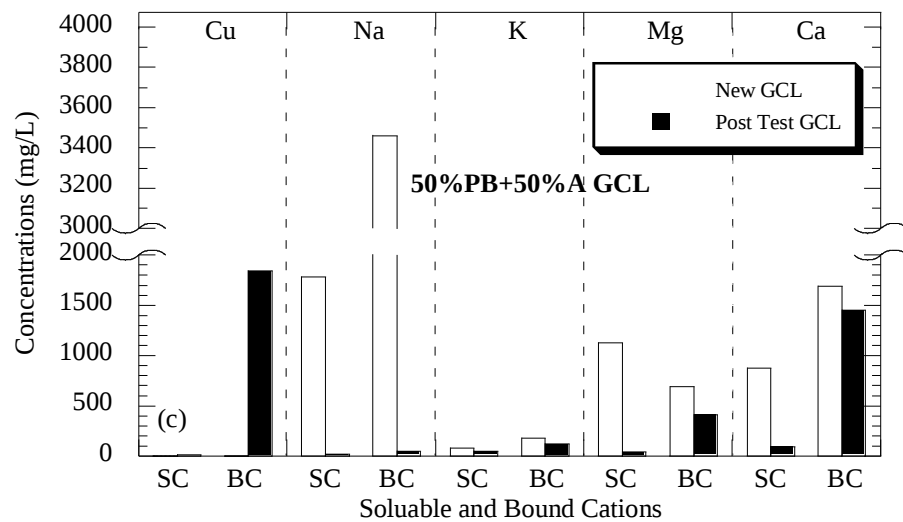
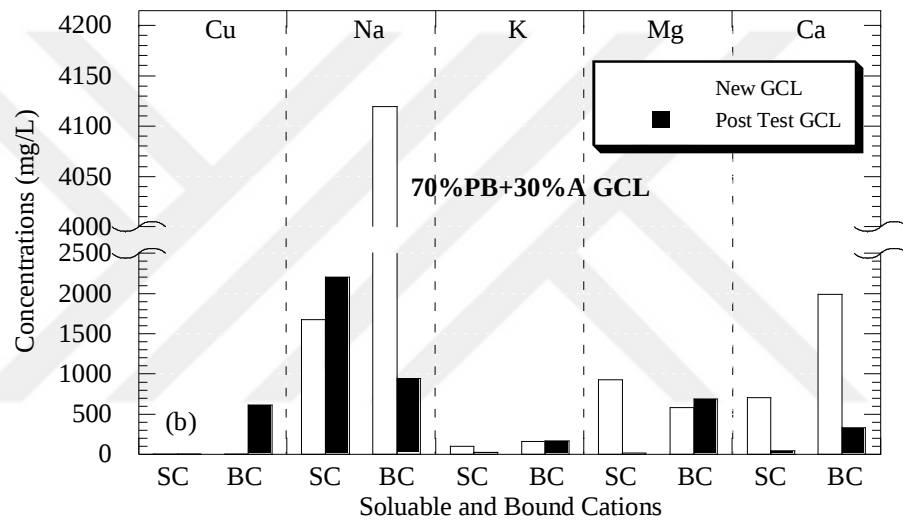
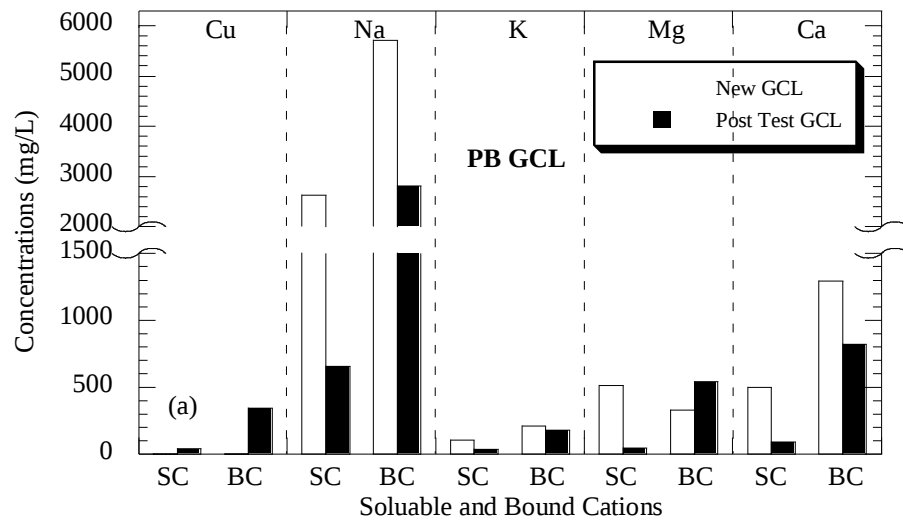


Figure 6.12 Soluble and Bound cation concentrations of brand new and post test GCLs: a) PB, b) 70%PB+30%A and c) 50%PB+50%A

#### 6.4 Discussion of the test results with salt solutions

A comparison of three different salt solutions having divalent cations in the same molar concentrations is given in Figure 6.17. When the permeant was 50 mM  $\text{CaCl}_2$  solution, the hydraulic conductivity of PB GCL was observed to be about 2-3 times greater than attapulgite mixed GCLs. In the case of using 50 mM  $\text{MgCl}_2$  solution, the hydraulic conductivity value of 70%PB+30%A GCL was about 1.5-2 times greater than other GCLs. In addition, the hydraulic conductivities of 50%PB+50%A GCL with 50 mM  $\text{CuCl}_2$  solution were about 5 orders of magnitude greater than the others. It can be concluded that the hydraulic conductivities of PB, 70%PB+30%A, and 50%PB+50%A GCLs had more or less the same hydraulic conductivity with 50 mM  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solutions, which is significantly greater than the allowable limits of barriers (i.e.  $1.0 \times 10^{-9}$  m/s). Unlike these solutions,  $\text{CuCl}_2$  solution had negative effect on the hydraulic conductivity of 50%PB+50%A GCL. Other two GCLs had low hydraulic conductivity because of clogging of the influent tubings (Figure 6.11 and Figure 6.12).

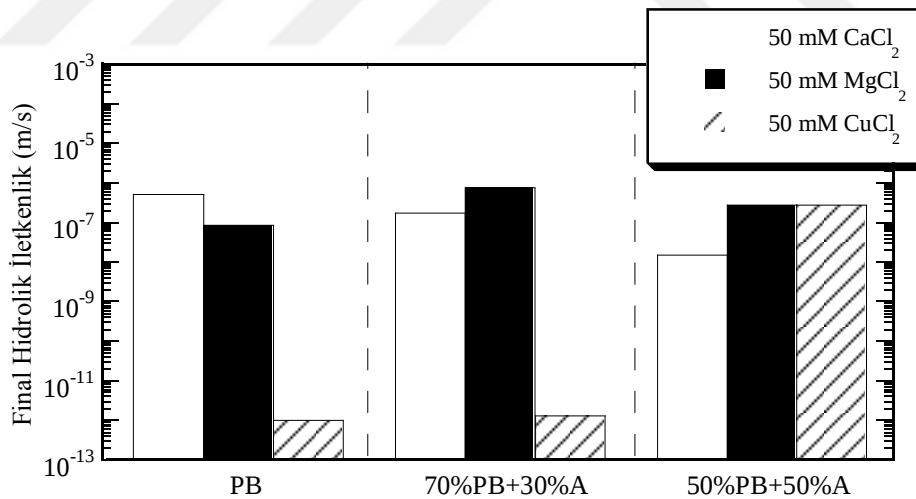


Figure 6.1713 The effect of divalent solutions on the hydraulic conductivities of geosynthetic clay liners

Studies conducted by many researchers have shown that GCL has barrier performance when the swell index is sufficiently high ( $\geq 15$  mL/2g) (Jo et al., 2001; Katsumi et al. 2007). It has been reported that there were differences in the swell index values of GCLs between DIW and salt solutions used in the swell index tests

of bentonites. Due to the chemical content of the salt solutions, the swell index values of bentonites are very low because divalent cations do not allow bentonite particles to swell.

The results obtained from the swell index test of bentonites are shown in Figure 6.18 together with their hydraulic conductivity values. As can be seen in Figure 6.18, as the swell indices increase, the hydraulic conductivities of the GCLs decrease. On the contrary, as the swell indices decrease, the hydraulic conductivities increase. In this study, the swell index values of the salt solutions ranged from 5 mL/2g ile 10 mL/2g, while the hydraulic conductivity values were measured between  $1.1 \times 10^{-6}$  m/s and  $1.1 \times 10^{-8}$  m/s. However, this differs only in 50 mM  $\text{CuCl}_2$ . The swell index values of the GCLs with the  $\text{CuCl}_2$  solution are similar to those of the other divalent salt solutions, but their hydraulic conductivities (excluding 50%PB+50%A) are about 5 orders of magnitude lower than the others.

The general behavior given in Figure 6.18 is also compared with the literature. Accordingly, the relationship given by Katsumi et al. (2008) is drawn on the figure as well. The behavior obtained from this study is similar to some extent with the swell index-hydraulic conductivity behavior of GCLs, when GCL contains 100% bentonite (with no attapulgite additive). However, some values of this study are also apart from the Katsumi's trend which is due to the use of attapulgite mixed GCLs in this study.

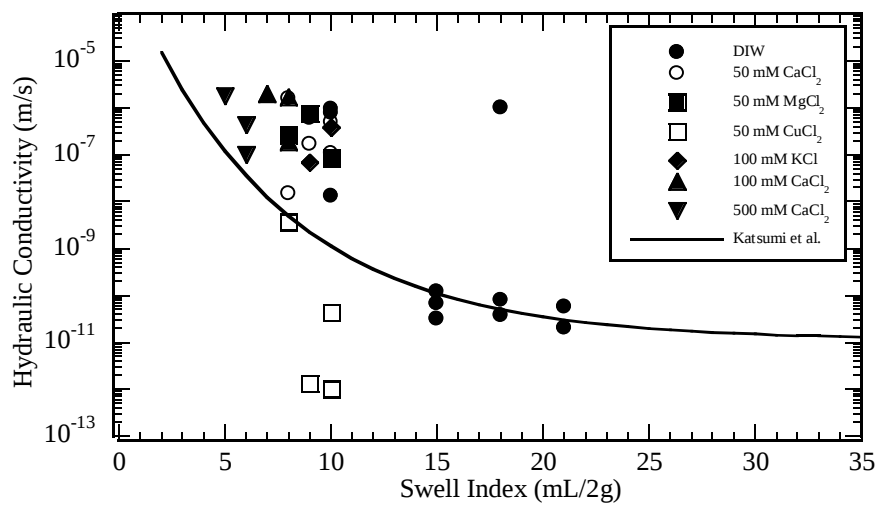


Figure 6.18 Relationship between the swell index and the hydraulic conductivity of GCLs

In Figure 6.18, it is not possible to understand the effect of attapulgite mixtures on the swell index and hydraulic conductivity. For this reason, the same figure is redrawn by showing the attapulgite mixtures separately (Figure 6.19). It should be noted, however, that for each type of GCL, deionized water and salt water are evaluated together. PB GCL is expected to be closer to the line of the equation proposed by Katsumi et al. (2008), because this equation is proposed for GCLs containing bentonite only. However, as can be seen in Figure 6.18, while the results of PB GCL with DIW follow the curve, the results obtained with the salt solutions are among the points at which the attapulgite mixtures accumulated.

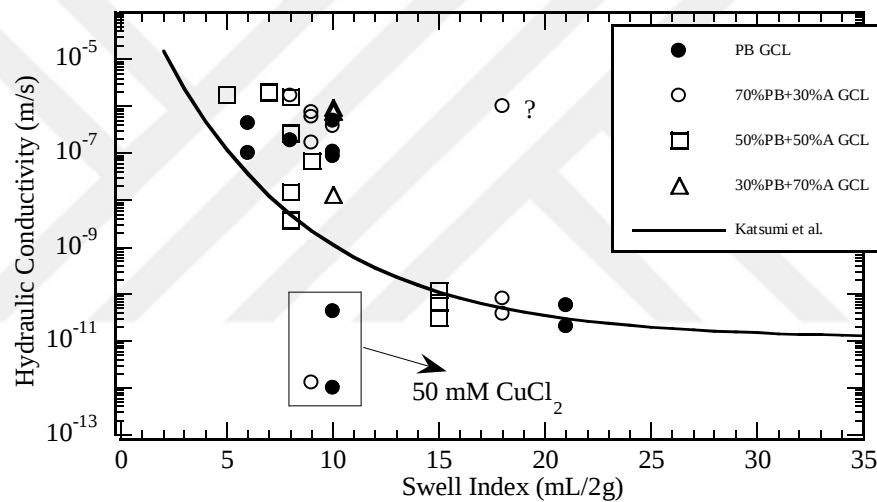


Figure 6.19 Swell index vs. hydraulic conductivity in terms of attapulgite content in GCLs

During the hydraulic conductivity tests, the changes in the height and water contents of the GCLs may give some information about the hydraulic conductivity. For this reason, GCL heights and water contents were measured before and after the hydraulic conductivity tests (Table 6.1) and the results were evaluated together with the attapulgite content and hydraulic conductivity. In this evaluation, non-prehydrated and prehydrated GCLs were considered together.

Table 6.1 Initial and post-test height and water contents of GCLs

| Test No | GCL Type           | Permeant Solution        | GCL Height (cm) |                | Water Content (%) |                |
|---------|--------------------|--------------------------|-----------------|----------------|-------------------|----------------|
|         |                    |                          | H <sub>i</sub>  | H <sub>f</sub> | w <sub>i</sub>    | w <sub>f</sub> |
| 1       | PB                 | DIW                      | 1.03            | 0.93           | 9.4               | 80             |
| 2       | PB (24 hour)       | DIW                      | 0.69            | 0.93           | 9.4               | 105            |
| 3       | 70%PB+30%A         | DIW                      | 0.66            | 0.62           | 9.6               | 56             |
| 4       | 70%PB+30%A         | DIW                      | 1.05            | 1.04           | 9.6               | 59             |
| 5       | 70%PB+30%A(24hour) | DIW                      | 0.76            | 0.94           | 9.6               | 105            |
| 6       | 50%PB+50%A         | DIW                      | 1.19            | 0.84           | 9.5               | 69             |
| 7       | 50%PB+50%A         | DIW                      | 1.01            | 0.96           | 9.5               | 91             |
| 8       | 50%PB+50%A(24hour) | DIW                      | 0.74            | 0.9            | 9.5               | 115            |
| 9       | 30%PB+70%A         | DIW                      | 1.00            | 0.74           | 9.4               | 103            |
| 10      | 30%PB+70%A         | DIW                      | 0.71            | 0.64           | 9.4               | 118            |
| 11      | 30%PB+70%A(24hour) | DIW                      | 0.82            | 1.00           | 9.4               | 107            |
| 12      | 70%PB+30%A         | 100 mM KCl               | 0.78            | 0.78           | 9.6               | 97             |
| 13      | 50%PB+50%A         | 100 mM KCl               | 0.78            | 0.84           | 9.5               | 80             |
| 14      | PB                 | 50 mM CaCl <sub>2</sub>  | 0.71            | 0.68           | 9.4               | 83             |
| 15      | PB (24 hour)       | 50 mM CaCl <sub>2</sub>  | 0.62            | 0.82           | 9.4               | 76             |
| 16      | 70%PB+30%A         | 50 mM CaCl <sub>2</sub>  | 0.69            | 0.78           | 9.6               | 92             |
| 17      | 70%PB+30%A(24hour) | 50 mM CaCl <sub>2</sub>  | 0.7             | 0.76           | 9.6               | 96             |
| 18      | 50%PB+50%A         | 50 mM CaCl <sub>2</sub>  | 0.72            | 0.81           | 9.5               | 91             |
| 19      | 50%PB+50%A(24hour) | 50 mM CaCl <sub>2</sub>  | 0.82            | 0.89           | 9.5               | 87             |
| 20      | PB (24 hour)       | 50 mM MgCl <sub>2</sub>  | 0.72            | 0.80           | 9.4               | 72             |
| 21      | 70%PB+30%A(24hour) | 50 mM MgCl <sub>2</sub>  | 0.7             | 0.69           | 9.6               | 90             |
| 22      | 50%PB+50%A(24hour) | 50 mM MgCl <sub>2</sub>  | 0.86            | 0.91           | 9.5               | 90             |
| 23      | PB (24 hour)       | 50 mM CuCl <sub>2</sub>  | 0.81            | 0.99           | 9.4               | 80             |
| 24      | 70%PB+30%A(24hour) | 50 mM CuCl <sub>2</sub>  | 0.73            | 0.76           | 9.6               | 88             |
| 25      | 50%PB+50%A(24hour) | 50 mM CuCl <sub>2</sub>  | 0.81            | 0.96           | 9.5               | 91             |
| 26      | PB (24 hour)       | 100 mM CaCl <sub>2</sub> | 0.83            | 0.83           | 9.4               | 82             |
| 27      | 70%PB+30%A         | 100 mM CaCl <sub>2</sub> | 0.63            | 0.63           | 9.6               | 82             |
| 28      | 50%PB+50%A         | 100 mM CaCl <sub>2</sub> | 0.81            | 0.81           | 9.5               | 90             |
| 29      | PB                 | 500mM CaCl <sub>2</sub>  | 0.78            | 0.74           | 9.4               | 77             |
| 30      | PB (24 hour)       | 500 mM CaCl <sub>2</sub> | 0.7             | 0.73           | 9.4               | 71             |
| 31      | 50%PB+50%A         | 500 mM CaCl <sub>2</sub> | 0.92            | 0.90           | 9.5               | 86             |

The final water contents of GCLs permeated with DIW ranged from 58% to 118%, while the final water contents of the same GCLs permeated with salt solutions ranged from 71% to 97% (Figure 6.20a-b). In salt solutions, 50%PB+50%A GCL generally had the highest final water content. Independent of the types and

concentration of the permeants, it was found that attapulgite increased the final water content of GCLs (Figure 6.20a). However, this increase did not affect the hydraulic conductivity (Figure 6.20b).

Figure 6.20b also shows that the final water contents of prehydrated GCLs permeated with DIW are greater than those of non-prehydrated GCLs. However, when  $\text{CaCl}_2$  was used as the permeant, the final water contents of non-prehydrated PB and 50%PB+50%A GCLs were 83% and 91%, and their hydraulic conductivity values were  $5.0 \times 10^{-7}$  m/s and  $6.1 \times 10^{-7}$  m/s, respectively. When the same GCLs were prehydrated and permeated with  $\text{CaCl}_2$ , the final water contents were 76% and 87% and the final hydraulic conductivity values were  $1.1 \times 10^{-7}$  m/s and  $1.5 \times 10^{-8}$  m/s, respectively. In contrast, a different situation was observed for the other attapulgite mixed GCL (70%PB+30%A) when permeated with 50 mM  $\text{CaCl}_2$ . In the non-prehydrated case, the final water content was 92% and the hydraulic conductivity was  $6.1 \times 10^{-7}$  m/s, whereas the final water content was slightly higher (96%) and the hydraulic conductivity value was 3.6 times less ( $1.7 \times 10^{-7}$  m/s) for prehydrated case. In addition to this, the hydraulic conductivity tests were carried out on the prehydrated GCLs with 50 mM  $\text{MgCl}_2$  solutions. In these tests, the final water content of PB GCL was 72% and final hydraulic conductivity was  $8.6 \times 10^{-8}$  m/s. The water contents of 70%PB+30%A and 50%PB+50%A GCLs were 90% and their final hydraulic conductivities were  $7.5 \times 10^{-7}$  m/s and  $2.7 \times 10^{-7}$  m/s. The hydraulic conductivity tests conducted with 50 mM  $\text{CuCl}_2$  solutions were prehydrated as well. The water content of these GCLs were 80% for PB GCL, 88% for 70%PB+30%A GCL, and 91% for 50%PB+50%A GCL. In addition, their hydraulic conductivity values were  $1.0 \times 10^{-12}$  m/s,  $1.3 \times 10^{-12}$  m/s and  $3.7 \times 10^{-9}$  m/s, respectively.

When the concentration was increased to 100 mM, the final water contents of non-prehydrated 70%PB+30%A and 50%PB+50%A GCLs were 82% and 90%, respectively, with  $\text{CaCl}_2$  solution and the final hydraulic conductivity values were measured  $1.7 \times 10^{-6}$  m/s and  $2.0 \times 10^{-6}$  m/s, respectively. The hydraulic conductivity tests were performed on prehydrated PB GCL. The final water content of prehydrated PB GCL was found to be 82% and the hydraulic conductivity was found

to be  $1.9 \times 10^{-7}$  m/s. Another salt solution used in the experiments is 100 mM KCl. The final water contents of non-prehydrated 70%PB+30%A and 50%PB+50%A GCLs were 97% and 89%, and the final hydraulic conductivity values were  $3.8 \times 10^{-7}$  m/s and  $6.8 \times 10^{-8}$  m/s, respectively. As the aggressive salt solution, 500 mM  $\text{CaCl}_2$  was preferred and the hydraulic conductivity tests were carried out both prehydrated and non-prehydrated GCLs. The final water contents of non-prehydrated PB and 50%PB+50%A GCLs were 77% and 86% and the hydraulic conductivity values were  $1.0 \times 10^{-7}$  m/s and  $1.8 \times 10^{-6}$  m/s, respectively. The prehydrated PB GCL had slightly lower final water content than non-prehydrated GCL with the same permeant (71%). The final hydraulic conductivity, however, was  $4.3 \times 10^{-7}$  m/s.

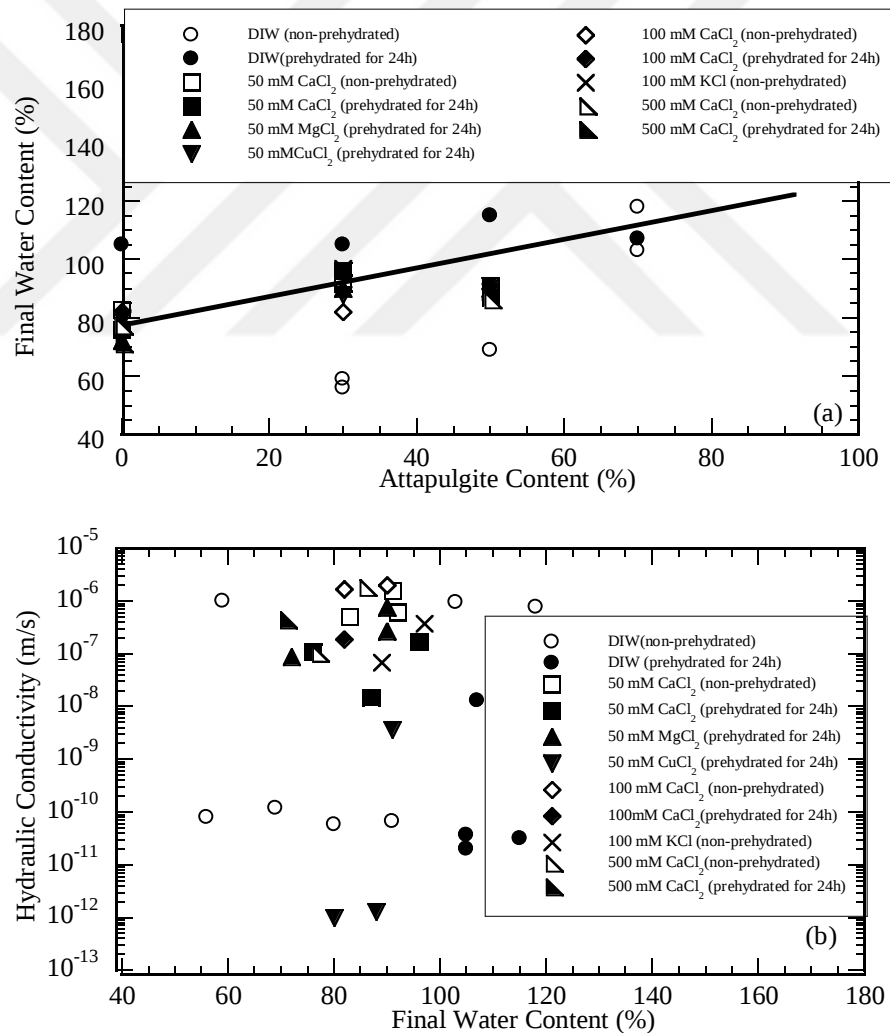


Figure 6.14 Relationship between: a) final water content and attapulgite content and b) hydraulic conductivity and final water content

Figure 6.21a shows the relationship between final GCL height and attapulgite content. The final heights of GCLs were generally higher when permeated with DIW rather than salts. The hydraulic conductivity tests with salt solutions, for example, 70%PB+30%A GCL had the lowest thickness of 0.69 cm. The reason for this is that the cations in the salt solutions suppress the absorbed water layer thickness around the bentonite.

The relationship between final GCL height and hydraulic conductivity is shown in Figure 6.21b. As can be seen in Figure 6.21b, the hydraulic conductivity to DIW did not change even though the final GCL thickness increased. However, the hydraulic conductivity to salt solutions decreased when the final GCL thickness increased.

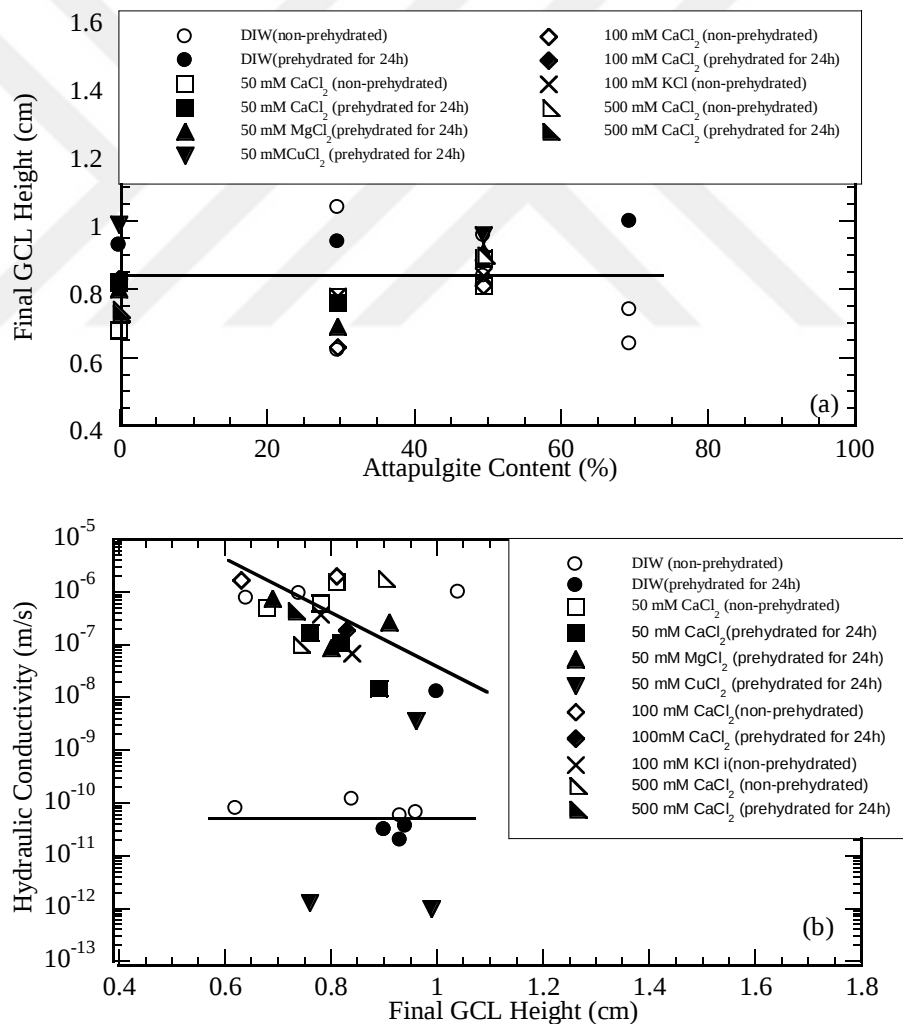


Figure 6.21 Relationship between: a) final GCL height and attapulgite content and b) hydraulic conductivity and final GCL height

## CHAPTER SEVEN

### SUMMARY AND CONCLUSIONS

In this study, the hydraulic conductivity of a polymer and attapulgite mixed polymer GCLs are presented. Hydraulic conductivity tests were carried out on four different GCLs with DIW. One of the GCLs was eliminated and the tests were continued with the other three GCLs when permeated with salt solutions.

The highlighted points obtained in this study are summarized below:

- As the attapulgite content in the GCL increased, the liquid limit, fine and clay contents of bentonite-attapulgite mixture decreased linearly.
- Except  $Mg^{2+}$ , soluble and bound cation concentrations of exchangeable cations were very close to each other.
- As the attapulgite content in the GCL increased, the cation exchange capacity (CEC) linearly decreased to about 45cmol/kg.
- The swell index of PB GCL, 70%PB+30%A GCL, 50%PB+50%A GCL and %30PB+%70A GCL in DIW were 21 mL/2g, 18 mL/2g, 15 mL/2g, and 10 mL/2g, respectively. That is, the swell indices decreased when attapulgite content increased.
- The swell index tests were also carried out with the 50 mM  $CaCl_2$ , 50 mM  $MgCl_2$  and 50 mM  $CuCl_2$  solutions. The results of these experiments were more or less the same for all solutions and were 10 mL/2g for PB, 9 mL/2g for 70%PB+30%A, 8 mL/2g for 50%PB+50%A, and 7 mL/2g for %30PB+%70A. That is, the swell indices slightly decreased when different solutions were used.
- Influence of prehydration on the hydraulic conductivity of GCLs was evaluated as well. The hydraulic conductivity of non-prehydrated and prehydrated GCLs were similar. The hydraulic conductivity of prehydrated PB GCL to DIW were 1.5-2 times

lower than that of non-prehydrated 70%PB+30%A and 50%PB+50%A GCLs to DIW.

- The hydraulic conductivity of prehydrated PB GCL to DIW was  $2.0 \times 10^{-11}$  m/s. Among attapulgite mixed GCLs, the hydraulic conductivity of 70%PB+30%A and 50%PB+50%A GCLs to DIW were 1.5-2.0 times higher, whereas that of 30%PB+70%A GCL was 3-4 orders of magnitude greater than the hydraulic conductivity of PB GCL. This shows that hydraulic conductivity of GCL to DIW can be acceptable when it contains 50% attapulgite at most.
- To investigate the effect of cell pressure on the hydraulic conductivity, the cell pressure gradually increased until 280 kPa and GCLs were permeated with DIW. Based on the results, the hydraulic conductivities decreased as the effective stress was increased.
- The hydraulic conductivity tests conducted with 50 mM  $\text{CaCl}_2$  solution were carried out on both non-prehydrated and prehydrated GCLs. Although the hydraulic behaviors were somewhat different, the final hydraulic conductivities of non-prehydrated to prehydrated GCLs were a factor of 3.6 for PB and 4.5 for 70%PB+30%A. However, this difference was around two orders of magnitude between non-prehydrated and prehydrated 50%PB+50%A GCLs ( $1.6 \times 10^{-6}$  versus  $1.5 \times 10^{-8}$  m/s).
- Hydraulic conductivity behaviors of GCLs were almost the same between 50 mM to 500 mM  $\text{CaCl}_2$  solutions. Although hydraulic conductivity rapidly increased when permeant was changed from DIW to 50 mM  $\text{CaCl}_2$  solution, the final hydraulic conductivities were very close to each other and were approximately  $2.0 \times 10^{-7}$  m/s.
- Similar final hydraulic conductivity values were attained even though the hydraulic conductivity behaviors of prehydrated GCLs were different with 50 mM  $\text{CaCl}_2$  and 50 mM  $\text{MgCl}_2$  solutions. This value is 3-4 orders of magnitude higher than the hydraulic conductivity of these GCLs to DIW.

- When 50 mM  $\text{CuCl}_2$  solution was used as the permeant, the initial hydraulic conductivity of PB GCL was  $7.6 \times 10^{-11}$  m/s, however, this value decreased dramatically during subsequent permeation. The reason of this decrease was due to the clogging of the influent tubings with copper ions. Copper precipitation occurred which stopped the flow. A similar situation was also observed with 70%PB+30%A GCL. In contrast, there was no obstruction with 50PB+%50A GCL.
- Katsumi et al. (2018) previously defined a relationship between hydraulic conductivity and swell index. The findings of this study partially in agreement with this relationship. Since this study uses bentonite-attapulgite mixtures, some of the data reported herein were apart from the tendency reported by Katsumi et al. (2008).
- Final water content of GCLs increased as the attapulgite content increased. However, there is no definite relationships exist between hydraulic conductivity and the final water content or the final height of GCL.

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## APPENDICES

### APPENDIX A-THE STEPS OF SAMPLE PREPARATION FOR HYDRAULIC CONDUCTIVITY TEST

1) The top pedestal was used to trace circle on GCL. Then GCL was carefully cut out along the trace. Deionized water was used to prevent loss of bentonite when cutting (Figure 1).



Figure 1 Cutting circle GCL (Personal archive, 2015)

2) Two heavy type nonwoven geotextiles were cut with the same diameter of GCL in order to use them as a porous stone during hydraulic conductivity tests. Then, GCL was sandwiched between these two geotextile and placed in this manner in flexible wall permeameters (Figure 2a/b).

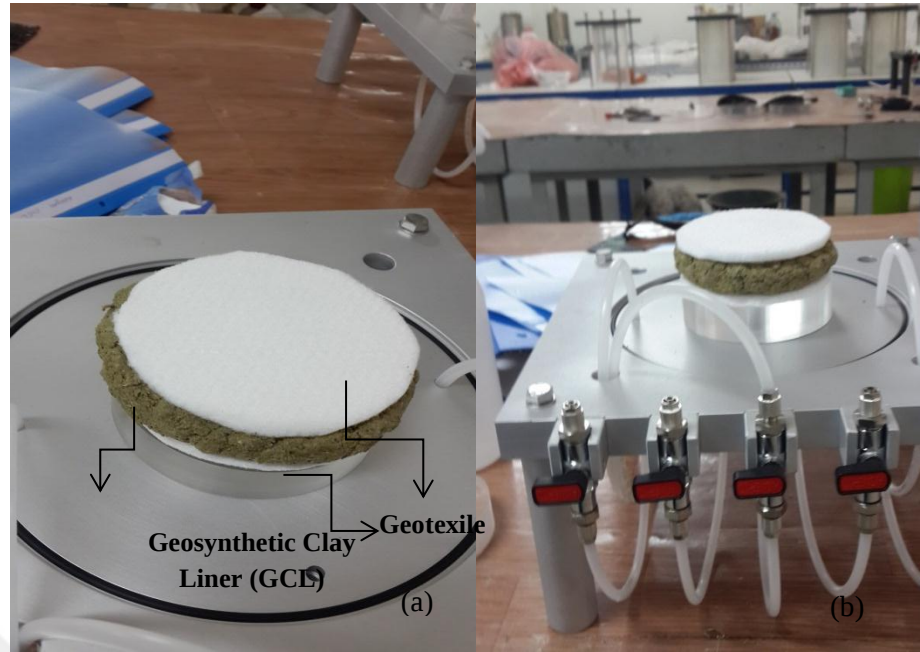


Figure 2 a/b GCL between two geotextiles (Personal archive, 2015)

3) Top pedestal was placed and then bentonite paste was applied along the perimeter of the specimen to prevent the side-wall leakage (Figure 3).



Figure 3 Applying bentonite paste to specimen (Personal archive, 2015)

4) Latex membrane was fitted on the sample. Two O-rings were placed over top and base pedestal (Figure 4).



Figure 4 Fitting latex membrane and sliding O-rings (Personal archive, 2015)

5) The tubings were attached to the top pedestal (Figure 5).

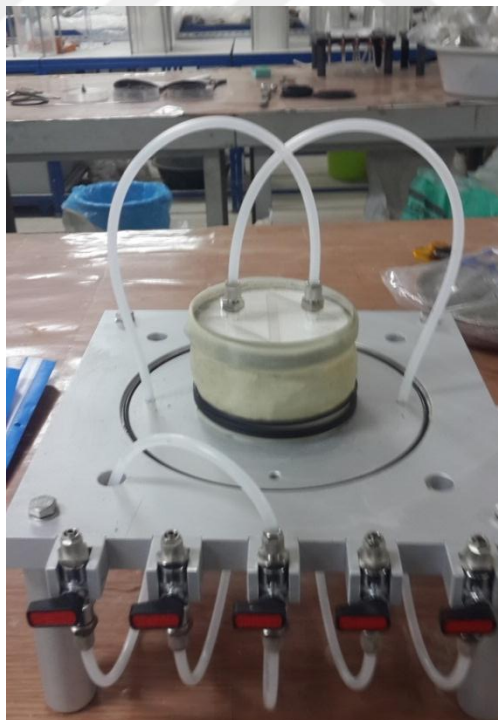


Figure 5 Attaching the tubing to top pedestal (Personal archive, 2015)

6) Acrylic cell was placed on base plate. Then, the top plate was placed on the acrylic cell. Ensure the acrylic cell is in contact with the top plate O-rings (Figure 6).

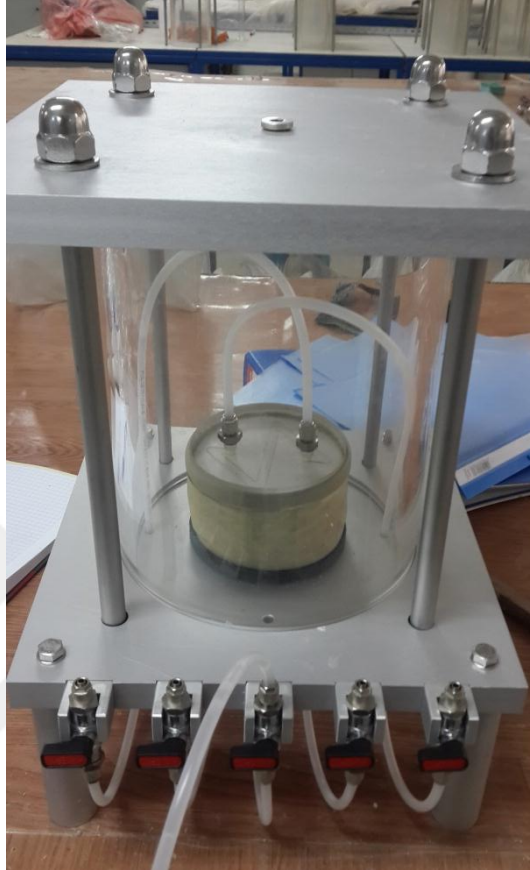


Figure 6 Placing a acrylic cell (Personal archive, 2015)

7) The permeameter was filled with tap water slowly. Cell pressure was applied via cell pressure line. Inflow line was filled with permeant and flow was started (Figure 7).

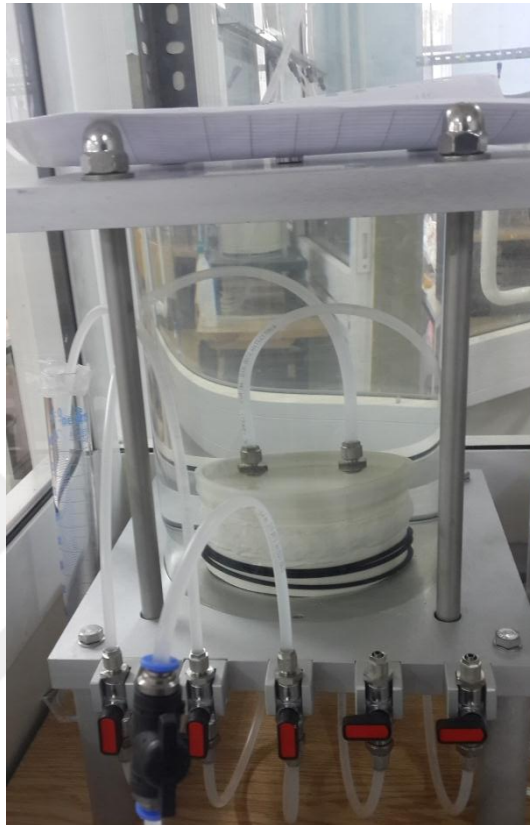


Figure 7 Insertion of the permeameter cell (Personal archive, 2015)