DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

FACTORS CONTROLLING THE CATION EXCHANGE BETWEEN GEOSYNTHETIC CLAY LINERS AND COMPACTED SUBSOILS DURING HYDRATION

by
Yasin KARAKUŞ

August, 2021
İZMİR

FACTORS CONTROLLING THE CATION EXCHANGE BETWEEN GEOSYNTHETIC CLAY LINERS AND COMPACTED SUBSOILS DURING HYDRATION

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M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **“FACTORS CONTROLLING CATION EXCHANGE BETWEEN GEOSYNTHETIC CLAY LINERS AND COMPACTED SUBSOILS DURING HYDRATION”** completed by **Yasin KARKAUŞ** under supervision of **Assoc. Prof. Ali 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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Assoc. Prof. Ali Hakan ÖREN

Supervisor

....

Assoc. Prof. Okan ÖNAL

(Jury Member)

....

Assoc. Prof. Hasan Fırat PULAT

(Jury Member)

Prof.Dr. Özgür ÖZÇELİK

Director

Graduate School of Natural and Applied Sciences

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Yasin KARAKUŞ

FACTORS CONTROLLING CATION EXCHANGE BETWEEN GEOSYNTHETIC CLAY LINERS AND COMPACTED SUBSOILS DURING HYDRATION

ABSTRACT

In this study, hydration experiments were conducted using three different GCLs to investigate hydration time, bentonite mass per unit area (MPUA), subsoil water content ($w_{subsoil}$), and vertical stress. As a result of these experiments, it was observed that as the hydration time increased, the water content of the GCLs increased, but the water content reached equilibrium after the 4th week. It was observed that the final water content (w_{final}) of GCLs increased with the increase of water content in the subsoil. It was also observed that the increase in MPUA caused a decrease in the w_{final} of the GCLs. It was found that the increase in vertical stress caused a slight decrease in the w_{final} by limiting the swelling of the bentonites. As a result of bound cation tests, although it was observed that the cation exchange decreased with increasing water content of the subsoils in the early stages of hydration, the opposite result was obtained in the 180-day hydration experiments. Moreover, the water content of the subsoils at the end of the hydration period was determined as a function of depth. It was observed that the water content of the subsoil decreased with increasing MPUA of the hydrated GCL.

Keywords: Geosynthetic clay liner, hydration, cation exchange, mass per unit area, swell index, subsoil water content, vertical stress

HİDRASYON SIRASINDA GEOSENTETİK KİL ÖRTÜ VE SIKIŞTIRILMIŞ ALT ZEMİN ARASINDAKİ KATYON DEĞİŞİMİNİ KONTROL EDEN FAKTÖRLER

ÖZ

Bu çalışmada, katyon değişimini etkileyen parametrelerden hidrasyon süresi, birim alan başına bentonit kütlesi (BABBK), alt zemin su içeriği ve düşey yük etkisini incelemek amacıyla üç farklı GKÖ ile hidrasyon deneyleri yürütülmüştür. Bu deneyler sonucunda, hidrasyon süresi arttıkça GKÖ'lerin su içeriği arttığı, ancak 4. haftadan sonra su içeriğinin dengeye ulaştığı gözlemlenmiştir. Alt zemin su içeriğinin artmasıyla GKÖ'lerin nihai su içeriğinin arttığı görülmüştür. Ayrıca, BABBK artışının GKÖ'lerin nihai su içeriğinde azalmaya sebep olduğu saptanmıştır. Düşey yükteki artışın ise bentonitlerin şişmesini kısıtlayarak nihai su içeriğinde hafifçe azalmaya sebep olduğu gözlemlenmiştir. Yapılan bağlı katyon deneyleri sonuçları hem mol fraksiyonu hem katyon konsantrasyonu açısından incelenmiştir. Bu incelemeler sonucunda, hidrasyonun erken dönemlerinde alt zemin su içeriği arttıkça katyon değişiminin azaldığı görülse de 180 günlük hidrasyon deneylerinde tam tersi bir sonuç elde edilmiştir. Öte yandan, düşey yükteki artış, GKÖ ile alt zemin arasındaki teması iyileştirerek katyon değişiminin gerçekleşmesini kolaylaştırmıştır. Ek olarak, hidrasyon süresi sonunda alt zeminlerin su içerikleri derinliğe bağlı olarak belirlenmiştir. Hidrate edilen GKÖ'nün BABBK'sı arttıkça alt zemin su içeriğinin düştüğü görülmüştür.

Anahtar kelimeler: Geosentetik kil örtü, hidrasyon, katyon değişimi, BABBK, şişme indisi, alt zemin su içeriği, düşey yük

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CHAPTER ONE
INTRODUCTION

1.1 Introduction

With the rapid increase in human population after 1970s, the growing volume of production and consumption brought many problems for the environment. Among these problems, the waste generation stands out as a major problem which threatens the world. The nations of the modern world have been looking forward to find out ways to dispose of the wastes without harming the environment.

Engineers, who want to stop the migration of contamination thorough the groundwater, have used compacted clay layers as a barrier material in landfills due to their low permeability. However, due to insufficient impermeability and for economic reasons, compacted clay liners were superseded by geosynthetic clay liners (GCLs) in the beginning of 2000s.

GCLs are composite materials with a thickness between 5 and 10 mm, produced by sandwiching bentonite between two geotextiles. GCLs have many advantages when compared to the compacted clay liners. Due to their capacity to hold water up to 10 times of their weight and low permeability (~2×10^{-11} m/s), GCLs are extensively used as a barrier material in solid waste and hazardous waste storage areas, irrigation canals, water transmission lines, and in ponds (Anderson et al., 2012; Estornell & Daniel, 1993; Petrov & Rowe, 1997; Rayhani et al., 2011; Rowe et al., 2011; Scalia IV & Benson, 2010). However, some factors affect the barrier performance of GCLs. There are physical factors such as mass per unit area (MPUA) of GCL, the initial water content of bentonite, the water content of subsoil, etc. In addition, there are several chemical factors namely polymer content of bentonite, concentrations of exchangeable cations of bentonite. In this study, both physical and chemical factors were investigated.

1.2 **Scope of the Study**

The primary purpose of this study is to elucidate the cation exchange behavior of geosynthetic clay liners (GCLs) (Figure 1.1) under some circumstances when placed over a compacted silty sand. For this aim, laboratory hydration tests were conducted with three different GCLs. These GCLs were hydrated 30, 90, 180, and 360 days over the subsoil (i.e., compacted silty sand). The parameters, that may influence the cation replacement between subsoil and GCL, were subsoil water content ($w_{subsoil}$), mass per unit area (MPUA) of GCL and vertical stress applied on GCL during hydration. To determine the water content change in GCL with time, GCLs were removed from the mold and the masses of GCLs were recorded. At the end of the hydration, GCLs were dried and bound cations as well as swell indices of the bentonites were determined. The details are given in further sections.

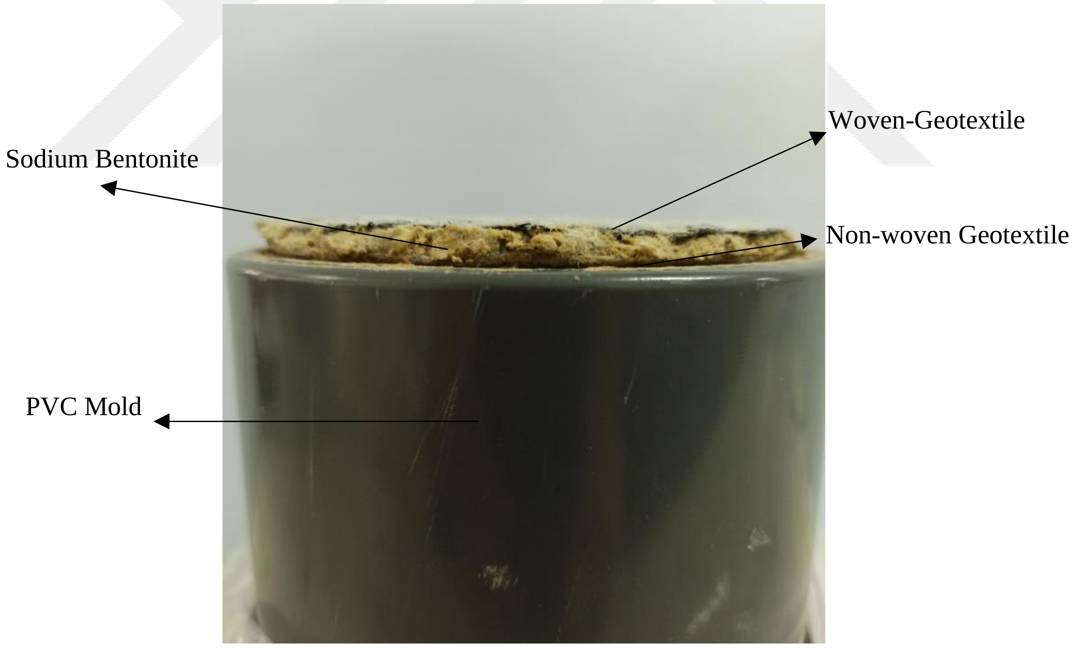

Figure 1.1 Geosynthetic clay liner (Na-GCL) placed on a PVC mold (Personal archive, 2021)

CHAPTER TWO
MATERIALS AND METHODS

2.1 Materials

2.1.1 Geosynthetic Clay Liners

Three GCLs were investigated, namely that GCL1 (Na-GCL), GCL2 (Na/Ca-GCL), GCL3 (P-GCL) in this study. GCLs were taken from local manufacturer. Mass per unit area of the GCLs (ASTM D 5993-14) were ranged between 3.8 and 5.1 for GCL1; 3.0 and 7.1 for GCL2; 2.9 and 4.3 for GCL3. The liquid limit of the bentonites was determined in accordance with ASTM D4318 and was 231%, 240%, and 222% for GCL1, GCL2, and GCL3, respectively. The swell index was 21.5 mL/2g for GCL1; 25.0 mL/2g for GCL2; and 26.5 mL/2g for GCL3.

All GCLs investigated in this study had been manufactured by needle-punching. GCLs had nonwoven cover geotextile and woven carrier geotextile. The average initial thickness of the GCLs were 0.61, 0.65, and 0.56 for GCL1, GCL2, and GCL3, respectively. GCL1 has powdered sodium bentonite (D_{60} = 0.0048 mm). GCL2 also has powdered sodium bentonite (D_{60} = 0.0031 mm). Due to the considerable amount of calcium content of this bentonite (20.9%) and its white color, this GCL was named as Na/Ca-GCL. The last GCL has polymer-treated powdered sodium bentonite (D_{60} = 0.0013 mm). There is no information about the polymer type of the bentonite due to the desire of the manufacturer to keep proprietary knowledge safe. However, to determine the polymer content of GCL3, loss on ignition (LOI) test was conducted. LOI of virgin polymer bentonite was determined as 7.3% at 550˚C. The properties of GCLs investigated are summarized in Table 2.1. Additionally, particle size distributions of the GCLs are shown in Figure 2.1.

Table 2.1 Properties of GCLs investigated

GCL Properties	Na-GCL	Na/Ca-GCL	P-GCL
MPUA (kg/m^2)	3.8-5.1	3.0-7.1	2.9-4.3
Carrier Geotextile	Woven	Woven	Woven
Cover Geotextile	Non-woven	Non-woven	Non-woven
Initial water content (%)	12.6±4.7%.	16.7±5.1	13.6±1.9
Liquid Limit, w_L (%)	231	240	222
Plastic Limit, w_P (%)	61	53	50
Clay Fraction (%)	45	70	70
Swell Index (mL/2g)	21.5	25.0	26.5
Loss on Ignition, LOI (%)	-	-	7.3
Manufacture type	Needle-punched	Needle-punched	Needle-punched

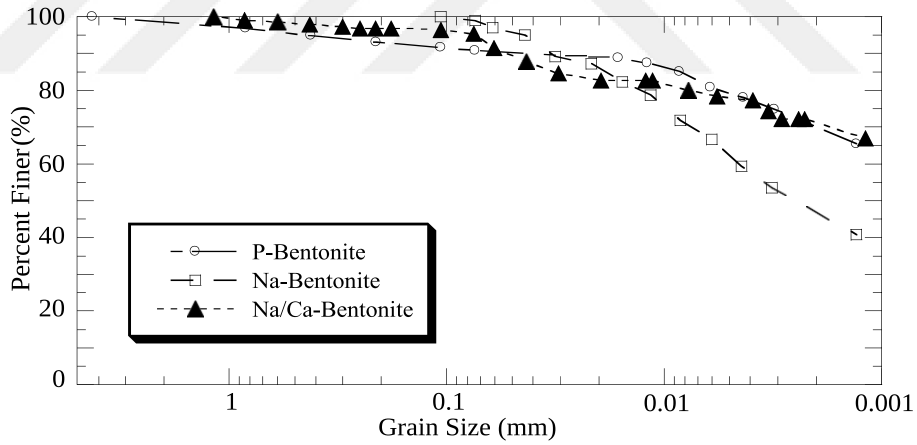

Figure 2.1 Particle Size Distributions of bentonites used in this study

2.1.2 ***Subsoil***

Silty sand taken from a landfill was used as the subsoil in hydration tests. The grain size distribution curve of subsoil was obtained following ASTM D 6913-17. As a result of the wet sieving and hydrometer tests, the fine content of subsoil was determined 41.5%. The grain size distribution of silty sand is given in Figure 2.2. Liquid and plastic limits of the subsoil (ASTM D4318) were determined 31% and non-plastic (NP). Subsoil was compacted with Standard Proctor compaction effort using PVC mold (ASTM D698-12, 2020). The optimum water content (w_{opt}) and maximum dry unit weight of the subsoil (γ_{max}) were obtained as 12% and 19.1 kN/m^3, respectively. The compaction curve is given in Figure 2.3.

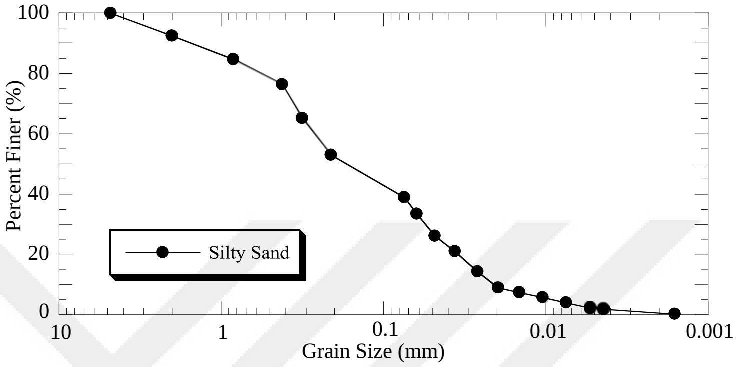

Figure 2.2 Grain Size Distribution of Silty Sand Subsoil

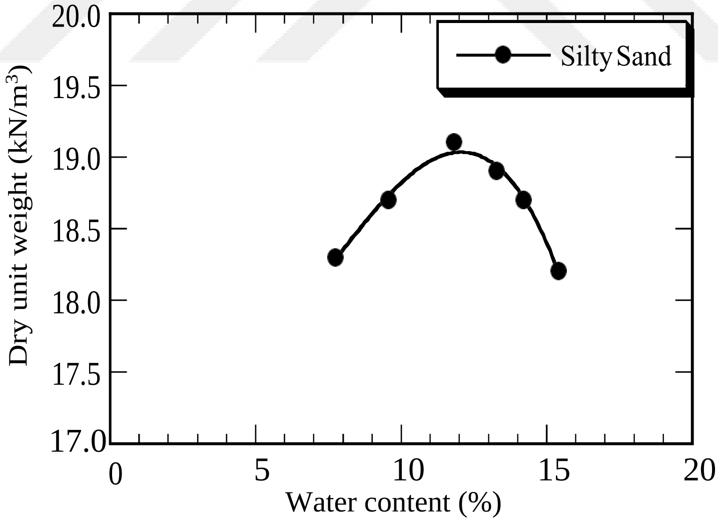

Figure 2.3 Compaction Curve of Silty Sand

After determining w_{opt}, four different subsoil water contents ($w_{subsoils}$) were selected two of which are on dry and two are on wet side of optimum to conduct hydration tests. The selected subsoil water contents ($w_{subsoils}$) in this study were 8%, 11%, 14%, and 17%, which correspond to −4%, −1%, +2%, +5% water contents relative to the optimum, respectively. Then, subsoils were compacted into the PVC molds as described above. Since water contents were determined after 24h of curing, they slightly deviated from target water contents. The real water contents were within the range of 7.4%-8.3%, 10.8%-11.8%, 13.6%-13.9%, and 16.5%-17.2%. To prevent confusion, the water contents will be given as the “target water contents” henceforth.

2.2 **Methods**

2.2.1 ***Preparation of GCL sample***

Circular-shaped GCLs were cut from the roll using a 110 mm diameter steel ring. After GCL was extracted from the roll, the diameter of the GCL was decreased to 100 mm using a scissor. Finally, the sides of the GCL were moistened with DIW to prevent loss of bentonite. Then, GCL was left for air drying until the weight change was negligible. The GCL rolls are shown in Figure 2.4.

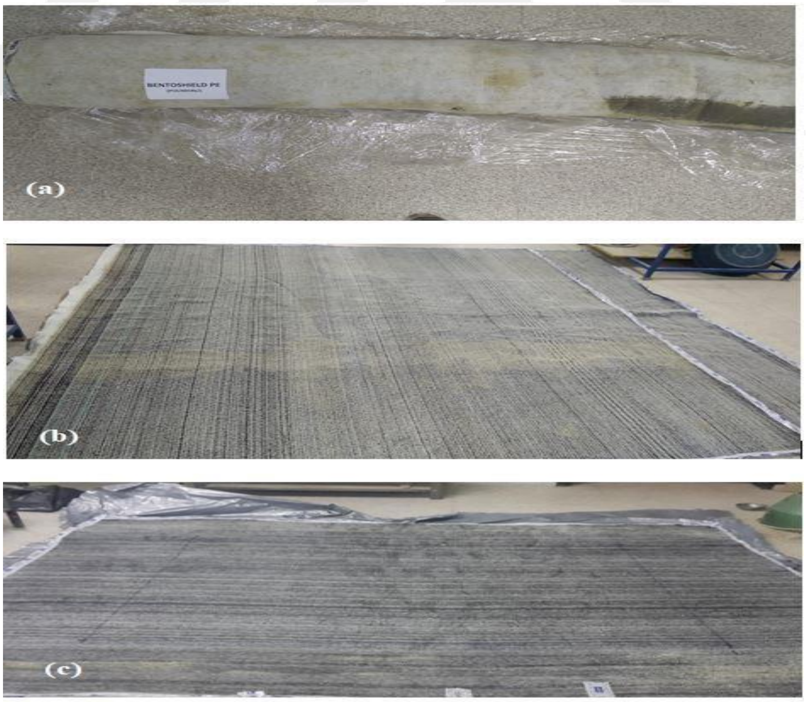

Figure 2.4 GCL rolls used in the study: (a) P-GCL (b) Na-GCL (c) Na/Ca-GCL (Personal archive, 2020)

The target MPUAs in this study were 3.0, 4.0, 5.0, 6.0, and 7.0 kg/m^2. The closest MPUAs were selected from a set of cut samples and used in hydration tests. The MPUAs were varied between 2.92 and 3.17 kg/m^2, 3.91, and 4.16 kg/m^2, and 5.03 and

5.14 kg/m^2. Only one samples for MPUA 6.0 kg/m^2 and 7.0 kg/m^2 were used. For simplicity, MPUA of 3.0, 4.0, 5.0, 6.0, and 7.0 will be used in the further sections.

2.2.2 ***Hydration Test Setup***

Hydration tests were conducted in isothermal conditions. Firstly, silty sand subsoil was oven-dried at 105±5˚C. After that, the subsoil was wetted by using a tap water filled spray bottle to bring the water content of the subsoil to the target water content. Subsoil left for conditioning for one night to ensure the homogeneous distribution of water in the soil. Then, the silty sand subsoil was compacted with Standard Proctor Compaction Energy. Once the subsoil was prepared, GCLs of 100 mm diameter cut from the roll was placed on the compacted subsoil. Finally, 20 mm-thick polyoxymethyle (POM) cap was placed on the GCL to imitate geomembrane in the field applications and to provide a basement for the applied vertical load. To provide the isothermal conditions, PVC molds were wrapped with plastic bags. O-rings were attached to the top and bottom of the mold to solidify the impermeability of the air. Additionally, in order to supply a sufficient contact between GCLs and subsoils 1 kPa vertical stress was applied. In addition to 1 kPa, 2, 5, and 10 kPa stresses were also applied to investigate the influence of vertical stress. An illustrative representation of the hydration test setup is given in Fig 2.5. Hydration test setup was open periodically to measure the mass of the GCLs. At the end of the hydration durations, GCLs were oven-dried to determine the water contents. The subsoils were divided into 5 layers and the water contents of these layers were also detected.

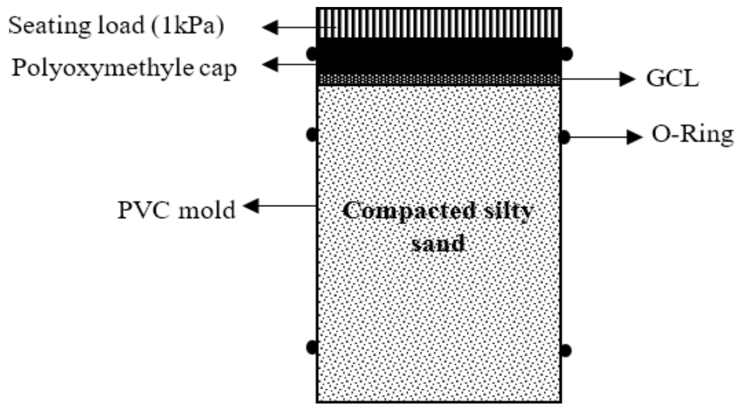

Figure 2.5 Isothermal hydration test setup

2.2.3 ***Bound Cation Tests***

Bound cation tests were conducted on virgin and hydrated bentonite extracted from the GCLs (ASTM: D7503-18, 2020). For this purpose, 1 M ammonium acetate (NH_4OAc) stock solution was prepared in a volumetric flask. Initially, 10 g of air-dry bentonite and 40 ml of NH_4OAc was mixed vigorously in a plastic bottle and the suspension was shaken in an end-over-end shaker at 30 rpm for 5 min. Then, the suspension was left curing for 24h. After 24h, the suspension was shaken for another 15 min at 30 rpm. The suspension was filtered through a 2.5 μm ashless filter paper which was placed on a Buchner funnel. Bentonite was further washed with 30 ml of NH_4OAc solution four times by applying 10 kPa vacuum pressure. The filtrate was analyzed in inductively coupled plasma optical emission spectrophotometry (ICP-OES) to determine the major bound cations (i.e., Na^+, K^+, Ca^{2+}, and Mg^{2+}).

2.2.4 ***Major Cations of Subsoil***

The batch elusion test was used to detect the major cations of the pore fluid (i.e., Na^+, K^+, Ca^{2+}, and Mg^{2+}). To do this test, a slurry with 1.3:1.0 liquid to solid ratio was prepared in plastic bottles. Then, plastic bottles were shaken in an end over end shaker at 30 rpm for 24h. Sand grains rapidly settled at the bottom of the bottles and the liquid above the sediment was transferred to centrifuge tubes. Since subsoil contains considerable number of fine particles, the blurred water was centrifuged under 2000 rpm and was filtered through 0.45 μm filter paper. The filtrate was transferred to another tube and the water was analyzed in ICP-OES following the Standard Method 3120B Baird et al., 2017) to determine the major cations. This process was replicated 6 times. The average cation concentrations of 6 tests are Ca^{2+}: 284.1±15 mg/L, Na^{+}: 13.8±1 mg/L, Mg^{2+}: 30.4±2 mg/L, and K^{+}: 36.4±2 mg/L.

2.2.5 ***Swell Index Test***

At the end of the hydration durations, bentonites were extruded from the GCLs. These bentonites were oven-dried at 105˚C during overnight. Once they cooled, bentonites were grinded until 100% passing a 100 mesh U.S standard sieve with a laboratory mortar and pestle. Afterward, 2 grams of bentonite was weighed and poured into a graduated cylinder filled with deionized water (DIW) up to 90 mL level. This pouring process was done gradually. At each step, 0.1 gram of bentonites was poured into the cylinder, and a minimum of 10 minutes has waited. When all of the bentonite samples were poured, the graduated cylinder filled with DIW up to 100 mL level. The open end of the graduated cylinder was closed with a parafilm to prevent evaporation. After 24 hours, cylinders were tipped and rolled slowly at a 45˚ angle to homogenize the settlement of clay minerals. Finally, swell indices were recorded. The details of this test can be found in ASTM D 5890. A general view of swell index tests is shown in Figure 2.6.

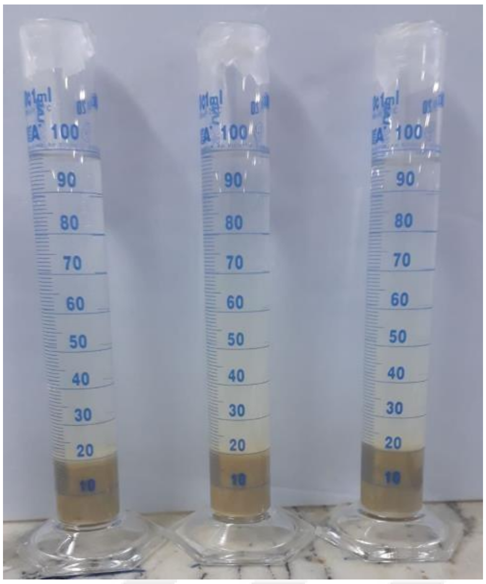

Figure 2.6 A general view of post swell index tests (Personal archive, 2020)

2.2.6 **Loss on Ignition Test**

In order to detect the polymer content of polymer-treated bentonite (GCL3), loss on ignition tests were conducted as proposed by (Scalia et al., 2014). To do this, 2.0 gram of oven-dried bentonite was used. Then, oven dried bentonite was transferred to muffle furnace for further drying which was heated up to 550˚C. Following the ignition about 4 hours, bentonite was weighted and loss on ignition was calculated as the percentage of mass lose.

CHAPTER THREE
THE ROLE OF MASS PER UNIT AREA AND TYPE OF GEOSYNTHETIC CLAY LINERS (GCLS) ON THE GCL-SUBSOIL INTERACTION

3.1 Background

GCLs, which have been used since 1990s, have many advantages when compared to the compacted clay liners. Due to their ability to absorb water up to 10 times of their weight and low permeability (~2×10^{-11} m/s), GCLs have been extensively used as a barrier material in solid waste and hazardous waste storage areas, irrigation canals, water transmission lines, and in ponds (Anderson et al., 2012; Estornell & Daniel, 1993; Petrov & Rowe, 1997; Rayhani et al., 2011; Rowe et al., 2011; Scalia IV & Benson, 2010).

Hydraulic conductivity is the governing factor determining the GCL field efficiency. Therefore, factors affecting the hydraulic conductivity of GCLs need to be well known. One of the most important factors that should be taken into consideration is the hydration performance of GCL on site. There are some studies carried out to determine the hydration behavior of GCL not only in the laboratory but also in the field (Barclay & Rayhani, 2013; Benson et al., 2010; Chevrier et al., 2012; Kul & Oren, 2019; Lee et al., 2005; Rowe et al., 2019; Ruhl & Daniel, 1997; Sarabian & Rayhani, 2013; Tian et al., 2019; von Maubeuge & Ehrenberg, 2014). These studies found that GCL hydration performance depends on the bentonite quality, particle size, mass per unit area, physicochemical properties (cation exchange capacity, polymer content, liquid limit etc.) and confining stress acting on the GCL.

Studies conducted on the exhumed GCLs have revealed that cation exchange inevitably occurs between GCL and subsoil during hydration process. Hence, this exchange reaction affects the barrier property of the GCL. Scalia & Benson (2011) conducted bound cation tests on GCLs exhumed after 4.1 to 11.1 years of installation. It was found that while mole fractions of the sodium decreased dramatically from 0.74

to less than 0.10, calcium mole fractions increased from 0.22 to more than 0.60. Rowe et al. (2017) determined the exchangeable cations of the bentonites of exhumed GCLs after 5-years. The sodium fraction of the virgin GCL1 was 0.67. However, it was completely exchanged with other cations (Ca^{2+}, Mg^{2+}, K^{+}) within 5 years, and sodium fraction decreased to zero. From lessons learned from conducted studies so far, the replacement of monovalent cations (Na^{+}, K^{+}) with the divalent cations (Ca^{2+}, Mg^{2+}) may cause serious damage on the GCLs resulting in an increase in the hydraulic conductivity.

Many researchers have investigated the parameters affecting the cation exchange reaction that took place between GCL and subsoil during hydration (Bradshaw et al., 2013; Kul & Oren, 2019; Rowe et al., 2019; Rowe & Abdelatty, 2012). To examine the effect of cation concentration of the subsoil on cation exchange, Abdelatty (2012) hydrated the GCLs up to 1100 days, and conducted bound cation tests on those GCLs. The results revealed that as the calcium concentration of the subsoil increased, cation exchange between GCL and subsoil increased. Bradshaw (2013) conducted hydration tests up to 365 days with four subsoils. At the end of the hydration durations, bound cation concentrations of GCLs were more or less the same regardless of subsoil type. Rowe et al. (2019) investigated the effect of subsoil water content ($w_{subsoil}$) on cation exchange during hydration. As a result of the hydration tests, GCLs placed on wetter subsoils exposed higher cation replacement.

To investigate the effect of MPUA on the hydration behavior of the GCLs, Azad et al. (2011) conducted hydration tests. As a result of these tests, the gravimetric water content of the GCLs decreased with an increase in MPUA. Apart from these studies, scarce studies are available which investigates the effect of MPUA on the cation exchange reaction of GCL. Therefore, the MPUA effect on GCL hydration needs to be investigated.

The purpose of this study is to evaluate the hydration of the three GCLs depending on the MPUA. These GCLs with MPUAs varying between 2.9 and 7.1 kg/m^2 were hydrated for 180 days. In this study, silty sand subsoils were compacted at 14% water content which was 2% wet of optimum. Additionally, 1 kPa vertical stress was applied to ensure the good contact between GCL and subsoil. At the end of the hydration duration, bound cations and swell indices of the bentonites were determined. Thus, it was aimed to observe the role of MPUA and GCL type on cation exchange between GCL and compacted subsoil.

3.2 Hydration of GCLs

The interaction between GCLs and subsoil were investigated in terms of MPUA and GCL type. For this purpose, GCLs were hydrated over the same subsoil (i.e., silty sand) for 180 days. The ranges of MPUA of bentonite were between 2.8-5.1 kg/m^2 for the GCL1 (Na-GCL); 3.1-7.1 kg/m^2 for GCL2 (Na/Ca-GCL); and 2.9-4.25 kg/m^2 for GCL3 (P-GCL). The details of hydration tests and the final water content (w_{final}) is summarized in Table 3.1.

Table 3.1 Final water contents (w_{final}) and saturation degrees of GCLs at the end of hydration

GCL Type	Mass Per Unit Area (kg/m^2)	Hydration Duration (days)	w_{final} (%)	w/w_{ref} (%)	Tests
GCL1	2.80	180	91.4	44.5	SB18
GCL1	3.91	180	78.0	42.1	SB20
GCL1	4.72	180	76.6	46.1	SB22
GCL2	3.05	180	121.7	57.1	SC4
GCL2	4.04	180	105.7	53.4	SC3
GCL2	4.99	180	112.1	65.6	SC5
GCL2	5.71	180	102.6	71.2	SC6
GCL2	7.12	180	99.8	77.9	SC7
GCL3	2.87	180	80.8	34.6	PS6
GCL3	3.80	180	78.5	35.7	PS3

The hydration behaviors of GCLs are shown in Figure 3.1a-c. The water contents of GCLs increased expeditiously up to 10 days and reached to an equilibrium point afterward (Figure 3.1). The water content of GCL1 and GCL3 reached their peak water contents within 30 days of hydration. Then, they tended to decrease considerably until 180 days (Figure 3.1). In contrast, except MPUA of 3.0 kg/m^2, GCL2 kept water uptake during 180 days. GCL2 with MPUA of 3.0 kg/m^2 also continued to water uptake until 150 days. Thereafter, it started to decrease until the end of test. The reduction in the water content with time may be due to cation exchange that took place between GCL and subsoil (Rowe & Abdelatty, 2012). In addition to this, dismantling of test set up for mass measurement inevitably change the hydration condition every time which may also cause evaporation. Thus, this may be also responsible for this loss of water as well. No matter is the cause of reduction in the water content, hydration tests showed that hydration behavior of GCL depends on the amount and type of cations present in the exchange complex of bentonite. These findings are consistent with the former studies (Anderson et al., 2012; Azad et al., 2011; Rayhani et al., 2011).

Effect of MPUA on the hydration was more noticeable for GCL1 and GCL2 than for GCL3. For GCL1, the highest w_{final} (i.e., 91.4%) was obtained at the lowest MPUA (i.e., 3.0 kg/m^2), while the lowest w_{final} (76.7%) was obtained at the highest MPUA (i.e., 5.0 kg/m^2) (Figure 3.1a). For GCL2, the range of MPUA was quite broad (3.0 to 7.0 kg/m^2) with respect to other GCLs. At the end of 180 days of hydration, w_{final} of GCL3 was 121.7 and 99.8% at MPUA of 3.0 and 7.0 kg/m^2, respectively (Figure 3.1b). If one investigates the GCL3 in terms of MPUA, it can be said that in the first 30 days of hydration, the influence of MPUA was quite prominent. However, after 45 days, water content of the GCLs followed the same hydration path as shown in Figure 3.1a (Figure 3.1c). At the end of the 180 days of hydration, influence of MPUA disappeared and w_{final} of GCL3 converged to same value (80.8% vs 78.5%) for MPUA of 3.0 and 4.0 kg/m^2.

Regardless of GCL type, the highest w_{final} was obtained with a GCL having the lowest MPUA. In contrast, the lowest w_{final} was obtained when MPUA was the highest. When w_{final} is plotted as a function of MPUA, a reduction in the w_{final} with a MPUA increase was seen (Figure 3.2). Figure 3.2 also shows that w_{final} of GCL1 and GCL3 overlaps, whereas that of GCL2 stays above GCL1 and GCL3 at all considered MPUA range. This indicates the role of exchangeable cations present in bentonites. The color of GCL1 and GCL3 resembles within each other. However, it is known that GCL1 is conventionally sodium and GCL3 was polymer treated. Based on personal communication done with the local manufacturer, the same bentonite was used in GCL3 which had been mixed with sodium polyacrylamide type of polymer. Therefore, it can be argued that polymer treatment did not change neither hydration behavior nor w_{final} of GCL3 when compared to those of conventional GCL (i.e., GCL1).

On the other hand, the bentonite in GCL2 is totally different from GCL1 and GCL3. The color of GCL was whitish and calcium concentration was rather high. This GCL was also supplied from the same manufacturer and the company noticed that this GCL is naturally abundant of calcium. The cation analysis conducted on the brand new GCLs partially supported this information. GCL2 was sodium abundant but has appreciable amount of calcium (Table 3.2). That is why it was called as Na/Ca GCL herein. It is interesting to note the hydration behavior as well as w_{final} of this GCL is totally different than GCL1 and GCL3. Since GCL2 has appreciable amount of calcium, it was expected that GCL2 would have lower w_{final} with respect to GCL1 and GCL3. However, 3.1 and 3.2 show that, at any MPUA range, w_{final} of GCL2 was greater than w_{final} of GCL1 and GCL3.

Table 3.2 Cation Concentration of GCLs

GCL Type	**Bound Cation Fractions (cmol/kg$^+$)**			
	Na^+	**Ca^{2+}**	**Mg^{2+}**	**K^+**
GCL1	88.7	16.6	5.3	1.9
GCL2	97.3	26.6	0.6	2.4
GCL3	82.8	28.9	7.7	1.7

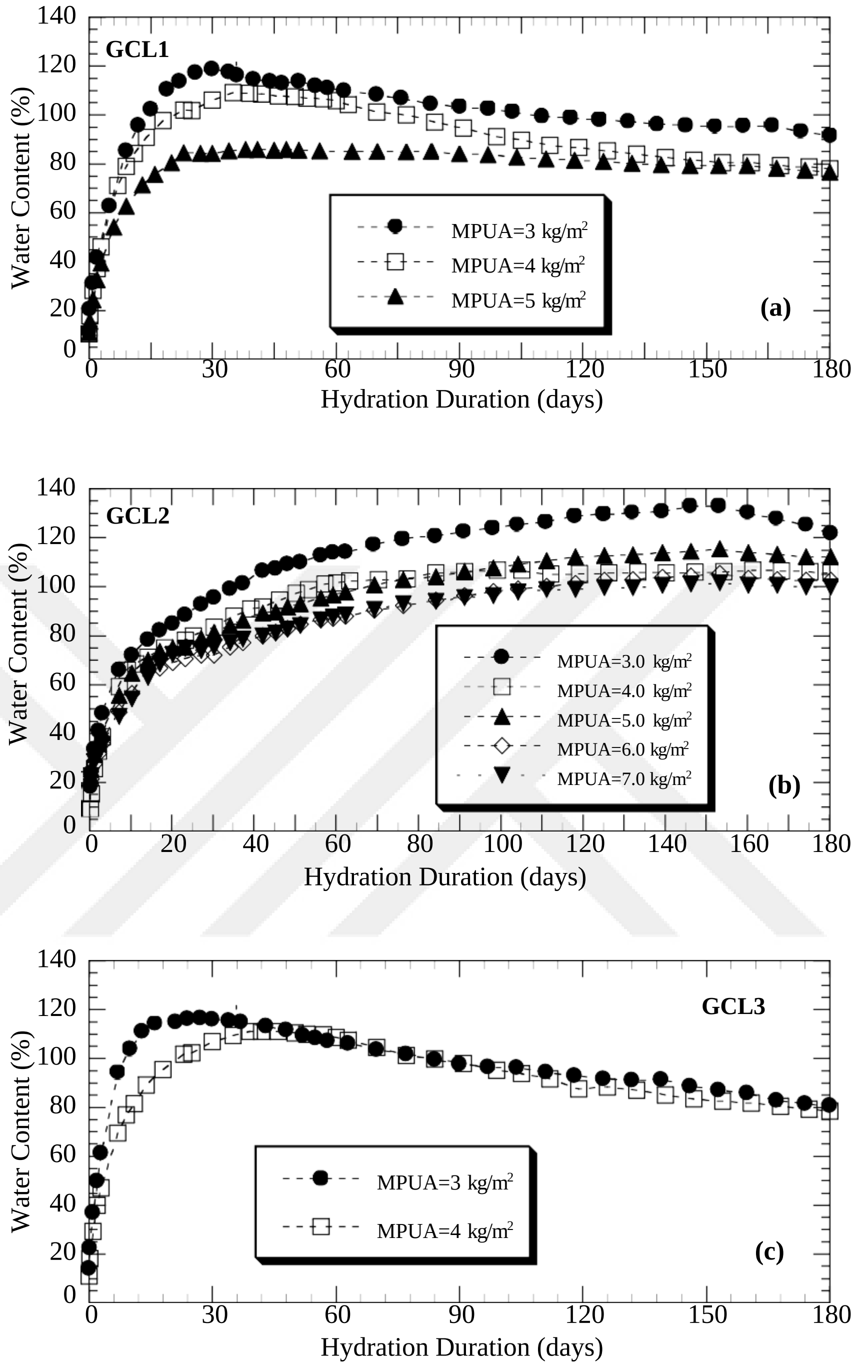

Figure 3.1 Hydration behaviors of three GCLs: (a) Na-GCL (b) Na/Ca-GCL (c) P-GCL

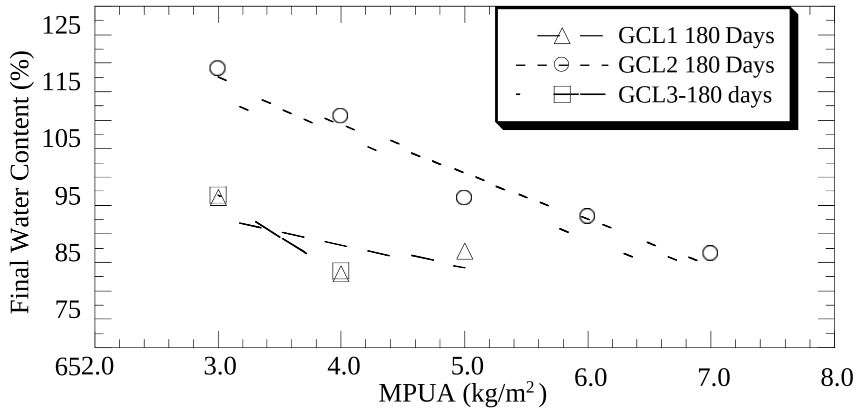

Figure 3.2 Relationship between final water contents (w_{final}) and MPUA of the GCLs investigated

3.3 **Cation Exchange During Hydration**

The major bound cations (i.e., Na^+, Ca^{2+}, K^+, Mg^{2+}) of GCLs were determined at the end of the hydration tests. The results are presented in terms of mole fractions of cation (%) in Table 3.3. If one investigates these exchange reactions in detail, it can be seen that most of the replacement occurred between Na^+ and Ca^{2+} ions. Thus, this study was focused on the changes in the concentration of these two major bound cations. Table 3.3 also gives the sum of monovalent cation fractions of Na^+ and K^+ undertotal monovalent cation fractions (X_M) and the sum of divalent cation fractions of Ca^{2+} and Mg^{2+} as the total divalent cation fractions (X_D).

The influence of MPUA on the cation exchange reaction is shown from Figure 3.3 through Figure 3.5 for GCL1, GCL2 and GCL3, respectively. X_M and X_D of GCL1 with MPUA of 3.0, 4.0 and 5.0 kg/m^2 were ~70% and ~30%, respectively (Fig 3.3). Thus, it can be concluded that MPUA had no influence on the cation exchange reaction of GCL1 when hydrated for 180 days.

Table 3.3 Bound cation fractions virgin and hydrated GCLs

GCL Type	MPUA (kg/m^2)	Hydration Duration (days)	Bound Cation Fractions (%)					
			Na^+	Ca^{2+}	Mg^{2+}	K^+	X_M	X_D
GCL1	Virgin	-	78.8	14.7	4.7	1.7	81	19
GCL1	2.80	180	69.3	21.6	7.7	1.3	71	29
GCL1	3.91	180	68.1	23.1	6.6	2.2	70	30
GCL1	4.72	180	69.3	22.7	7.0	1.0	70	30
GCL2	Virgin	-	76.7	20.9	0.5	2.6	79	21
GCL2	3.05	180	70.8	22.3	2.6	4.3	74	26
GCL2	4.04	180	71.2	25.2	1.0	2.6	74	26
GCL2	4.99	180	70.7	22.5	2.5	4.3	73	27
GCL2	5.71	180	71.1	23.0	3.5	2.5	74	26
GCL2	7.12	180	72.1	22.3	3.3	2.3	74	26
GCL3	Virgin	-	68.4	23.4	6.4	1.4	70	30
GCL3	2.87	180	63.4	25.6	8.5	2.5	66	34
GCL3	3.80	180	65.4	26.0	6.6	2.0	67	33

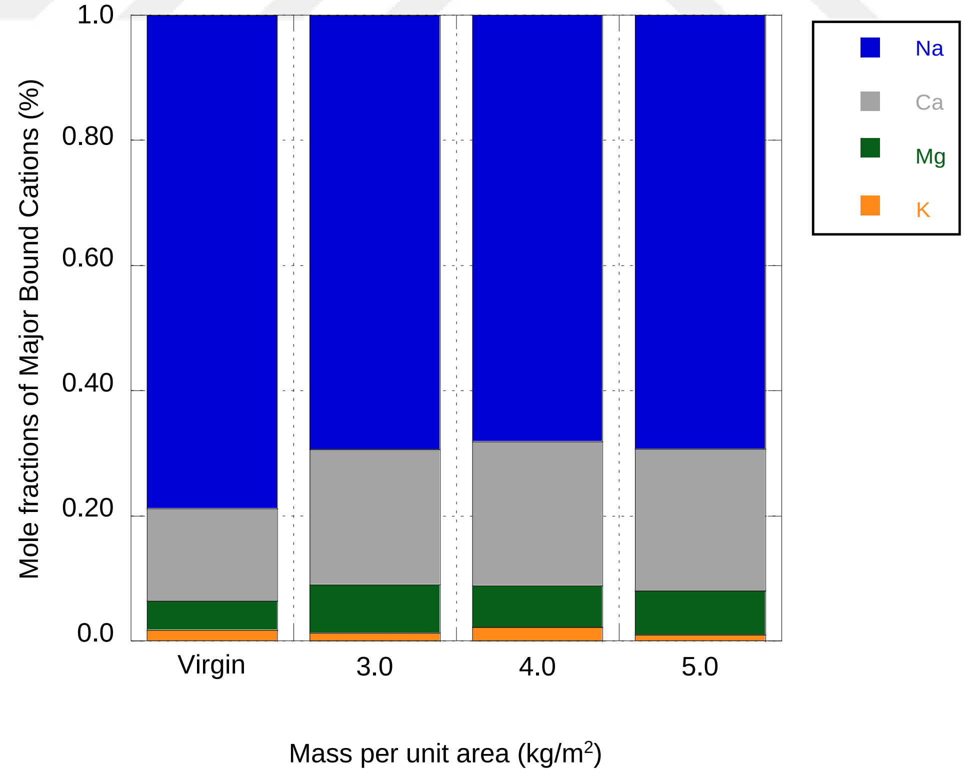

Figure 3.3 Mole fractions of GCL-1 after 180 days of hydration

The finding highlighted above was also supported by the cation analysis conducted on GCL2. The MPUA range of GCL2 was rather high when compared to GCL1 and GCL3 (3.0 to 7.0 kg/m^2). However, the influence of MPUA was still not noticeable even at greater MPUAs (Figure 3.4). For instance, X_M was 74% for MPUA 3.0 kg/m^2 while it was 74, 73, 74 and 74% for MPUA 4.0, 5.0, 6.0, and 7.0 kg/m^2, respectively.

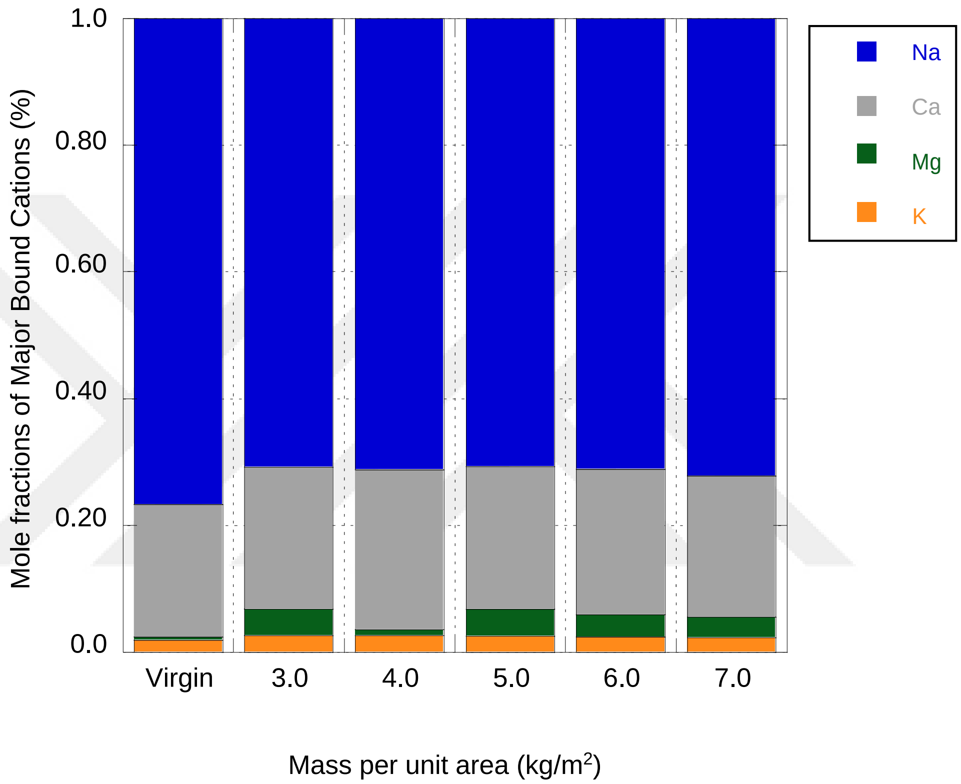

Figure 3.4 Mole fractions of GCL-2 after 180 days of hydration

The hydration, so does the cation exchange, behavior of GCL3 was only investigated on MPUA of 3.0 and 4.0 kg/m^2. At the end of the 180 days of hydration, GCL3 with MPUA of 4.0 kg/m^2 exhibited similar cation exchange reaction than GCL3 with MPUA of 3.0 kg/m^2 (66 vs. 67%) (Figure 3.5).

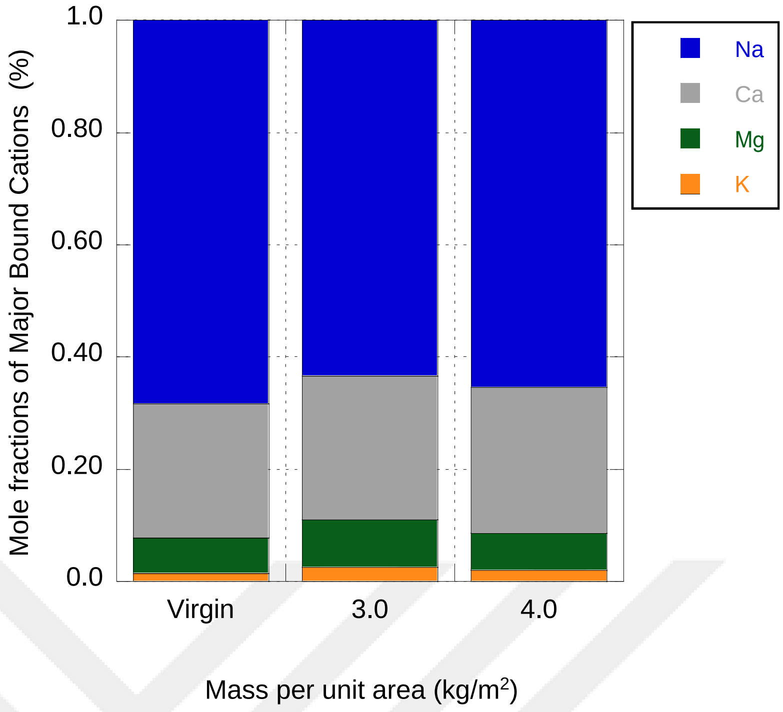

Figure 3.5 Mole fractions of GCL-3 after 180 days of hydration

Since GCL3 contains polymer-treated bentonite, polymer elution has become a parameter that needs to be investigated. Because, sodium-polyacrylamide was used as the polymer material, and elution of this polymer may cause unexpected changes in Na^+ concentration in GCL rather than cation exchange reaction. To examine the polymer elution, polymer contents of bentonites were determined with the loss on ignition (LOI) tests. These tests were conducted with both virgin and hydrated bentonites. The LOI of virgin bentonite (i.e., virgin GCL3) was detected 7.3%. However, the LOI of hydrated bentonites in GCL3 was 4.9 and 4.2% for MPUA of 3.0 and 4.0 kg/m^2, respectively. Reduction in the LOI fractions shows possibility of polymer elusion during hydration. It should be pointed out that these values did not shows the polymer loading on the bentonite. Because, at 550 ^{o}C, strongly bound water molecules abandons the bentonite; calcite decomposes; organic matters combust (Wang et al., 2019). However, Gustitus et al., (2021) investigated the relationship between LOI and polymer loading. According to their proposed relationship, almost 7.0 g polymer/kg bentonite should exist in virgin GCL3 and this value decreased to approximately 5 g polymer/kg bentonite after hydration. When these results are taken into account, it can be said that an elution occurred during the hydration, and this phenomenon may cause a decrease in monovalent cation concentration in GCL3. The eluted polymers are expected to accumulate in the compacted subsoil.

Based on above findings, it is possible to say that MPUA alone has negligible influence on the exchange reaction of GCL1, GCL2 and GCL3.

In this study, the effect of GCL type on cation exchange is also examined. To do this, X_M of the GCLs were compared within each other. In Figure 3.6, X_M of each GCL is presented for any MPUA investigated. As can be seen in this figure, except MPUA 5.0 kg/m^2, the least cation exchange occurred for GCL2. These results imply that GCL type has a substantial effect on cation exchange.

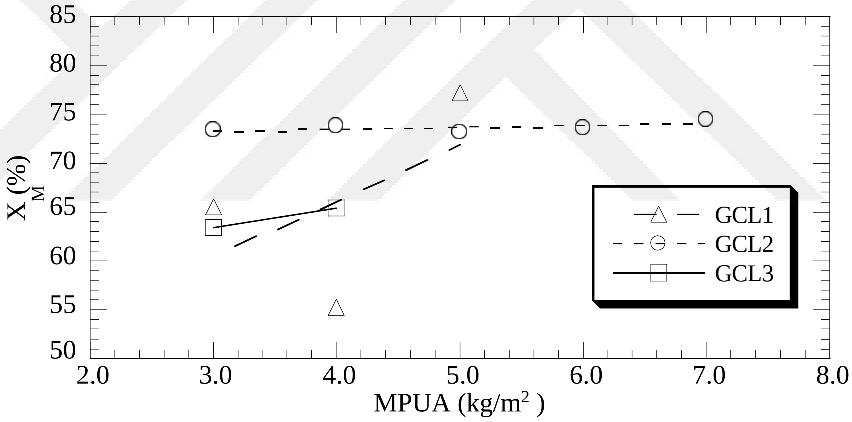

Figure 3.6 Influence of GCL Type on cation exchange in terms of decrease in monovalent cation concentration of bentonites

3.4 **Physical and chemical changes in subsoil after hydration**

At the end of the hydration tests, each subsoil was divided into 5 layers and water content of these layers were determined. The water content of the subsoils was shown from Fig 3.7 to Fig 3.9 for each MPUA and GCL type. In these figures, initial water content of the subsoil is shown with solid line (i.e., 14%).

Although GCL with lower MPUA had greater water content than the GCL with higher MPUA, it absorbs less water with respect to other when mass of water was compared. Since mass of bentonite is more in GCL with higher MPUA, the water content was obtained always less for such GCL. That means GCLs with higher MPUA absorb more water from the underlying soil, and thus, subsoil loses more water during hydration. Therefore, the subsoil below GCL with higher MPUA dries more than the subsoil below GCL with lower MPUA. This expected behavior for the subsoil was observed for each GCL type investigated (Figure 3.7-3.9). Although the $w_{subsoil}$ vary with depth, the average $w_{subsoil}$ will be expressed herein. For example, GCL1 with MPUA 4.0 and 5.0 kg/m^2 reduced from 14% to 11.3 and 10.4%, respectively (Figure 3.7). Note that $w_{subsoil}$ for GCL1 with MPUA of 3.0 was not determined after hydration. It had not been decided to measure the $w_{subsoils}$ at the time of terminating the hydration of GCL1 with MPUA of 3.0 kg/m^2. The subsoil was kept, but not sealed properly. Thus, $w_{subsoil}$ is not given in Figure 3.7.

MPUA effect on subsoil drying was quite prominent for the subsoils below GCL2 (Figure 3.8). Subsoil below GCL2 with MPUA 3.0 kg/m^2 dried least (i.e., 11.5%) while subsoil below the GCL2 with MPUA 7.0 kg/m^2 dried most (i.e., 8.5%), and the others followed this order (Figure 3.8). The first layer of subsoil contacting with GCL2 with MPUA of 3.0 kg/m^2 is significantly lower than other layers. Although slight reduction generally occurred in the first layers of GCLs, such a significant reduction was not observed. The cause of this significant reduction in GCL2 with MPUA of 3.0 kg/m^2 is not known.

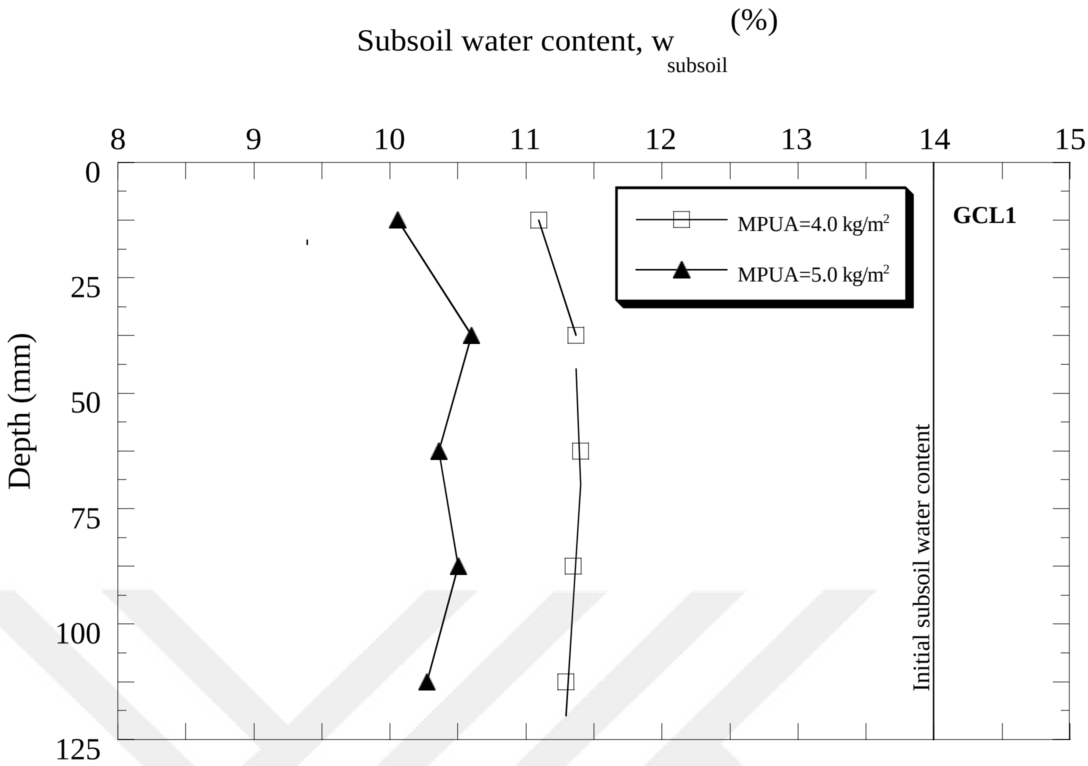

Figure 3.7 Subsoil water contents ($w_{subsoil}$) depending on depth at the end of the 180 days of hydration of GCL1

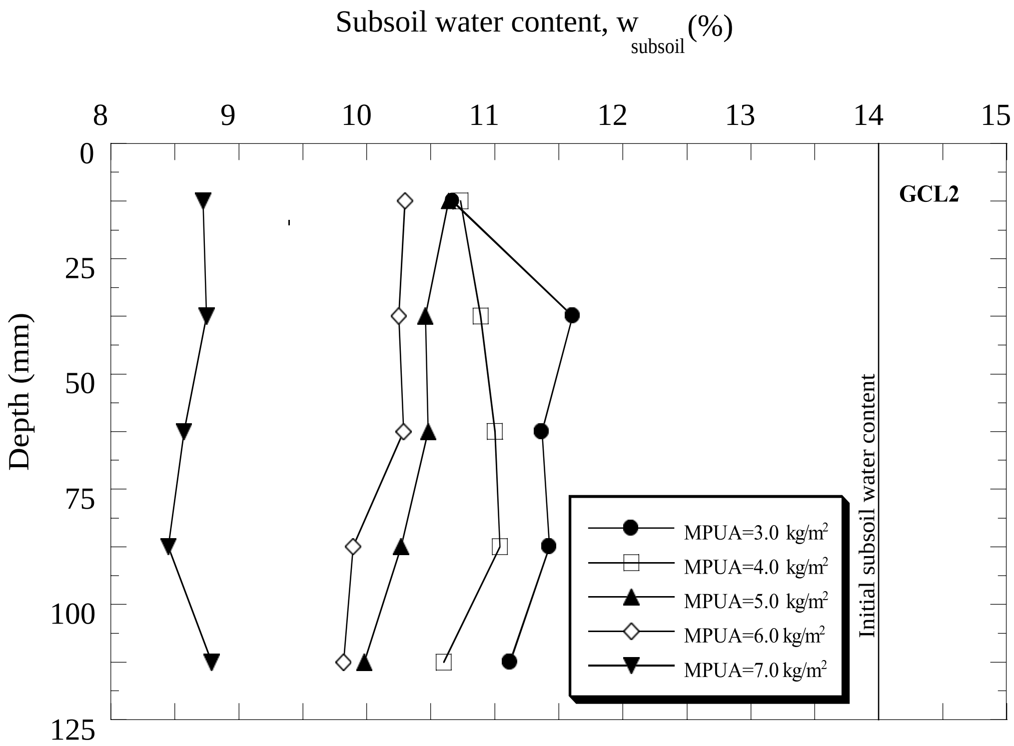

Figure 3.8 Subsoil water contents ($w_{subsoil}$) depending on depth at the end of the 180 days of hydration of GCL2

The change of $w_{subsoil}$ across the depth for polymer GCL (GCL3) was the same as previously observed for GCL1 and GCL2 (Figure 3.9). Figure 3.9 also shows that the greater MPUA of GCL3 led to have lower $w_{subsoil}$.

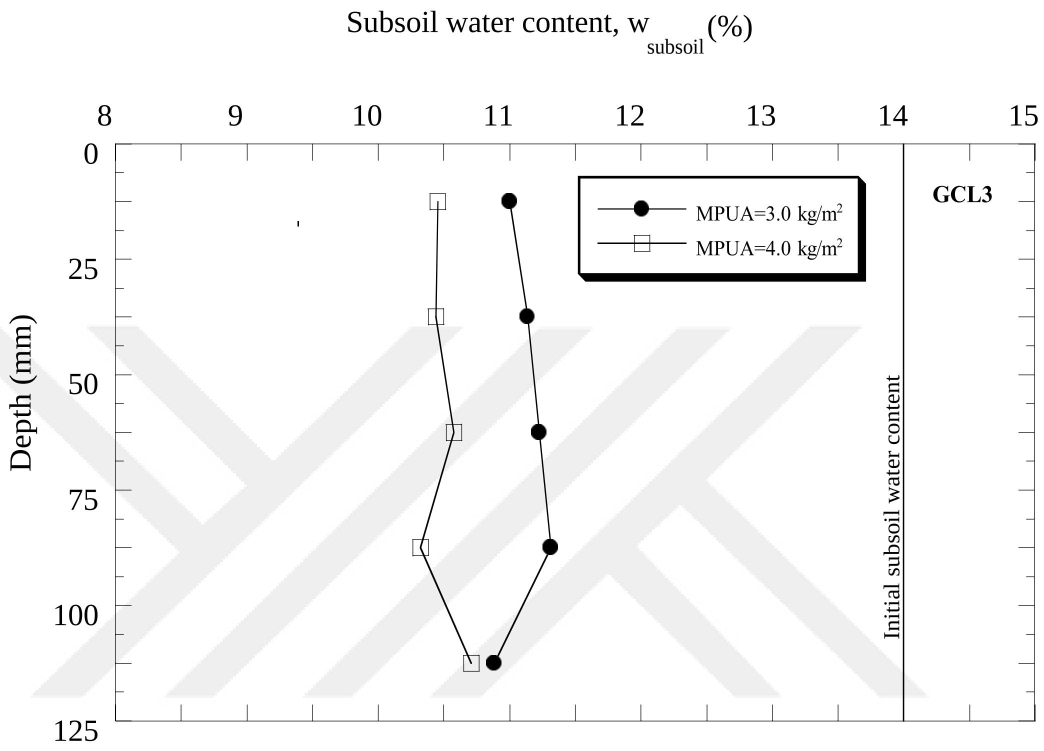

Figure 3.9 Subsoil water contents ($w_{subsoil}$) depending on depth at the end of the 180 days of hydration of GCL3

Batch elusion tests were conducted to determine the exchangeable cations of the subsoils. Thus, cation exchange between subsoil and GCLs can be explained in terms of cation concentration of subsoil. Since the concentration of the K^+ and Mg^{2+} cations were relatively low in the subsoil, and most of the exchange occur between Ca^{2+} and Na^+ cations, only Ca^{2+} and Na^+ were taken into account. These concentrations are presented across the depth and depending on the MPUA of GCL in Figure 3.10 – 3.12.

Figure 3.10 through 3.12 show that the concentrations of Ca^{2+} of subsoil decreased and Na^+ increased significantly during hydration. This implies that more exchange occurred between GCL and subsoil. In other words, GCL released Na^+ through the subsoil and adsorb Ca^{2+} from the underlying soil. Figure 3.10 shows the cation concentration of the subsoils underlying GCL1 which was hydrated for 180 days. In the first 50 mm of the subsoil, it can be seen that GCL with higher MPUA decreased the Na^+ concentration of subsoil more than the GCL with lower MPUA. Na^+ concentration in the first 50 mm of subsoils was average of 109 and 82 mg/L for GCLs with MPUA 3.0 and 5.0 kg/m^2, respectively. In this region of the subsoil, Ca^{2+} concentration decreased significantly to the average of 100 and 29, respectively. Especially for GCL with MPUA of 5.0 kg/m^2, Ca^{2+} concentration approached to zero which means that cation exchange completed. Between 50 and 125 mm, however, Na^+ concentration of the subsoil interacted with MPUA of 5.0 kg/m^2 was greater than the subsoil interacted with MPUA of 3.0 kg/m^2 GCL. The Na^+ concentration of the subsoil interacted with MPUA of 3.0 kg/m^2 GCL had a S-type curved shape, whereas that of the subsoil interacted with MPUA of 5.0 kg/m^2 had a flat shape (vertical). This shows that cation exchange between GCL with MPUA of 3.0 kg/m^2 and subsoil was not completed. Ca^{2+} concentration in the first 50 mm of the subsoil was about three times more for 3.0 kg/m^2 than for 5.0 kg/m^2. This difference in Ca^{2+} concentration also supports that cation exchange reaction was still under progress when the test was terminated. Between 50 and 125 mm, Ca^{2+} concentrations converged at a same value (~75 mg/L) for both GCLs.

Figure 3.10 also shows that cation exchange reaction is more obvious and rapid on top part of subsoil (close to GCL contact plane) where Ca^{2+} and Na^+ concentration of the subsoil reached its minimum and maximum value herein.

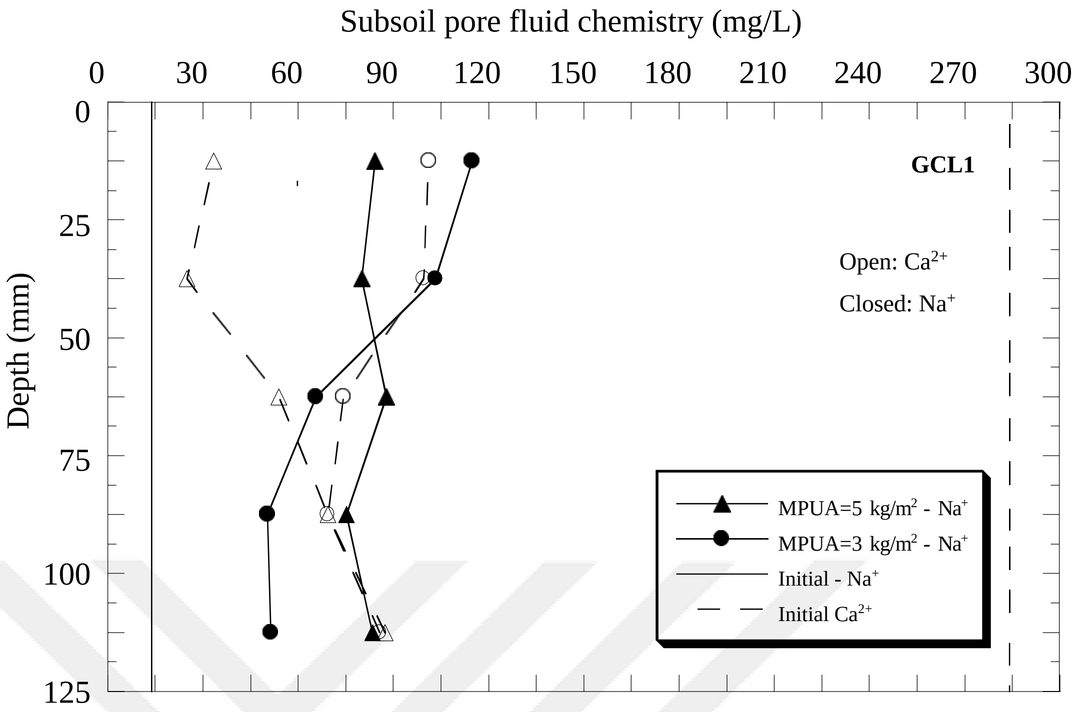

Figure 3.10 Change in concentration of two major cations (Na+ and Ca2+) of subsoils at the end of the 180 days of hydration of GCL1

The exchangeable cation concentrations across the depth of subsoil after interacting with GCL2 resembles to GCL1 as shown in Figure 3.11. Na^+ concentration decreased from top to bottom of the subsoil, whereas Ca^{2+} concentration had a zigzag shape. However, on top of the subsoil, which is close to contact plane of subsoil and GCL2, Ca^{2+} and Na^+ reached its minimum and maximum values regardless of MPUA range.

When this interaction is evaluated in terms of MPUA, then it can be seen that Ca^{2+} concentration of subsoil decreased from 284 mg/L to 61, 46, and 40 mg/L for MPUA 3.0, 5.0, and 7.0 kg/m^2, respectively (Fig 3.11). In contrast, Na^+ concentration of subsoil increased from 14 mg/L to 130, 153, 198 mg/L for the same MPUA range, respectively. This behavior is also similar to subsoil/GCL1 interaction mentioned above (Figure 3.10). That is, the higher the MPUA of GCL, the lower is the Ca^{2+} and the higher is the Na^+ in the subsoil.

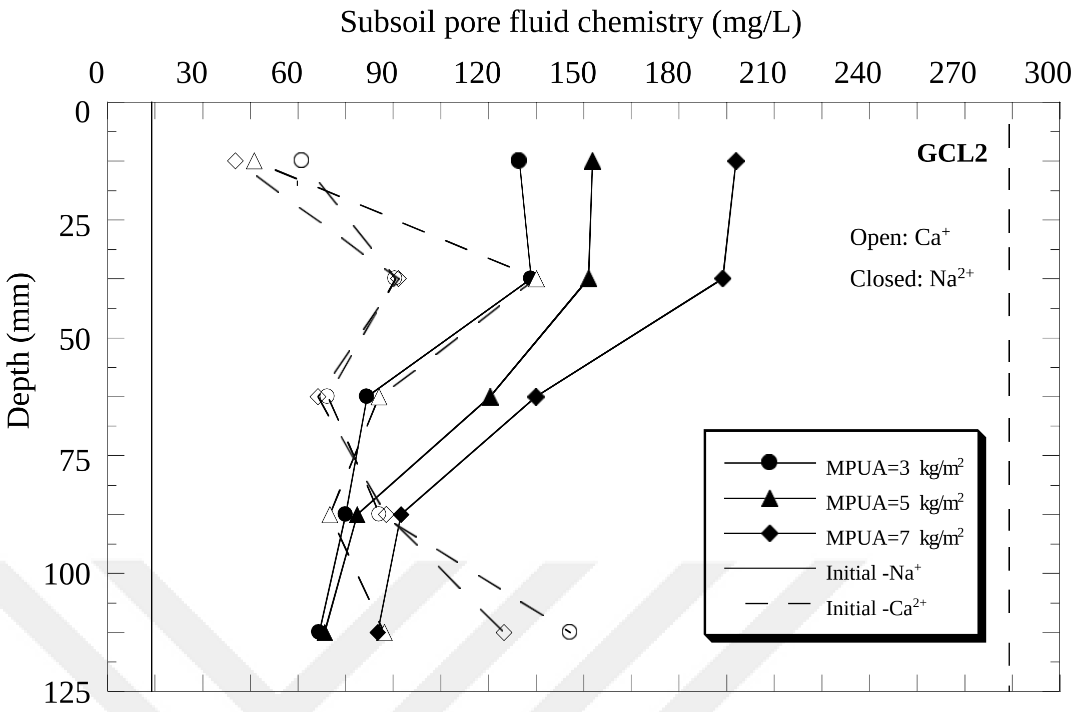

Figure 3.11 Change in concentration of two major cations (Na^+ and Ca^{2+}) of subsoils at the end of the 180 days of hydration of GCL2

The variation of Ca^{2+} and Na^+ cations across the depth of subsoils interacted with GCL3 was limited (i.e., curves are flat shape) when compared to subsoils interacted with GCL1 and GCL2. Ca^{2+} concentrations decreased from 284 mg/L to 53 and 35 mg/L for GCL3 with MPUA of 3.0 and 4.0 kg/m^2, respectively. Unlike other subsoils studied, Na^+ concentrations were rather fluctuated within MPUA. That is, at top and bottom of the subsoil, Na^+ concentration was greater for MPUA of 3.0 kg/m^2 than for MPUA of 4.0 kg/m^2. Between top and bottom, however, it was greater for MPUA of 4.0 kg/m^2 than for MPUA of 3.0 kg/m^2. The possible reason for this fluctuation can be attributed to polymer elution.

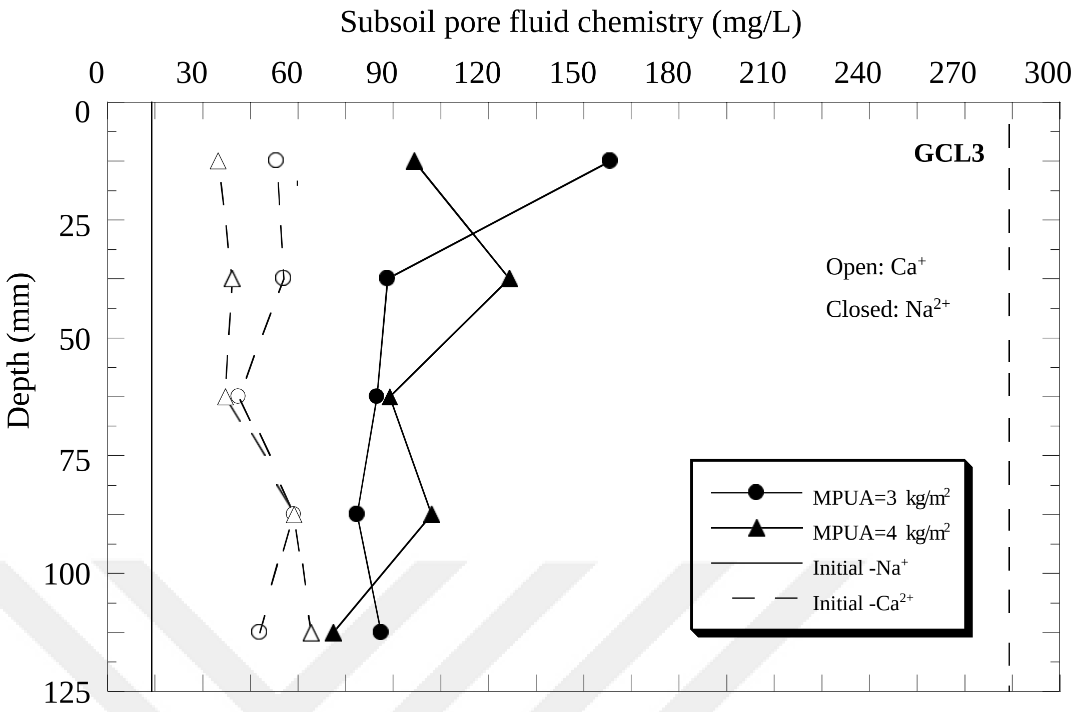

Figure 3.12 Change in concentration of two major cations (Na+ and Ca2+) of subsoils at the end of the 180 days of hydration of GCL3

In summary, declining trend of Ca^{2+} concentration with increasing in MPUA was observed for each of the GCL type investigated. At this point, it should be indicated that while the effect of MPUA was not prominent with the bound cation tests conducted with bentonite extruded from GCLs, it became noticeable with the batch elusion tests conducted on silty sand subsoil. Based on above findings, it is possible to say that GCLs with higher MPUA absorbs more mass of water from underlying soil, resulting in a more replacement between Na^{+} of GCL and Ca^{2+} of subsoil.

3.5 Conclusions

In this study, the influence of GCL type and MPUA of GCLs on the interaction between subsoil and GCL were investigated. For this purpose, three different GCLs with different MPUA were hydrated 180 days in PVC molds under 1 kPa vertical stress. At the end of the hydration duration, water contents and bound cations of the bentonites extruded from the GCL were determined. Additionally, water content and pore water chemistry of the subsoil were obtained across the depth. Thus, the cation exchange behavior of GCLs was also explained with a change in subsoil chemistry.

As a result of these experiments, the following conclusions, and recommendations can be made:

- The water content of the GCLs was rapidly increased in the first 30 days. Thereafter, a decrease was observed in the water contents of GCL1 and GCL3. This decrease can be attributed to cation exchange that took place between GCL and subsoil or evaporation during weighing the GCLs.
- As the MPUA increased, the water content of GCLs decreased for each type of GCL.
- GCL type has a substantial effect on the w_{final} of GCLs. In this study, GCL2 has reached the highest w_{final}.
- When cation exchange was investigated in terms of mole fractions of bentonites, the influence of MPUA was not clearly observed. For instance, X_M of GCL2 with MPUA 3.0 kg/m^2 was 73% while it was 74% for GCL2 with MPUA 7.0 kg/m^2. The same conclusion can be drawn for GCL1 and GCL3.
- GCL type has a considerable effect on the cation exchange. GCL2 exposed less exchange than other GCLs investigated for each MPUA investigated (except for GCL1 with MPUA 5.0 kg/m^2).
- $w_{subsoils}$ were determined across the depth at the end of the hydration duration. As the MPUA of the GCL increased, the w_{final} of the subsoil decreased. Although GCL with higher MPUA had lower w_{final} than GCL with lower MPUA, it absorbs more mass of water from the subsoil, resulting lower $w_{subsoil}$ across the depth.
- For most of the tests, the lowest water contents were observed in the first layer of the subsoil (i.e., first 25 mm of the subsoil). The water content and cation exchanged changes were remarkably observed in this layer.
- As a result of batch elusion tests conducted with the subsoils at the end of the hydration duration, massive changes were detected in Na^+ and Ca^{2+} cation concentration. As the cation exchange occurs between GCLs and silty sand subsoil, GCL takes Ca^{2+} from the subsoil and release Na^+ through the subsoil.

Thus, Ca^{2+} concentration decreased and Na+ concentration increased in the subsoil.

- When the change in cation concentration of the subsoil investigates in terms of MPUA, the Ca^{2+} concentration of subsoils below the GCLs with higher MPUA decreased more for each type of GCLs. It can be deduced that GCLs with higher MPUA exposed more cation exchange than those with lower MPUA.

CHAPTER FOUR
COMBINED INFLUENCE OF SUBSOIL WATER CONTENT AND MASS PER UNIT AREA ON CATION EXCHANGE BEHAVIOR OF GEOSYNTETIC CLAY LINERS

4.1 Background

The hydraulic conductivity of GCL is crucial for maintaining the barrier property. Thus, the factors affecting the hydraulic conductivity need to be known. Hydration is one of the parameters that affect the permeability of GCL. When GCL is installed on a subsoil, it takes water from subsoil due to the suction head difference between GCL and subsoil. This water uptake phenomenon is called as hydration. The hydration process consists of two phases: vapor and liquid (Rouf et al., 2016; Bouazza et al., 2017, Acikel et al., 2018). When GCL has adequate contact with the subsoil and when subsoil has enough water, then hydration occurs in the liquid phase. If there is no sufficient contact between the subsoil and GCL or even good contact but subsoil has no adequate water to moisten the bentonite, hydration occurs in the vapor phase. The type and water content of subsoil; normal stress acting on GCL; initial water content, type, and mass per unit area (MPUA) of GCL; and daily thermal cycles applied on GCLs are the main factors that affect hydration (Rayhani et al., 2011; Anderson etal., 2012; Barclay & Rayhani, 2013; Bradshaw et al., 2013; Bradshaw & Benson, 2014; Rowe et al., 2019; Sarabian & Rayhani, 2013).

Hydration is governed by crystalline and osmotic swelling of bentonite particles. Zhou (1995) stated that when clays are subjected to a concentrated brine or a solution dominated by divalent or multivalent cations, crystalline swelling occurs. If clay mineral encounters a dilute solution where sodium (Na^+) is predominant, this situation causes a robust repulsion between the layers and hence, osmotic swelling occurs. Crystalline swelling is commonly correlated with relatively lower water content (35%-50%), while the osmotic swelling is associated with relatively higher water content (35%-200%) (Yesiller et al., 2019). When cation exchange occurs between Na^+ and calcium (Ca^{2+}) cations, loss of hydrated water can raise a problem that affects the hydraulic conductivity of GCLs.

Cation exchange is a rapid, reversible, stoichiometric, and diffusion-controlled chemical process (Sparks, 2002). This exchange phenomenon depends on temperature, pressure, soil solution composition, and soil-solution mass ratio. Cation replacement occurs between one adsorbed readily exchangeable cation by another via an aqueous solution (Sposito, 1981). While analyzing the cation exchange of GCLs, generally Na^+, potassium (K^+), Ca^{2+}, and magnesium (Mg^{2+}) are primarily investigated cations and known as exchangeable cations.

Many studies reported in the literature highlight the importance of cation exchange during hydration (Benson & Meer, 2009; Bradshaw et al., 2013; James et al., 1997.). However, the combined role of subsoil water content ($w_{subsoil}$) and MPUA of GCLs in the hydration has been rarely investigated so far and thus, needs further attention. This study investigates the combined influence of $w_{subsoil}$ and MPUA of GCLs on the hydration water contents of GCLs and cation exchange that occurs between subsoil and GCL during hydration. For this purpose, GCLs within the range of 2.9–5.1 kg/m^2 MPUAs were hydrated over compacted silty sand, which had been prepared at four $w_{subsoils}$ such as 8%, 11%, 14%, and 17%. After hydration, the exchangeable cations of bentonite were detected and the results were evaluated with changes in the swell indices as well.

4.1.1 ***Influence of MPUA and Subsoil Water Content on Hydration***

Rayhani et al. (2011) investigated factors affecting GCL hydration. Three GCLs were hydrated on silty sand and poorly graded sand subsoils for up to 70 weeks. The MPUA of GCLs used in this study ranged between 3.4 and 5.6 kg/m^2. Silty sand subsoil, which has 11.6% optimum water content was compacted at four water contents: 5%, 10%, 16%, and 21%. The results showed that an increase in the $w_{subsoil}$ increased the final water content (w_{final}) of GCLs. Additionally, although the influence is not as obvious as $w_{subsoil}$, GCL water content also increased as the MPUA decreased.

Anderson et al. (2012) placed three GCLs on clayey sand subsoil (SC) to investigate the effects of product type and initial moisture content of subsoil on the hydration of GCLs. The MPUA of the GCLs were ranged between 3.7 and 5.5 kg/m^2. Subsoils were compacted at four water contents, such as 5%, 10%, 15%, and 20%. In this study, isothermal and cyclic-heating tests were conducted in PVC cells. It was observed that as the $w_{subsoil}$ increased, w_{final} of the GCLs increased.

Sarabian and Rayhani (2013) revealed the influence of MPUA and $w_{subsoil}$ on the hydration water content of GCL. They investigated the hydration behavior of two GCLs under both isothermal conditions and daily thermal cycles. The MPUAs of the GCL-1 and GCL-2 were 3.9 kg/m^2 and 5.4 kg/m^2, respectively and the subsoils were compacted at different water contents (i.e., 10%, 30%, 45%, and 60%). It was pointed out that the hydration rate of GCLs and their w_{final} was affected considerably by the $w_{subsoil}$. Additionally, the w_{final} of GCL-1, which had relatively lower MPUA with respect to GCL-2, was greater than the w_{final} of GCL-2.

4.1.2 ***Cation Exchange during Hydration***

James et al. (1997) conducted hydration tests on GCLs that were used to ensure seals to roofs of five water service reservoirs. Because of cation exchange, Na^+ content of bentonite decreased from 63% to 43%, while Ca^{2+} content increased from 41% to 51%. It was indicated that the replacement of Na^+ with Ca^{2+} resulted in shrinkage and cracking of the bentonite in GCL.

Meer and Benson (2007) performed bound cation tests on exhumed GCLs. It was observed that all GCLs were exposed to cation exchange with the subsoils. Ca^{+2} and Mg^{+2} was replaced with Na^+ in bentonite. Even for some bentonite, the mole fraction of Na^+ reduced to 0.02 (e.g., for D2 sample). It was also pointed out that the hydraulic conductivity of exhumed GCLs was strongly associated with the gravimetric water content of the GCL. To emphasize the importance of water content, it was indicated that when the gravimetric water content of GCLs was greater than 100%, the hydraulic conductivity values were obtained relatively lower.

Scalia and Benson (2011) reported that the water content of the GCLs increased as the $w_{subsoil}$ increased. Bound cation tests conducted on exhumed GCLs showed that monovalent cation fraction of the bentonite reduced from 0.76 to around 0.05 (e.g., for the samples extracted from Site E-03). It was recommended that GCLs should be placed on the subgrade with water content higher than the optimum water content to ensure the barrier feature.

To highlight the influence of cation exchange between GCL and subsoil during hydration, Rowe and Abdelatty (2012) considered two scenarios. In the first scenario, GCL was placed on a Ca^{2+} rich soil (1700 mg/l Ca^{2+}) and hydrated for 1100 days. In this scenario, Na^{+} fraction decreased from 77% to 26% in the first 475 days and from 26% to 20% between 475 and 1100 days. In the second scenario, 30 cm foundation soil (300 mg/l Ca^{2+}) was placed between GCL and Ca^{2+} rich soil and thus, GCL was hydrated from foundation soil. For this scenario, Na^{+} fraction decreased from 77% to 47% in the first 453 days and from 47% to 40% between 453 and 1100 days. While Na^{+} fraction decreased, Ca^{2+} fraction of the bentonite increased in both cases. However, placing the foundation soil between GCL and Ca^{2+} rich soil delayed the cation exchange.

Bradshaw et al. (2013) evaluated the cation exchange by conducting the hydration test on Na-GCLs. GCL with MPUA of 3.7 kg/m^2 was hydrated on four subgrades, namely, Torpedo sand, Red Wing clay, Boardman silt, Cedar Rapids clay. As a consequence, it was reported that cation exchange occurs in the first 30 days of hydration. This outcome shows that cation exchange starts in the early stages of hydration. To reduce the cation exchange, it was recommended to compact subsoil on its wet side of optimum water content.

Kul and Oren (2019) examined the hydration behavior of two GCLs on zeolite. The bentonite MPUA of the LP-GCL and HP-GCL were within the range of 3.2–4.3 kg/m^2 and 2.7–3.0 kg/m^2, respectively. GCLs were hydrated up to 90 days. It was reported that there was a considerable amount of cation exchange occurred between LP-GCL and subsoil in the early stages of hydration, whereas no exchange occurred between HP-GCL and subsoil. For LP-GCL, while a slight change was seen in the first 7 days, monovalent cation fractions decreased from 0.87 to 0.76 at the end of 30 days and to 0.61 at the end of 90 days of hydration.

Rowe et al. (2019) investigated the effects of the water content of the subgrade on the long-term hydration of five GCLs. GCLs were prehydrated on silty sand subsoil at two distinct water contents (5% and 16%) to show the effect of $w_{subsoil}$ on cation exchange before hydraulic conductivity tests. MPUA of the GCLs was within the range of 4.4 – 5.2 kg/m^2. They reported that since cation exchange could not occur via vapor transport, the monovalent fraction of GCLs which were hydrated in dry subsoils was considerably greater than that of the GCLs hydrated in wet subsoils (e.g., ~64% vs 35% for GCL1).

4.2 **Hydration Behavior of GCLs**

The results of 16 hydration tests conducted under this study are summarized in Table 4.1. Table 4.1 also presents the degree of potential hydration of GCLs in terms of w_{final}/w_{ref}. w_{final} is the water content of GCL at the end of hydration and w_{ref} is the hydration potential of GCL1 (Na-GCL) which was determined by inundating the GCL with deionized water under a specified vertical stress (Rayhani et al., 2011). For MPUA of 3.0, 4.0, and 5.0 kg/m^2, w_{ref} was obtained as 206, 185, 166%, respectively. Hydration performance of Na-GCL was initially investigated considering three hydration periods namely 30, 90, and 180 days to assess the reproducibility of the tests and to determine the change in cation exchange within 180 days of hydration (from SB1 to SB-5 in Table 4.2). For this purpose, GCLs with MPUA of 4.0 kg/m^2 were hydrated over silty sand compacted at two distant $w_{subsoils}$ (i.e., 8 and 17%). Figure 4.1 shows these hydration behaviors of GCLs as a function of time.

The hydration behaviors of GCLs shown in Figure 4.1a-b are consistent with the previous findings reported in the literature (Anderson et al., 2012; Rayhani et al., 2011; Rowe & Abdelatty, 2012; Sarabian & Rayhani, 2013). The water content of the GCLs rapidly increased in the first 7 days of hydration due to the suction difference between the GCL and compacted subsoil. After that, with the decrease in suction difference, the hydration rate decreased. After 30 days of hydration, there was no change measured in GCL water content. For the GCLs between 90 and 180 days, there were only approximately 5% decrease in water content. Rowe and Abdelatty (2012) reported such kind of decrease in the water contents with time. They attributed this reduction to the loss of bound water because of cation exchange during hydration (Rowe & Abdelatty, 2012).

Table 4.1 Final water content (w_{final}) and hydration potential of GCLs after hydration.

Test #	MPUA (kg/m²)	Subsoil Water Content, $w_{subsoil}$ (%)	Hydration Duration (days)	Final water content of GCL, w_{final} (%)	w_{final}/w_{ref}^{*}
SB1	3.99	8.2	30	69.6	37.6
SB2	4.09	8.3	90	62.8	33.9
SB3	4.16	8.3	180	60.6	32.8
SB4	3.91	16.5	30	108.8	58.8
SB5	3.95	16.6	90	97.8	52.8
SB6	4.02	16.6	180	104.2	56.3
SB7	2.92	7.4	30	69.3	33.6
SB8	3.07	11.8	30	97.4	47.3
SB9	3.17	13.9	30	109.6	53.2
SB10	2.93	17.1	30	111.5	54.1
SB11	3.96	10.8	30	88.3	47.7
SB12	3.91	13.6	30	97.3	52.6
SB13	5.11	7.7	30	64.2	38.7
SB14	5.11	11.6	30	77.8	46.9
SB15	5.03	13.8	30	91.8	55.3
SB16	5.14	17.2	30	94.1	56.7

* w_{ref} at 1 kPa in DI water

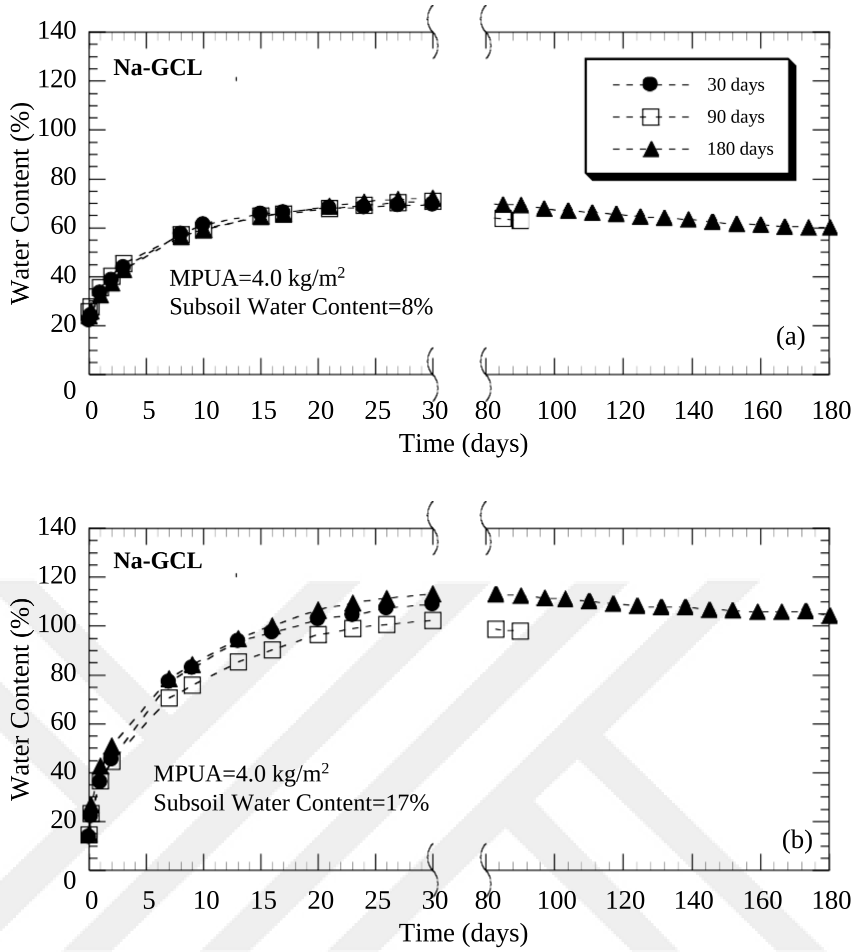

Figure 4.1 Water sorption ability of Na-GCLs when hydrated over silty sand compacted at: (a) 8% water content and (b) 17% water content

The reproducibility of hydration tests can be evaluated considering the behaviors within 30 days of hydration. The negligible change in the hydration behaviors was observed when $w_{subsoil}$ was 8% (Figure 4.1a), whereas slight differences in the water contents were measured when $w_{subsoil}$ was 17% (Figure 4.1b). The differences in the water contents of samples were 11%, which is possibly due to small variations in the $w_{subsoil}$ and MPUAs (Table 4.1b). Thus, this amount of change in w_{final} of GCLs is satisfactory. Since hydration behavior and cation replacement (will be explained later) changed negligibly after 30 days of hydration, it was decided to perform 30 days for the rest of the hydration tests.

Previous studies consider a unique MPUA of GCL and investigate the hydration behavior at different $w_{subsoil}$ (Anderson et al., 2012; Rayhani et al., 2011; Sarabian & Rayhani, 2013). In this study, however, the hydration behavior was measured considering different $w_{subsoil}$ and MPUA conditions. The influence of MPUA on the hydration behaviors of GCLs is shown in Figure 4.2a-d for each $w_{subsoil}$. Except 8% $w_{subsoil}$, GCL water contents increased as the MPUA decreased. Among 30 days of hydration (Table 4.1), the least GCL water content was obtained 64.2% when MPUA of GCL was 5.0 kg/m^2 and $w_{subsoil}$ was 8% (Figure 4.2a).

It can also be seen from Figure 4.2a-d that w_{final} of GCLs increased as the $w_{subsoil}$ increased. Depending on the MPUA, the range of w_{final} significantly increased from 64.2-69.6% to 77.8-97.4% when the $w_{subsoil}$ was increased from 8% to 11%, respectively (Table 3.1). The range of w_{final} further increased to 91.8-109.6% as the $w_{subsoil}$ increased from 11% to 14%. As can be seen from Table 3.1, this increment in the w_{final} is less pronounced (94.1-111.5%) when $w_{subsoil}$ was increased from 14% to 17%. The findings of this study regarding the influence of MPUA and $w_{subsoil}$ on the hydration of GCL are consistent with the literature (Anderson et al., 2012; Rayhani et al., 2011; Sarabian & Rayhani, 2013).

The combined influence of $w_{subsoil}$ and MPUA on the w_{final} of the GCLs is shown in Figure 4.3 by drawing a surface plot. Rather than a linear fit, the general shape of surface plot is quadratic. The slope of $w_{subsoil}$-w_{final} is steeper than that of MPUA-w_{final}. This implies that the influence of $w_{subsoil}$ on the w_{final} is more prominent than that of MPUA. The highest w_{final} was obtained when $w_{subsoil}$ was 17% and MPUA of GCL was 3.0 kg/m^2 (i.e., 111.5%). In contrast, the lowest w_{final} was obtained when $w_{subsoil}$ was 8% and MPUA of GCL was 5.0 kg/m^2 (64.2%).

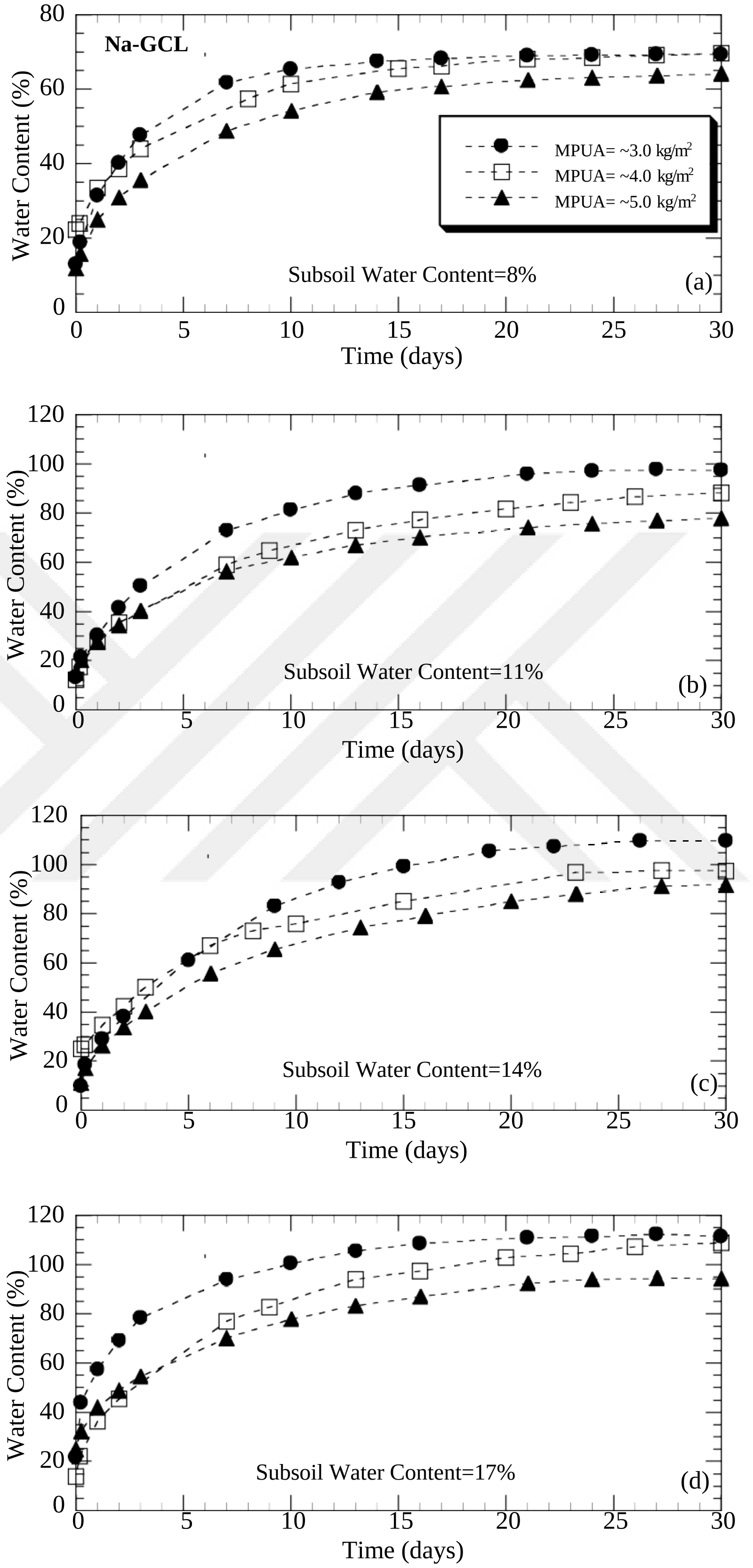

Figure 4.2 Influence of mass per unit area (MPUA) on the hydration performances when hydrated over silty sand compacted at: (a) 8%, (b) 11%, (c) 14%, and (d) 17%

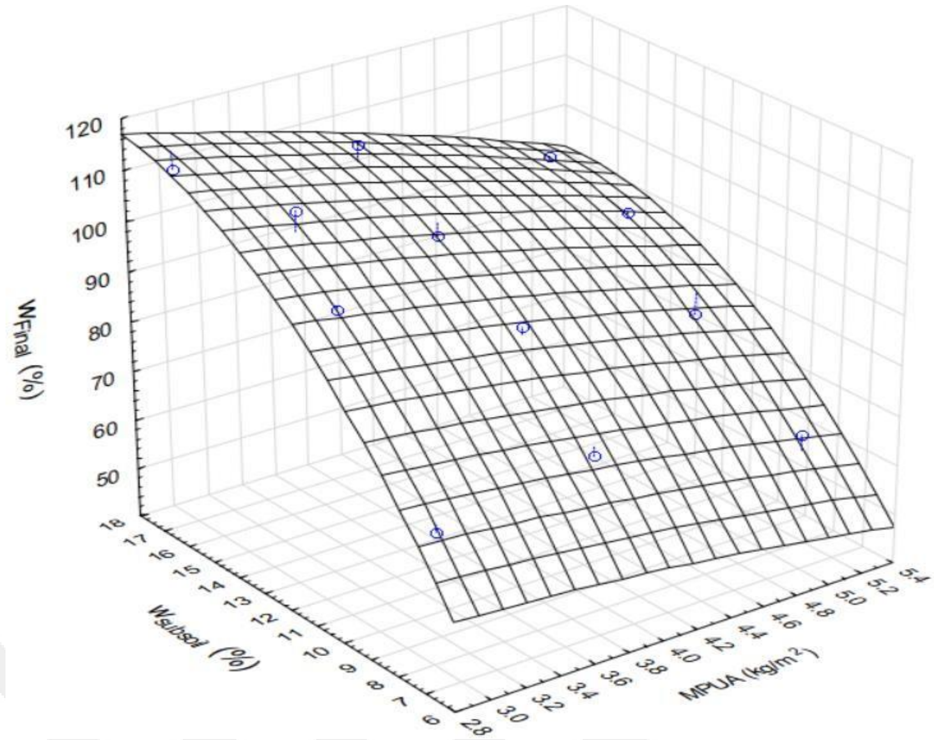

Figure 4.3 Influence of subsoil water content ($w_{subsoil}$) and mass per unit area (MPUA) of GCL on the final water content of GCL (w_{final})

4.3 Cation Exchange During Hydration

The bound cations (Na^+, Ca^{2+}, Mg^{+2}, and K^+) of virgin and hydrated bentonite are presented in Table 4.2 in terms of mole fractions. The change in mole fractions with hydration duration is also shown in Fig 4.4a-b. Cation exchange reaction mainly occurred between Na^+ in GCL and Ca^{2+}/Mg^{2+} in subsoil (Figure 4.4a-b). Mole fractions of K^+ negligibly changed during hydration (Table 4.2). As shown in Figure 4.4a-b, cation exchange was completed within 30 days of hydration regardless of $w_{subsoil}$. In other words, although cation exchange occurred rapidly in the first 30 days of hydration, the mole fractions of cations slightly changed after 90 and 180 days of hydration. For example, Figure 4.4a and Table 4.2 shows that mole fractions of monovalent cations (i.e., Na^+ and K^+, X_M) decreased from 0.81 (virgin) to 0.67 and then to 0.65 and mole fractions of divalent cations (Ca^{2+} and Mg^{2+}, X_D) increased from 0.19 (virgin) to 0.33 and then to 0.35 (SB1-2) after 30 and 90 days of hydration, respectively. In contrast, X_M increased from 0.65 to 0.71 and X_D decreased from 0.35

to 0.29 between 90 and 180 days of hydration (SB3). The source of this difference between 90 and 180 days could be due to small deviations in the $w_{subsoil}$ and MPUA of GCLs. Such differences between the hydration durations were minor when $w_{subsoil}$ was 17%. Following the rapid reduction in the X_M (0.81 to 0.74) or increment in X_D (0.19 to 0.26) within 30 days of hydration (SB4), X_M and X_D slightly changed to 0.72 and 0.28 (SB5 and SB6) in the following hydration durations (i.e., 90 and 180 days), respectively.

The reasons why cation exchange completed within 30 days may be the volume of subsoil used for hydration (i.e., 0.0012 m^3) and Ca^{2+} concentration in the pore fluid of subsoil (i.e., 284 mg/L). The volume of the subsoil used in (R.K. Rowe & Abdelatty, 2012) was 0.28 m^3 and Ca^{2+} concentration was 1750 mg/L in calcium rich silty sand. Although tests were conducted up to 1100 days (Rowe & Abdelatty, 2012), the cation replacement of Na^+ with Ca^{2+} completed around 500 days. In another study, Rowe et al. (2019) hydrated GCLs over silty sand up to 187 weeks. The volume of subsoil was 6.7 times greater (0.01 vs. 0.0012 m^3) and Ca^{2+} concentration was slightly lower than this study (234 mg/L vs. 284 mg/L). Although they reported the exchangeable mole fractions of hydrated GCLs, the time when the cation exchange completed is unknown. Bradshaw et al. (2013) reported the change of mole fractions of exchangeable cations of GCLs hydrated over different types of subsoils. The volume of subsoil was 0.001 m^3 and for Red Wing Clay, Ca^{2+} concentration was 0.6 mM. They reported that X_M increased and X_D markedly decreased up to 90 days of hydration and negligibly changed between 90 and 365 days. Based on their finding, 90 days can be taken as the time required to complete the cation exchange reaction. Although volume and Ca^{2+} concentration of Red Wing Clay is closer to this study, the equilibrium time obtained in both studies is still different which is possibly due to the use of different subsoil types during hydration. This study and the studies reported in the literature show that subsoil dimensions and pore fluid chemistry of subsoils could influence the time required to complete the cation exchange reaction that occurs between GCL and subsoil.

Bradshaw et al. (2013) suggest that subsoils should be compacted at or wet of optimum to minimize the influence of cation exchange. The impact of $w_{subsoil}$ on cation exchange of GCLs has been reported by Rowe et al. (2019). GCL-1 was hydrated over 5% and 16% $w_{subsoil}$ for 87 and 157 weeks and GCL-4 were hydrated over the same subsoil conditions for 87 and 187 weeks, respectively. The water contents after hydration were 55 and 87% for GCL-1 and 52 and 93% for GCL-4 when hydrated over 5% and 16% $w_{subsoil}$, respectively. They reported that bound Na^{+} percentage was greater and Ca^{2+} percentage was lower for GCLs hydrated over 5% $w_{subsoil}$ than for GCLs hydrated over 16% $w_{subsoil}$. They attributed this conclusion to the vapor phase of hydration, which is favored on drier subsoil conditions.

In contrast, this finding of this study shows that cation exchange at 17% $w_{subsoil}$ was lower than that at 8% $w_{subsoil}$ (Figure 4.4a-b and Table 4.2). That means the cation exchange is more favorable when GCLs were hydrated over a subsoil compacted on dry side of optimum water content. In addition to subsoil volume, there are some other differences between Rowe et al. (2019) and this study such as drier subsoil conditions and hydration duration. The drier subsoil conditions applied herein is 8% and greater than that in Rowe et al. (2019). Even after 180 days of hydration, as shown in Figure 4.5, $w_{subsoil}$ decreased to an average of 6.5% across the depth of sample, which is still greater than that of Rowe et al.'s (2019) initial $w_{subsoil}$ (the post-test $w_{subsoil}$ was not given in their study). Additionally, the hydration duration applied in this study was up to 180 days (or 26 weeks), which is significantly lower than that of Rowe et al. (2019).

Table 4.2 Swell Index and exchangeable mole fractions of virgin and hydrated GCLs.

Test #	MPUA (kg/m^2)	$w_{subsoil}$ (%)	Swell Index (mL/2g)	Hydration Duration (days)	Bound cation fractions (%)					
					Na	Ca	Mg	K	X_M	X_D
Virgin	-	-	21.5	-	78.8	14.7	4.7	1.7	81	19
SB1	3.99	8.2	18.0	30	64.8	25.5	7.8	1.7	67	33
SB2	4.09	8.3	18.5	90	63.3	26.4	8.5	1.8	65	35
SB3	4.16	8.3	18.0	180	69.3	23.8	5.1	1.8	71	29
SB4	3.91	16.5	19.0	30	72.3	18.9	6.7	2.0	74	26
SB5	3.95	16.6	17.5	90	70.2	21.2	6.7	1.9	72	28
SB6	4.02	16.6	17.5	180	70.3	21.2	6.4	2.1	72	28
SB7	2.92	7.4	17.5	30	63.4	26.5	8.2	1.9	65	35
SB8	3.07	11.8	18.5	30	66.4	24.9	6.8	1.9	68	32
SB9	3.17	13.9	18.5	30	71.4	20.6	6.2	1.9	73	27
SB10	2.93	17.1	18.5	30	77.4	13.7	6.8	2.2	80	20
SB11	3.96	10.8	18.5	30	66.7	23.2	6.8	3.1	70	30
SB12	3.91	13.6	18.5	30	68.7	22.2	6.9	2.3	71	29
SB13	5.11	7.7	18.5	30	67.0	24.5	7.1	1.5	68	32
SB14	5.11	11.6	18.5	30	66.8	24.3	7.2	1.7	69	31
SB15	5.03	13.8	18.5	30	71.1	20.6	6.6	1.7	73	27
SB16	5.14	17.2	19.0	30	71.9	20.6	4.2	3.4	75	25

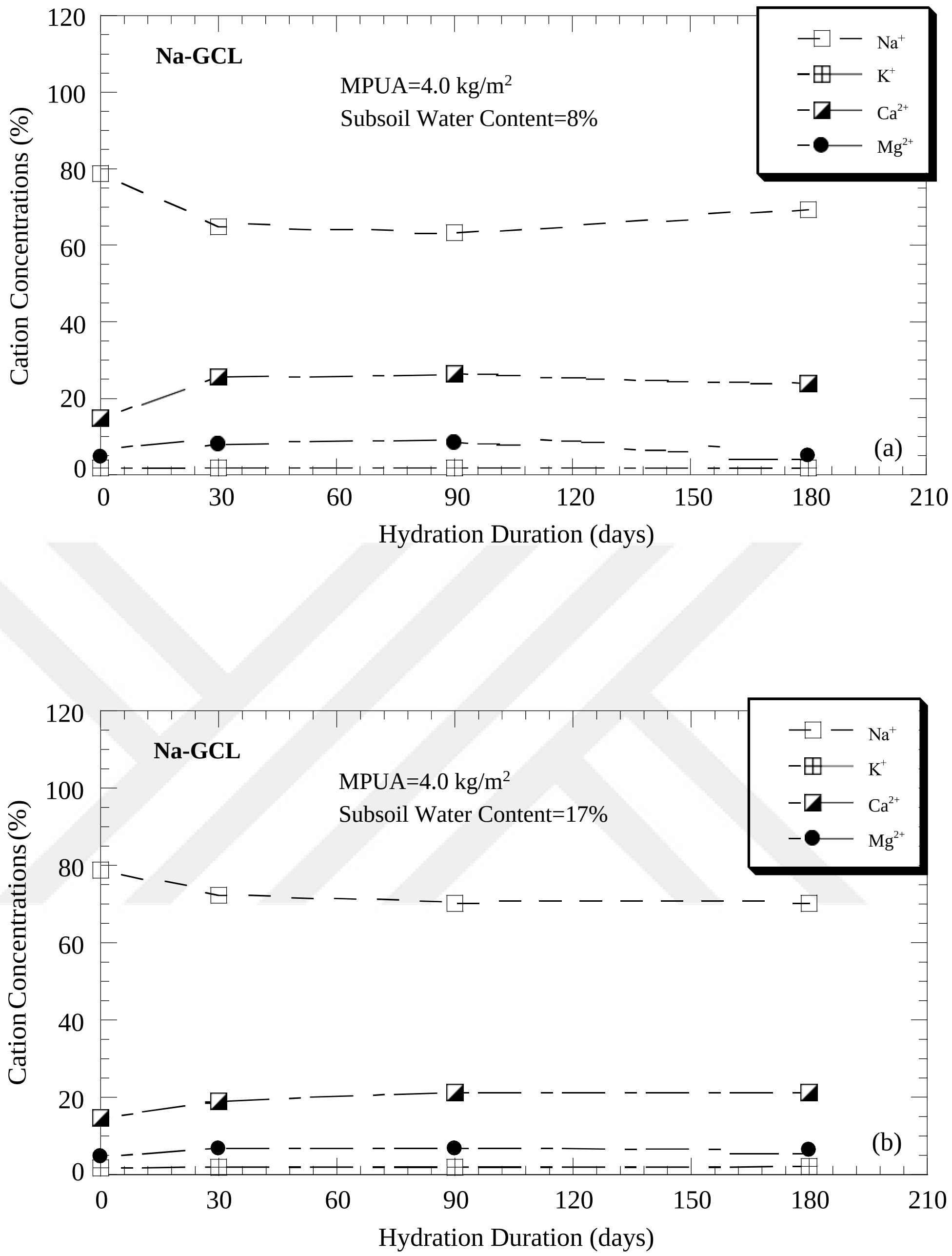

Figure 4.4 Change in mole fractions of exchangeable cations of the GCLs with MPUA 4.0 kg/m^2 when hydrated over subsoil compacted at: (a) 8% and (b) 17% water content

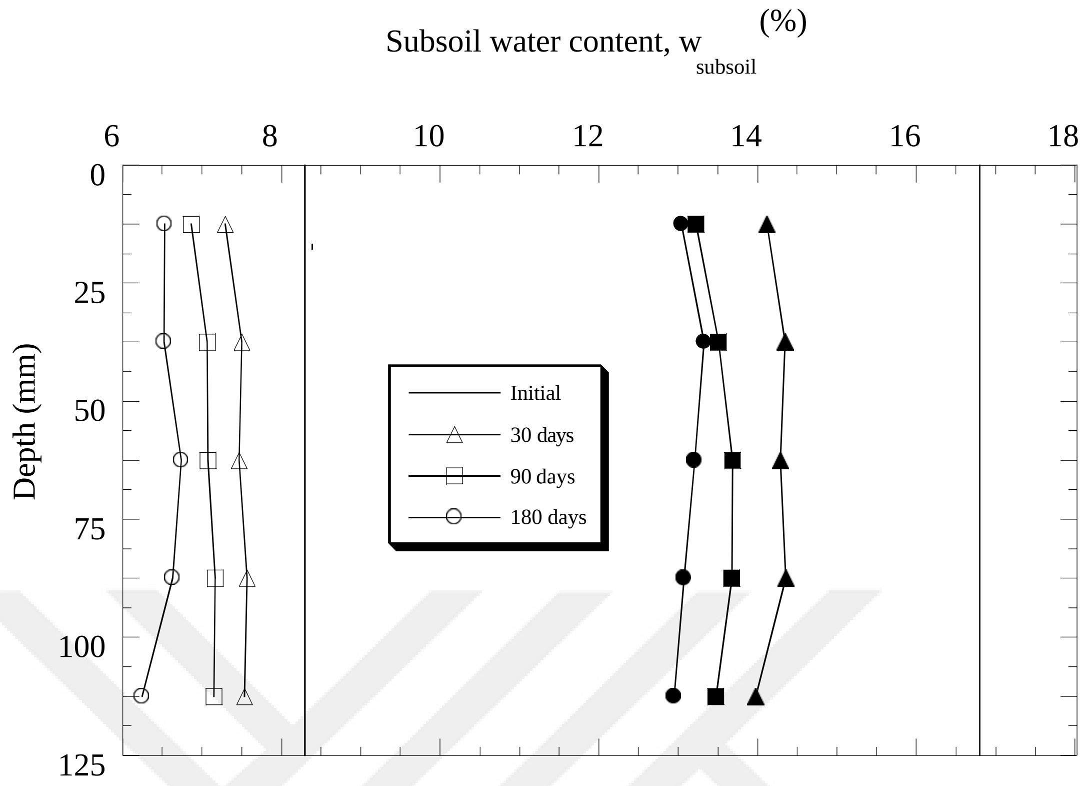

Figure 4.5 Change in subsoil water content ($w_{subsoil}$) with depth after hydration (SB1-SB6)

Acikel et al., (2018) reported that hydration initially occurs in the vapor phase up to 25%-30% water content (i.e., up to water entry value) and then it turns to the liquid phase where the water content of GCL further increases. In this study, however, GCL with lower MPUA and hydrated over 17% $w_{subsoil}$ reached 25%-30% water content less than a one-day hydration period (mostly within 4 h). Similarly, other GCLs, even GCL hydrated over 8% $w_{subsoil}$, reached the liquid phase in few days (Figure 4.1). Thus, it can be said that the hydration process and cation exchange was mainly governed by the liquid phase rather than a vapor phase during hydration (about 29 days) regardless of $w_{subsoil}$ and MPUA in this study. Therefore, the differences in the volume, pore fluid chemistry of subsoil, subsoil condition and hydration duration may be responsible for the difference in the cation exchange reaction.

To examine the effect of pore fluid chemistry of subsoil on the cation exchange reaction, Ca^{2+} rich silty sand was prepared with a similar concentration reported in Rowe and Abdelatty (2012) (1700 mg/L Ca^{2+}). Then, the subsoils were compacted at 8 and 17% water contents. GCLs with MPUA of 4.0 kg/m^2 were hydrated for 30 days over the Ca^{2+} rich subsoils and then exchangeable mole fractions of GCLs were determined as mentioned before. X_M and X_D of GCLs hydrated over Ca^{2+} rich subsoil is given in Figure 3.6 compared to those hydrated over conventional (untreated) subsoil (SB1 and SB4 in Table 4.2). X_M and X_D of GCL hydrated over Ca^{2+} rich soil compacted at 8% were 69 and 31%, respectively. When GCL was hydrated over subsoil compacted at 17%, then X_M and X_D were obtained as 67 and 33%, respectively. Although the difference in X_M and X_D of GCLs hydrated over 8% and 17% $w_{subsoil}$ is slight, the cation exchange reaction is favorable at 17% rather than 8%. This finding is the opposite of that determined by the conventional subsoil (Figure 4.6) and in agreement with the findings of Rowe et al. (2019). This situation shows that subsoil pore fluid chemistry can change the cation exchange reaction.

The exchangeable cations of GCLs hydrated over compacted silty sand at 11% and 14% $w_{subsoil}$ were also determined to validate the cation exchange reaction obtained at 8% and 17% $w_{subsoil}$. Since cation exchange was completed within 30 days of hydration at drier and wetter subsoil conditions and at MPUA of 4.0 kg/m^2, the rest of hydration tests was decided to be conducted just for 30 days.

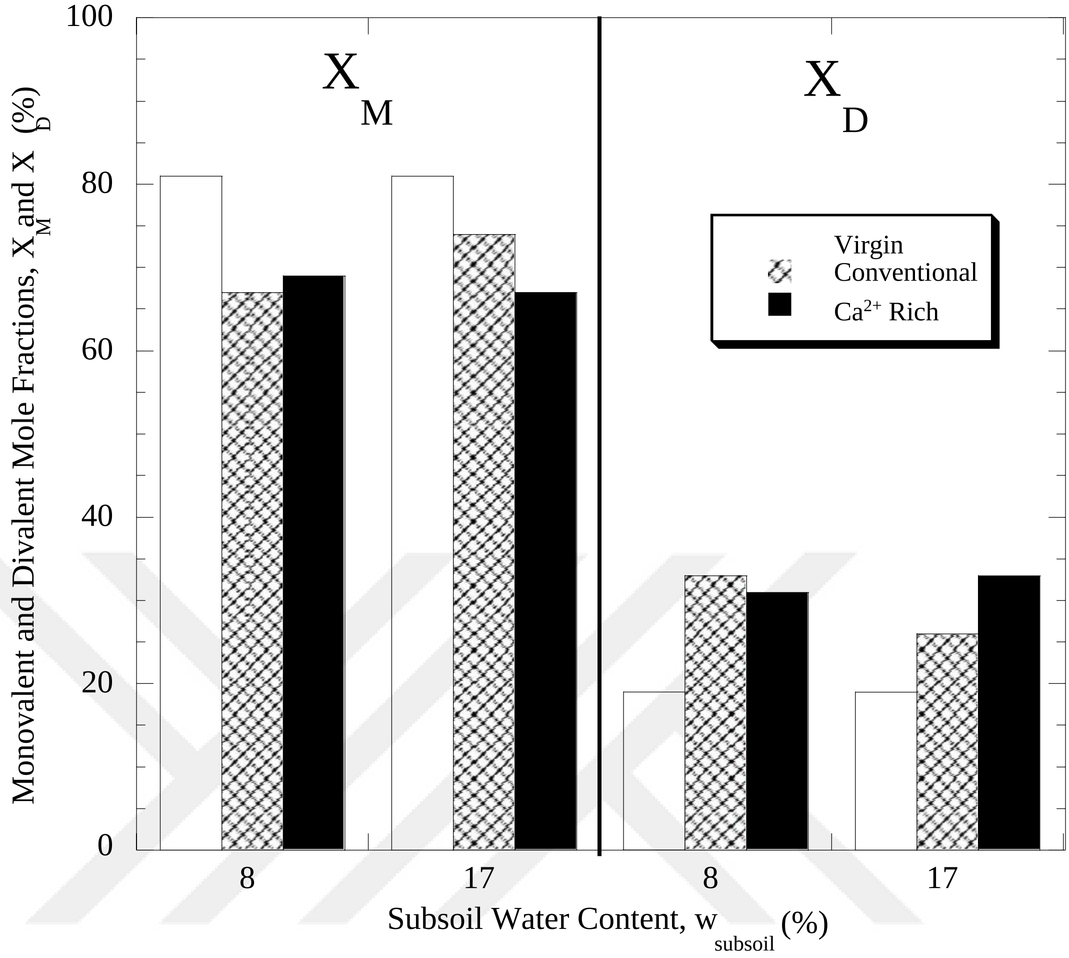

Figure 4.6 Change in monovalent (X_M) and divalent (X_D) fractions of exchangeable cations of GCLs when hydrated over conventional and Ca^{2+} rich subsoils

The influence of $w_{subsoil}$ on the cation exchange is evaluated together with MPUA and shown in Figure 4.7a-b just in case of 30 days of hydrated GCLs. Figure 4.7a-b indicates that X_M and X_D obtained for 11 and 14% $w_{subsoil}$ supported the findings previously shown in Figure 4.4a-b. That is, at any MPUA, X_M decreased and X_D increased with a decrease in $w_{subsoil}$. Note that the rate of change in X_M and X_D decreased through MPUA of 5.0 kg/m^2.

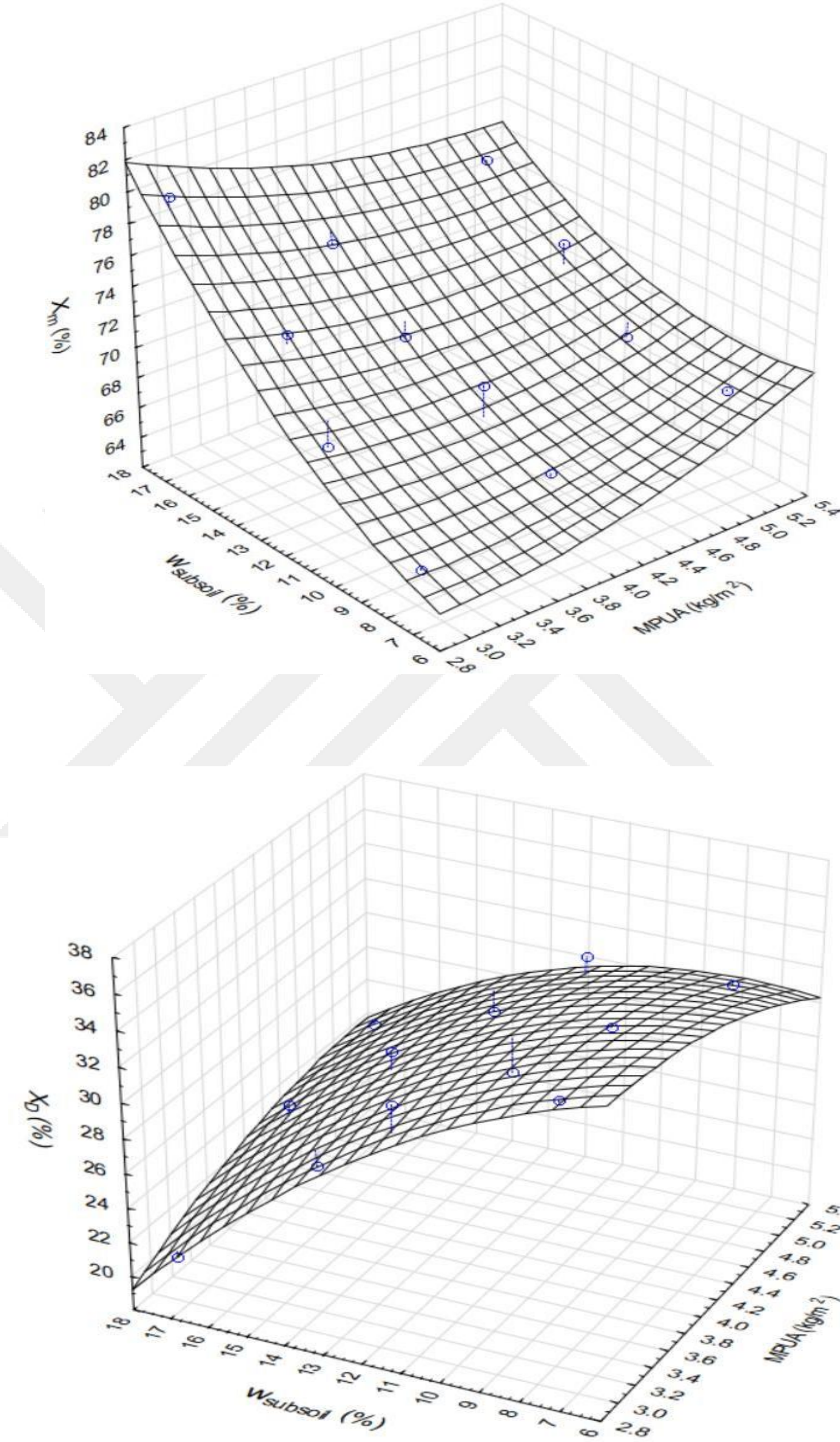

Figure 4.7 Change in mole fractions of exchangeable cations as a function of subsoil water content ($w_{subsoil}$) and mass per unit area (MPUA): a) Monovalent (X_M) and b) divalent (X_D) fractions

The influence of MPUA on cation exchange had two characteristics depending on $w_{subsoil}$ (Figure 4.7a-b). On drier side of optimum (i.e., 8%), X_M increased from 0.65 to 0.69 and X_D decreased from 0.35 to 0.32 as MPUA of GCL increased from 3.0 to 5.0 kg/m^2 (SB7, SB1, SB13 in Table 4.2). Comparing with X_M and X_D of virgin GCL (0.81 and 0.19, respectively), GCL with lower MPUA subjected to cation exchange more than the GCL with greater MPUA. Near optimum (i.e., 11%), X_M and X_D slightly changed, but still the behavior resembles to that obtained for 8% $w_{subsoil}$. X_M was 0.68, 0.70, and 0.69 and X_D was 0.32, 0.30, and 0.32 at MPUA of 3.0, 4.0, and 5.0 kg/m^2, respectively (SB8, SB11, and SB14 in Table 4.2). This trend starts to change on wet side of optimum (i.e., 14 and 17%). That is, when $w_{subsoil}$ was 14%, X_M was 0.73, 0.71, and 0.73, and X_D was 0.27, 0.29, and 0.24 at MPUA of 3.0, 4.0, and 5.0 kg/m^2, respectively (SB9, SB12, and SB15 in Table 4.2). Similarly, X_M was 0.80, 0.74, and 0.75, and X_D was 0.21, 0.26, and 0.25 at MPUA of 3.0, 4.0, and 5.0 kg/m^2, respectively, when $w_{subsoil}$ was 17% (SB10, SB4, SB16 in Table 4.2). As can be seen, the lowest X_M and highest X_D were obtained at MPUA of 4.0 kg/m^2 which makes the fit plane convex rather than concave as previously obtained for w_{final} vs. MPUA/$w_{subsoil}$ (Figure 4.4). This means that the cation exchange was more favorable in MPUA of 4.0 kg/m^2 and when $w_{subsoil}$ was on wet side of optimum. But, even on wet side of optimum for GCL with MPUA of 4.0 kg/m^2, the cation exchange was still lower than the GCLs hydrated over drier subsoil (i.e., 8%) (Figure 4.7a-b). Based on these findings, it can be stated that the abundance of bentonite particles in GCL with greater MPUA delays the cation exchange reaction with respect to the GCLs with lower MPUA.

Figure 4.4a-b and Figure 4.7 show that the cation exchange reaction depends on the $w_{subsoil}$ and MPUA of GCL. The lower the $w_{subsoil}$, the greater is the cation replacement occurred between GCL and subsoil and vice versa. Although not as pronounced as $w_{subsoil}$, cation exchange reaction is more pronounced at lower MPUA. Thus, the greatest cation replacement occurred when $w_{subsoil}$ and MPUA was both the lowest.

4.4 **Post Test Swell Index**

An indirect measure of cation exchange can be done by performing swell index tests on hydrated GCLs. The swell index of the virgin GCL was determined as 21.5 mL/2g. The swell indices of hydrated GCLs decreased to 17.5–19 mL/2g (Table 4.2). This reduction is because of the cation exchange that occurred between GCL and subsoil, indicating the swell index values are in agreement with the cation exchange results. Additionally, swell indices were lower for the GCLs hydrated over drier subsoil conditions than those hydrated on wet side of optimum. Although there is little difference between the values, the swell index of GCLs was 17.5, 18.0, and 18.5 mL/2g when $w_{subsoil}$ was 8%, whereas it was 18.5, 19.0, and 19.0 mL/2g when $w_{subsoil}$ was 17% for MPUA of 3.0, 4.0, and 5.0 kg/m^2, respectively.

The influence of $w_{subsoil}$ and MPUA on swell index of hydrated GCLs is shown in Figure 4.8. A surface plot drawn through the data points shows that swell index increased as the MPUA increased. This increment is more when $w_{subsoil}$ was 8% and less when $w_{subsoil}$ was 17%. Similarly, swell index decreased when $w_{subsoil}$ decreased from 17% to 8%. This decrement is more when MPUA was 3.0 kg/m^2 and less when MPUA was 5.0 kg/m^2. Thus, swell index can be accepted as a notable indicator of cation exchange.

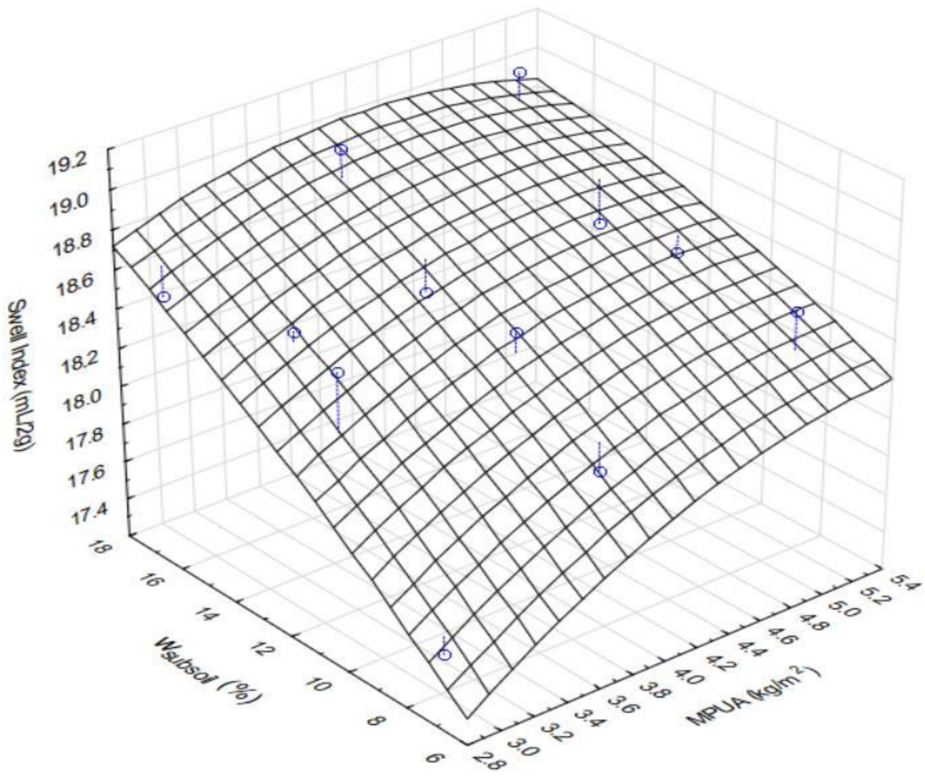

Figure 4.8 Swell indices of the GCLs at the end of the 30 days of hydration

4.5 **Conclusions**

This study discusses the influence of $w_{subsoil}$ and MPUA on hydration performance, cation exchange and swell indices of GCLs. GCLs with MPUA of 3.0, 4.0, and 5.0 kg/m^2 were hydrated on compacted silty sands, which were prepared at four water contents (8, 11, 14, and 17%). When the hydration duration was terminated, bound cations were determined on the bentonite extruded from the GCL. Swell index tests were also conducted on hydrated GCLs. The obtained results are summarized below:

- The water content of the GCLs was rapidly increased within 30 days of hydration. After that, no significant change was observed up to 180 days.
- As the $w_{subsoil}$ increased, the hydration rate of water uptake and w_{final} of the GCLs increased. For instance, at the end of 30 days of hydration, SB1 ($w_{subsoil}$=8%) reached 69.6%, while SB4 ($w_{subsoil}$=17%) reached 108.8% water content.

- MPUA has a negative impact on the w_{final} of GCLs. The increase in the MPUA led to decrease in w_{final} of GCLs. For example, w_{final} of SB9 (MPUA of 3.0 kg/m^2) was 109.6%, whereas w_{final} of SB15 (MPUA=5.0 kg/m^2) was 91.8%.
- In this study, the vapor phase of hydration was completed in few days at most. Subsequently, cation replacement between the subsoil and GCL was even in the short term of the hydration.
- At any MPUA, monovalent cation fraction (X_M) decreased and divalent cation fraction (X_D) increased with a decrease in $w_{subsoil}$ because of cation exchange.
- GCLs with lower MPUA exposed to cation exchange more than GCLs with greater MPUA. Thus, it can be said that greater amounts of bentonite content in the GCL decelerate the cation exchange reaction.
- Among all cases investigated, cation exchange occurred when both subsoil and MPUA are relatively lower.
- This study reveals that the volume of the mold and pore water chemistry of the subsoil may affect the time required to complete the cation exchange reaction occurs between subsoil and GCL.
- Swell indices of the bentonite extruded from hydrated GCLs were noticeably lower than that of virgin GCL even after 30 days of hydration. Swell indices decreased when X_D increased.

CHAPTER FIVE
FACTORS AFFECTING CATION EXCHANGE BETWEEN GEOSYNTHETIC CLAY LINERS AND COMPACTED SUBSOILS

5.1 Background

There are valuable studies investigating the cation exchange that occurs during hydration of GCLs (Bradshaw et al., 2013; Rowe et al., 2019; Rowe and Abdelatty, 2012). However, none of these studies investigate the parameters affecting cation exchange reaction. For this reason, this study aims to investigate some parameters such as hydration time, subsoil water content ($w_{subsoil}$), and vertical stress, affecting the cation exchange reaction. A sodium-rich GCL (i.e., GCL1) with MPUA of 4.0 kg/m^2 was hydrated for 30, 90, 180, and 360 days and the influence of $w_{subsoil}$ was investigated on this GCL. The influence of hydration duration on GCL1 is given together with MPUA in Chapter 4. However, the influence of hydration duration is given once more to evaluate the factors affecting cation exchange reaction in this chapter. In Chapter 4, the influence of $w_{subsoil}$ is given for short term hydration duration (i.e., 30 days). Although it is mentioned that cation exchange reaction was completed within 30 days of hydration, the influence $w_{subsoil}$ is evaluated for the long-term hydration duration herein (i.e., 180 and 365 days). For this purpose, the silty sand subsoil was again compacted at four different water contents: 8%, 11%, 14%, and 17%. Finally, the influence of vertical stress on the cation exchange reaction of GCL1 was determined by applying 1, 2, 5, and 10 kPa stress during hydration.

5.1.1 Influence of Hydration Duration and Subsoil Water Content

Since the studies that investigate the influence of hydration duration and $w_{subsoil}$ are given in Chapter 4 (Bradshaw et al., 2013; Rowe et al., 2019; Rowe & Abdelatty, 2012), there is no need to summarize those studies once again under this chapter. Thus, the studies related to the influence of vertical stress on the hydration behavior will be given herein (next section).

5.1.2 Influence of Vertical Stress

Based on author's knowledge, the effect of vertical stress on the cation exchange reaction of GCL has not been investigated so far. The reported studies deal with their hydration behavior. For example, Chevrier et al. (2012) conducted hydration tests under vertical stress ranging from 7.0 kPa to 28.2 kPa. As a result of these tests, it was found that the final water content (w_{final}) slightly decreased as the vertical stress increased. Note that hydration rate also increased with an increase in the vertical stress. The w_{final} under 7.0 and 28.2 kPa was 107% and 95%, respectively.

Sarabadani et al. (2014) conducted hydration tests on two different subsoils (sand and clay) and different GCLs. The stress range applied in these tests is between zero and 28 kPa. The tests showed that there is a positive relationship between the hydration rate and the vertical stress. Chevrier et al. (2012) argued that increasing vertical stress provides a good contact between GCL and subsoil. However, considering the equilibrium water contents of the GCLs in Sarabadani et al. (2014), it was found that the stress between 2 kPa and 5 kPa had a positive effect. Moreover, no significant change in the w_{final} was observed when the applied vertical stress exceeded 5 kPa.

5.2 Hydration Behavior of GCLs

Water contents of GCL1 hydrated for 30, 90, 180, and 360 days on a silty sand subsoil were determined by recording the mass of GCLs at specific time intervals (Table 5.1). These readings were used to plot time-dependent water content curves. During the first week of hydration, GCL1 swelled due to the rapid uptake of water from the subsoil due to the high suction pressure difference between the subsoil and the GCL. As this suction pressure difference decreased, the hydration rate of the GCLs decreased, and water contents came to equilibrium after approximately 30 days (Figure 5.1). These results are consistent with those reported in the literature (Anderson et al. 2012; Rayhani et al. 2011; Rowe et al. 2012).

Table 5.1 Final water content (w_{final}) of the Na-GCL at the end of the hydration durations

GCL	MPUA (kg/m^2)	Vertical Stress (kN/m^2)	$w_{subsoil}$ (%)	Hydration Duration (day)	w_{final} (%)	W/W_{ref} (%)	Test no#
Na-GCL	4.16	1	8.3	180	60.6	32.8	SB3
Na-GCL	4.05	1	11.0	180	69.9	37.8	SB23
Na-GCL	3.91	1	13.9	30	97.3	52.5	SB12
Na-GCL	4.31	1	13.8	90	84.2	45.5	SB19
Na-GCL	3.91	1	14.5	180	78.0	42.1	SB20
Na-GCL	3.91	1	14.5	360	61.9	33.5	SB24
Na-GCL	4.02	1	16.6	180	104.2	56.3	SB6
Na-GCL	4.72	1	13.9	180	76.6	46.1	SB22
Na-GCL	5.34	2	13.0	180	76.7	46.2	SB25
Na-GCL	5.00	5	14.3	180	75.3	45.3	SB26
Na-GCL	5.33	10	13.8	180	71.9	43.3	SB27

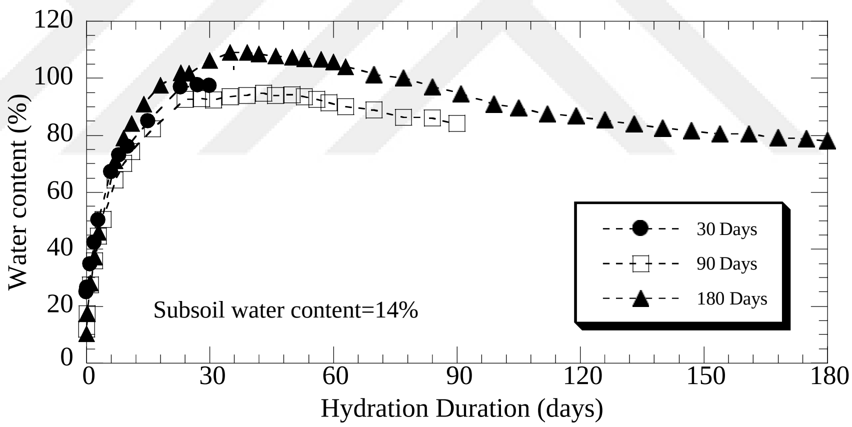

Figure 5.1 Hydration behavior of Na-GCL and its time-dependent water content

To see the effect of $w_{subsoil}$ on hydration, GCL1 with MPUA of 4.0 kg/m^2 was hydrated over the subsoil compacted at four different water contents and those GCLs were hydrated for 180 days (Figure 5.2). Note that one of a sample was hydrated for 365 days. As a result of hydration tests, it was observed that w_{final} of GCL1 increased as the $w_{subsoil}$ increased. It was also observed that the hydration rate was more for greater $w_{subsoil}$ than for lower $w_{subsoil}$. The w_{final} of GCL1 was 60.4% when $w_{subsoil}$ was 8.3% and was 69.6% when $w_{subsoil}$ was 11.0%. The effect of $w_{subsoil}$ was being more pronounced on the wet side of the optimum. For example, w_{final} was 78% when $w_{subsoil}$ was 14%, and was 104.2% when $w_{subsoil}$ was 17%.

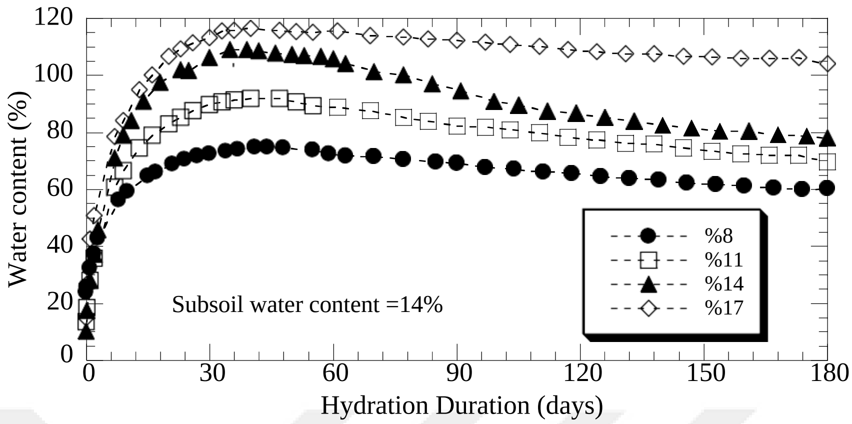

Figure 5.2 Investigating the hydration behavior of Na-GCL depending on subsoil water content

Another factor affecting the hydration behavior of GCL1 is the vertical stress. To see the effect of vertical stress, GCL1 with MPUA of 5.0 kg/m^2 were hydrated for 180 days under 1, 2, 5, and 10 kPa (Figure 5.3). Based on the findings, no significant difference was observed between the w_{final} of GCL1 hydrated under 1, 2, and 5 kPa stresses (76.6%, 76.7%, and 75.3%, respectively). However, the w_{final} for GCL1 hydrated under 10 kPa decreased to 71.9%, which is slightly less than w_{final} obtained under other stresses studied. Moreover, when Figure 5.3 was examined during 180-days of hydration period, the highest water contents were obtained for the GCL1 hydrated under 2 kPa stress, while the lowest water contents were observed for the GCL1 hydrated under 10 kPa stress. Therefore, it can be concluded that 2 kPa was the optimum stress for the hydration of GCLs. It is known that good contact with the subsoil ensures that hydration takes place in the liquid phase (Rouf et al. 2016). However, the obtained results showed that high stresses limit the swelling of bentonites, resulting lower w_{final} for GCL1.

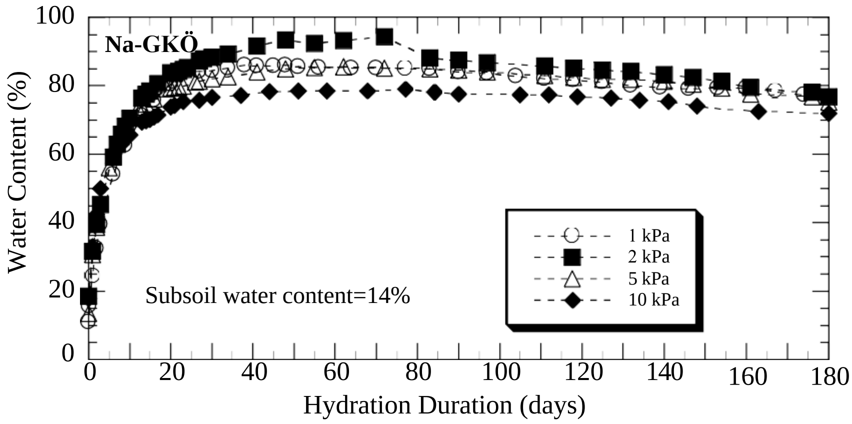

Figure 5.3 Investigating the Hydration behavior of Na-GCL depending on vertical stress

5.3 Cation Exchange during Hydration

The major bound cations (Na^+, Ca^{2+}, K^+, and Mg^{2+}) were determined for virgin and hydrated GCL1. In this study, cation exchange was investigated from two aspects: Mole fraction (%). The results from the bound cation tests are summarized in Table 5.2.

The cation exchange in the bound cations occurred mainly within the first 30 days. This conclusion is already highlighted in Chapter 4. However, the trend was not changed up to 365 days of hydration. X_M for virgin GCL1 was 81%. X_M then decreased to 70% after 30 days of hydration (Figure 5.4). In the meantime, X_D increased from 19% to 30%. The percentages of bound cations remained almost the same for 90 days and 180 days of hydration. For example, X_M was 71 and 70% at 90 days and 180 days of hydration, respectively. The cation exchange over the long term (i.e., 365 days) negligibly changed. X_M decreased and X_D increased slightly with respect to those at 180 days of hydration (X_M =66% and X_D =34%). These results differ somewhat from those in the literature. Because most of the cation exchange occurred in this study completed within the first 30 days. Although cation exchange reaction of GCL hydrated over Red Wing Clay completed after 90 days (Bradshaw et al., 2012), that of GCL hydrated over Cedar Rapids Clay did not complete even after 365 days.

Similarly, fully completion cation replacement between subsoil and GCL may need more than one year as well (Rowe & Abdelatty, 2012).

It is believed that cation exchange reaction depends on the pore water chemistry of the subsoil. The pore water chemistry of the subsoil used in this study was as follows: Ca^{2+} 284.1±15 mg/L; Na^{+} 13.8±1 mg/L; Mg^{2+} 30.4±2 mg/L; K^{+} 36.4±2 mg/L. Rowe and Abdelatty (2012) reported that high concentrations of divalent cations available in the subsoil rapids the cation exchange reaction. They placed a foundation soil (i.e., 200-300 mg/L) between calcium-rich soil (1700-1800 mg/L) and GCL which resulted in a delay of cation exchange reaction with respect to GCL in contact with calcium rich soil. The completion of cation exchange in the within 30 days may be due to relatively low concentration of divalent cations present in the subsoil used in this study. In addition, the volumes of molds used for hydration vary widely in the literature. The larger the mold the more is the calcium source in subsoil. For example, the volume of the hydration mold used in Rowe and Abdelatty (2012) is 282743 cm^3 and the Ca^{2+} amount present in the subsoil is 480663 mg Ca^{2+} when calcium rich soil is in contact with GCL. However, the volume of the mold used in this study is 1207 cm^3. The subsoil has 343 mg Ca^{2+}. This situation is believed to have a severe impact on the results.

Table 5.2 Bound cation concentrations and fractions of Na-GCLs

MPUA (kg/m^2)	Vertical Stress (kN/m^2)	$w_{subsoil}$ (%)	Hydration duration (days)	Bound Cations (%)					
				Na^+	Ca^{2+}	Mg^{2+}	K^+	X_M	X_D
Virgin	-	-	-	78.8	14.7	4.7	1.7	80.5	19.4
4.40	1	8.3	180	64.7	25.1	7.8	2.4	67.1	32.9
4.05	1	11.0	180	69.3	23.8	5.1	1.8	71.1	28.9
3.91	1	13.9	30	75.2	18.1	4.7	2.1	77.3	22.8
4.31	1	13.8	90	68.4	22.7	7.0	1.9	70.3	29.7
3.91	1	14.5	180	68.7	22.2	6.8	2.3	71.0	29.0
3.91	1	14.5	360	68.1	23.1	6.6	2.2	70.3	29.7
4.02	1	16.8	180	66.7	22.5	9.4	1.4	68.1	31.9
4.72	1	13.9	180	70.3	21.2	6.4	2.1	72.4	27.6
5.34	2	13.0	180	69.3	22.7	7.0	1.0	70.3	29.7
5.00	5	14.3	180	70.8	19.8	8.0	1.4	72.2	27.8
5.33	10	13.8	180	71.7	18.5	8.2	1.6	73.3	26.7

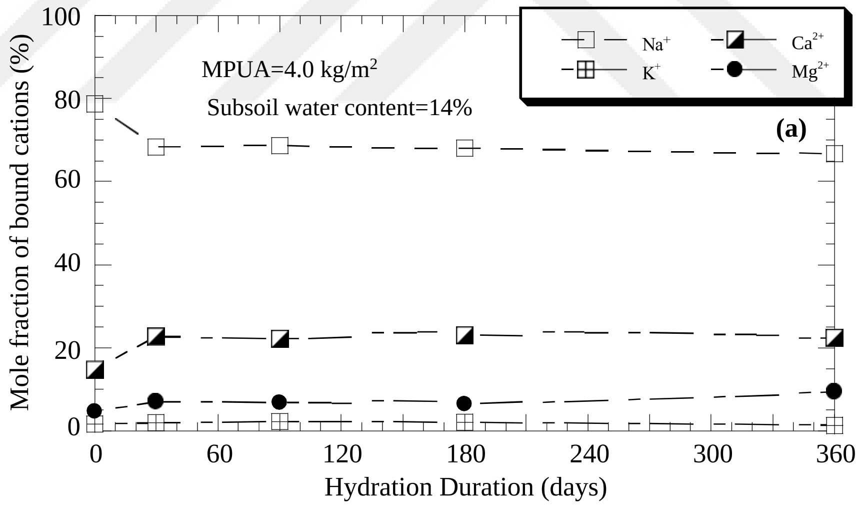

Figure 5.4 Investigating the effect of hydration duration on the cation exchange of GCL1 with MPUA of 4.0 kg/m^2

The effect of $w_{subsoil}$ on cation exchange is shown in Figure 5.5 in terms of mole fraction of bound cations. X_M of GCL1 was 71, 77, 70, 72% when hydrated over a subsoil compacted at 8, 11, 14, and 17% water content (Figure 5.5).

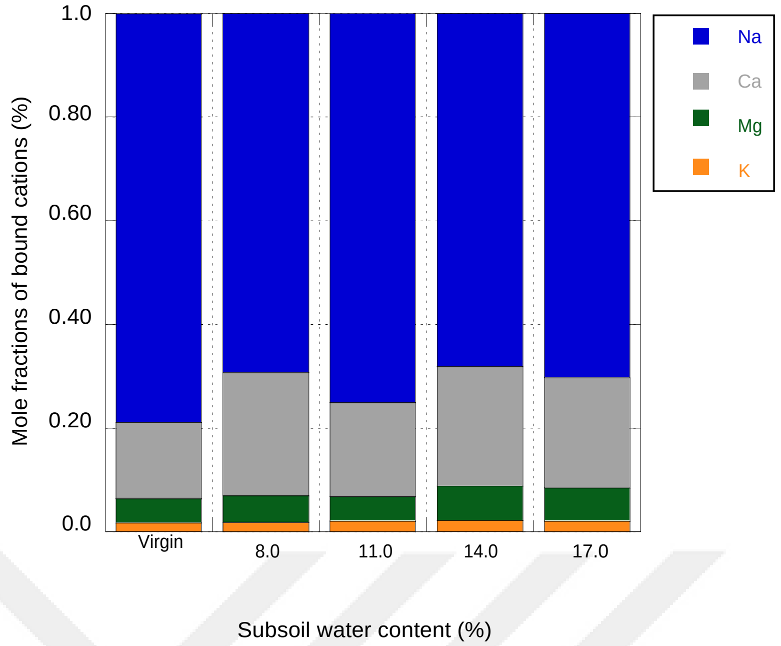

Figure 5.5 Investigating the subsoil water content ($w_{subsoil}$) effect on cation exchange with Na-GCL with MPUA 4.0 kg/m^2 in terms of mole fraction

Another parameter that is thought to affect the cation exchange between the subsoil and GCL1 is the vertical stress. When the results of the experiments conducted at the end of the hydration period with bound cations were examined in terms of mole fraction, no obvious difference was observed between vertical stresses. For example, X_M of Na-GCL was 70 and 72% when hydrated under 1 and 10 kPa stress, respectively. For the tests conducted under 2 and 5 kPa vertical stress, X_M was determined 72% and 73%, respectively (Figure 5.6). Considering these results, it is very difficult to talk about the influence of vertical stress on the cation exchange. It is known that at higher vertical stresses, there is a good contact between GCL and the subsoil. With the good contact, it is expected that the cations can be easily transported because water is present in the subsoil to allow hydration of the GCL in the liquid phase. Therefore, it is expected that more cation exchange occurs at high vertical stress level. However, Figure 5.6 shows that this effect is negligible.

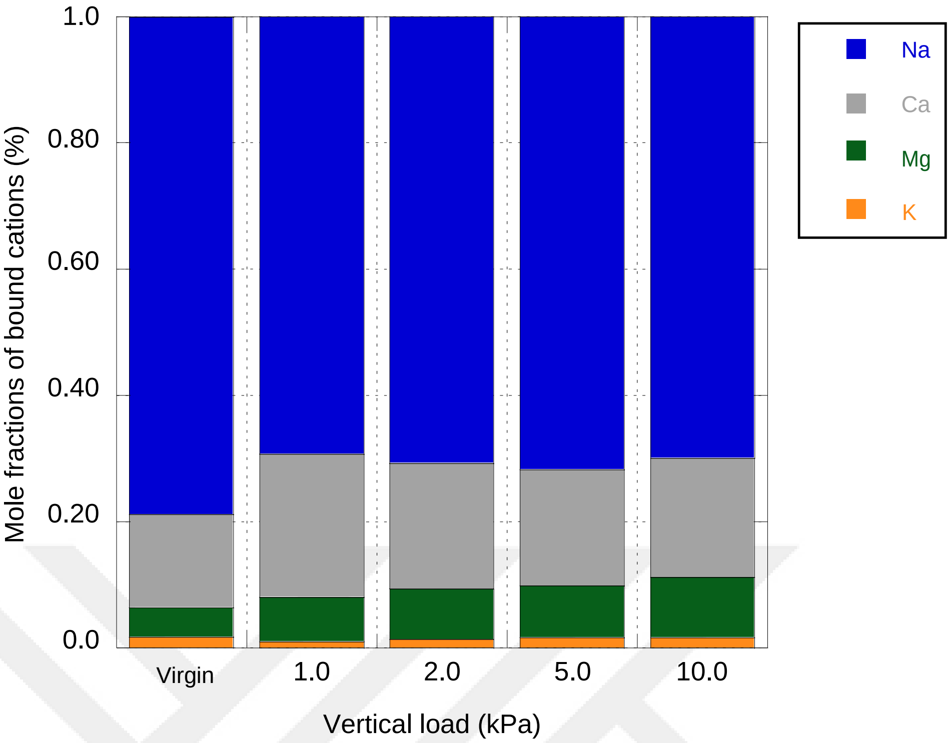

Figure 5.6 Investigating the vertical stress effect on cation exchange with Na-GCL with MPUA 5.0 kg/m2 in terms of mole fraction

5.1. Conclusions and Recommendations

In this study, the cation exchange between GCL1 and compacted subsoil was investigated as a function of $w_{subsoil}$, hydration time, and vertical stress. To investigate the influence of hydration time, GCL1 was hydrated with MPUA of 4.0 kg/m^2 for 30, 90, 180, and 360 days. To investigate the effect of the $w_{subsoil}$, silty sand was compacted at 8%, 11%, 14%, and 17%, and GCL1 was hydrated on these subsoils. Finally, to investigate the effect of vertical stress, GCL1 with an MPUA of 5.0 kg/m^2 was subjected to 1, 2, 5, and 10 kPa vertical stresses during the 180-day hydration period. At the end of the hydration period, the major bound cations of the bentonites were determined. The results were examined in terms of both mole fraction and cation concentration.

Based on the findings, the following conclusions can be made:

- As $w_{subsoil}$ increases, the w_{final} of the GCL1 increases.
- The effect of vertical stress on GCL hydration is negligibly important. When considering the w_{final}, it can be seen that increase in vertical stress limits the swelling of the GCLs, resulting in a slight decrease in the w_{final}.
- When examining the effect of hydration time on cation exchange, it was found that cation exchange between the GCL1 and subsoil was rapid during the first 90 days of hydration and did not change significantly thereafter. The reason why cation exchange was not observed after 90 days of hydration is probably due to relatively low number of divalent cations in the pore water of subsoil.
- The effect of vertical stress on the cation exchange is negligible. It is expected that good contact would be satisfied when vertical stress increased. However, such effect on cation exchange was not observed.

CHAPTER SIX
SUMMARY AND CONCLUSIONS

6.1 Summary and Recommendations

This study investigates and discusses the factors affecting cation exchange between GCLs and compacted subsoils during hydration. For this purpose, three GCLs, namely GCL1, GCL2, and GCL3, were hydrated for up to 360 days on compacted silty sand prepared at four different water contents. Based on the findings obtained so far, the following conclusions and recommendations can be made in terms of change in water contents and cation exchange reactions:

Conclusions Regarding to Water Content of GCL:

- GCLs rapidly absorbed water from the underlying soil during the early stage of hydration. Afterward, as the suction pressure of the silty sand and bentonite reached equilibrium, the water content of the GCL did not change significantly.
- As the MPUA of the GCLs increased, w_{final} of GCL decreased.
- As the $w_{subsoil}$ increased, w_{final} of the GCL also increased.
- As the vertical stress acting on the GCL during hydration increased, there was a slight decrease in the w_{final} of the GCL.

Conclusions Regarding to Water Content of Subsoil:

- As the MPUA of the GCLs increased, $w_{subsoil}$ decreased. This is because GCLs with higher MPUA absorbs more mass of water from subsoil.

Conclusions Regarding to Cation Exchange Reaction:

- Cation exchange reaction for all GCLs completed mostly within 30 days of hydration. Further hydration did not have remarkable influence on the cation exchange of GCLs.
- When the influence of MPUA is evaluated alone after hydrating the GCLs (GCL1, GCL2, and GCL3) in the long term (180 days), MPUA had no significant influence on the cation exchange reaction. Thus, the influence of

MPUA can be seen when evaluated together with another parameter such as $w_{subsoil}$.

- Cation exchange reaction changed depending on the GCL type. Although the mole fractions of monovalent and divalent cations (X_M and X_D) for GCL1 and GCL3 were close within each other, GCL2 had better performance by means of cation exchange. The highest X_M and the lowest X_D was obtained for GCL2.
- Although the influence of MPUA was not seen when compared X_M and X_D, MPUA changed the subsoil pore fluid chemistry within the applied hydration duration. The subsoils interacting with the GCLs with higher MPUA had more Na^+ and less Ca^{2+} than the subsoils interacting with the GCLs with lower MPUA. It can be inferred that GCLs with higher MPUA released more mass of Na^+ through the subsoil.
- When 30 days of hydration was examined, cation exchange was more pronounced when subsoil was compacted on dry side. This is opposite of the data given in the literature. That is, monovalent cation fraction of GCL1 decreased and divalent cation fraction increased with a decrease in $w_{subsoil}$ at any MPUA.
- For 30 days of hydration of GCL1 with lower MPUA exposed more cation exchange than GCL1 with higher MPUA. It can be said that greater amounts of bentonite content in the GCL decelerate the cation exchange reaction.
- When combined effect of subsoil water content and MPUA on cation exchange is examined, it is concluded that GCL1 exposed more cation exchange when MPUA and $w_{subsoil}$ were low.
- Vertical stress had no remarkable influence on the cation exchange of GCL1 when GCLs were hydrated for 180 days.

REFERENCES

Acikel, A. S., Gates, W. P., Singh, R. M., Bouazza, A., & Rowe, R. K. (2018). Insufficient initial hydration of GCLs from some subgrades: Factors and causes. *Geotextiles and Geomembranes*, *46*(6), 770–781.

Anderson, R., Rayhani, M. T., & Rowe, R. K. (2012). Laboratory investigation of GCL hydration from clayey sand subsoil. *Geotextiles and Geomembranes*, *31*, 31–38.

ASTM D4318. (2005). Standard test methods for liquid limit, plastic limit, and plasticity index of soils. Report 04, 1–14.

ASTM D5890. (2019). Standard test method for swell index of clay mineral component of geosynthetic clay liners, ASTM International, West Conshohocken, PA, 2019

ASTM D698-12. (2020). Standard test methods for laboratory compaction characteristics of soil using standard effort. 1. ASTM International, West Conshohocken, PA, USA 1–13.

ASTM D6913. (2017). Standard test methods for particle-size distribution (Gradation) of soils using sieve analysis, ASTM International, West Conshohocken, PA, 2017.

ASTM D7503. (2020). Standard test method for measuring the exchange complex and cation exchange capacity of inorganic fine-grained soils 1. ASTM International, West Conshohocken, PA, USA 1–5.

ASTM D854. (2014). Standard test methods for specific gravity of soil solids by water pycnometer, ASTM International, West Conshohocken, PA, 2014,

Azad, F. M., Rowe, R. K., El-Zein, A., & Airey, D. W. (2011). Laboratory investigation of thermally induced desiccation of GCLs in double composite liner systems. *Geotextiles and Geomembranes*, *29*(6), 534–543.

Barclay, A., & Rayhani, M. T. (2013). Effect of temperature on hydration of geosynthetic clay liners in landfills. *Waste Management and Research*, *31*(3), 265–272.

Benson, C. H., & Meer, S. R. (2009). Relative abundance of monovalent and divalent cations and the impact of desiccation on geosynthetic clay liners. *Journal of Geotechnical and Geoenvironmental Engineering*, *135*(3), 349–358.

Benson, C. H., Ören, A. H., & Gates, W. P. (2010). Hydraulic conductivity of two geosynthetic clay liners permeated with a hyperalkaline solution. *Geotextiles and Geomembranes*, *28*(2), 206–218.

Bradshaw, S. L., & Benson, C. H. (2014). Effect of municipal solid waste leachate on Hydraulic Conductivity and Exchange Complex of Geosynthetic Clay Liners. *Journal of Geotechnical and Geoenvironmental Engineering*, *140*(4), 04013038.

Bradshaw, S. L., Benson, C. H., & Scalia, J. (2013). Hydration and cation exchange during subgrade hydration and effect on hydraulic conductivity of geosynthetic clay liners. *Journal of Geotechnical and Geoenvironmental Engineering*, *139*(4), 526–538.

Bouazza, A., Ali, M. A., Gates, W. P., & Rowe, R. K. (2017). New insight on geosynthetic clay liner hydration: the key role of subsoils mineralogy. *Geosynthetics International*, *24*(2), 139–150.

Chevrier, B., Cazaux, D., Didier, G., Gamet, M., & Guyonnet, D. (2012). Influence of subgrade, temperature and confining pressure on GCL hydration. *Geotextiles and Geomembranes*, *33*, 1–6.

Estornell, B. P., & Daniel, D. E. (1992). Hydraulic conductivity of three geosynthetic clay liners. *Journal of Geotechnical Engineering 118, 1592-1606*

Gustitus, S. A., Nguyen, D., Chen, J., & Benson, C. H. (In Press). Quantifying polymer loading in bentonite-polymer composites using loss on ignition and total carbon analyses. *Geotechnical Testing Journal*, *44*(5)

Hollerbach, A., Baird, Z., & Cooks, R. G. (2017). Ion separation in air using a three-dimensional printed ion mobility spectrometer. *Analytical Chemistry*, *89*(9), 5058–5065.

James, A. N., Fullerton, D., & Drake, R. (1997). Field Performance of Gcl under ion exchange conditions. *Journal of Geotechnical and Geoenvironmental Engineering*, *1997*, *897-901*

Kul, T. O., & Oren, A. H. (2019). Hydration of geosynthetic clay liners (GCLs) on compacted zeolite. *Geosynthetics International*, *26*(1), 81–91.

Lee, J.-M., Shackelford, C. D., Benson, C. H., Jo, H.-Y., & Edil, T. B. (2005). Correlating index properties and hydraulic conductivity of geosynthetic clay liners. *Journal of Geotechnical and Geoenvironmental Engineering*, *131*(11), 1319–1329.

Petrov, R. J., & Rowe, R. K. (1997). Geosynthetic clay liner (GCL) chemical compatibility by hydraulic conductivity testing and factors impacting its performance. *Canadian Geotechnical Journal*, *34*(6), 863–885.

Rayhani, M. T., Rowe, R. K., Brachman, R. W. I., Take, W. A., & Siemens, G. (2011). Factors affecting GCL hydration under isothermal conditions. *Geotextiles and Geomembranes*, *29*(6), 525–533.

Rouf, M. A., Bouazza, A., Singh, R. M., Gates, W. P., & Rowe, R. K. (2016). Water vapour adsorption and desorption in GCLs. *Geosynthetics International*, *23*(2), 86–99.

Rowe, R K, Brachman, R. W. I., Hosney, M. S., Take, W. A., & Arnepalli, D. N. (2017). Insight into hydraulic conductivity testing of geosynthetic clay liners (GCLs) exhumed after 5 and 7 years in a cover. *Canadian Geotechnical Journal*, *1138*(March), 1118–1138.

Rowe, R. Kerry, & Abdelatty, K. (2012). Effect of a calcium-rich soil on the performance of an overlying GCL. *Journal of Geotechnical and Geoenvironmental Engineering*, *138*(4), 423–431.

Rowe, R. Kerry, Garcia, J. D. D., Brachman, R. W. I., & Hosney, M. S. (2019). Chemical interaction and hydraulic performance of geosynthetic clay liners isothermally hydrated from silty sand subgrade. *Geotextiles and Geomembranes*, *47*(6), 740–754.

Rowe, R. Kerry, Rayhani, M. T., Take, W. A., Siemens, G., & Brachman, R. W. I. (2011). GCL hydration under simulated daily thermal cycles. *Geosynthetics International*, *18*(4), 196–205.

Ruhl, J. L., & Daniel, D. E. (1997). Geosynthetic clay liners permeated with chemical solutions and leachates. *Journal of Geotechnical and Geoenvironmental Engineering*, *123*(4), 369–381.

Sarabian, T., & Rayhani, M. T. (2013). Hydration of geosynthetic clay liners from clay subsoil under simulated field conditions. *Waste Management*, *33*(1), 67–73.

Scalia IV, J., & Benson, C. H. (2010). Effect of permeant water on the hydraulic conductivity of exhumed GCLs. *Geotechnical Testing Journal*, *33*(3), 201–211.

Scalia, J., & Benson, C. H. (2011). Hydraulic conductivity of geosynthetic clay liners exhumed from landfill final covers with composite barriers. *Journal of Geotechnical and Geoenvironmental Engineering*, *137*(1), 1–13.

Scalia, J., Benson, C. H., Bohnhoff, G. L., Edil, T. B., & Shackelford, C. D. (2014). Long-term hydraulic conductivity of a bentonite-polymer composite permeated with aggressive inorganic solutions. *Journal of Geotechnical and Geoenvironmental Engineering*, *140*(3), 04013025.

Sposito, G., (2008). *The chemistry of soils* (2nd edition). New York: Oxford University Press

Sparks, D.L., (2003). *Environmental soil chemistry* (2nd edition). London: Academic Press

Tian, K., Likos, W. J., & Benson, C. H. (2019). Polymer elution and hydraulic conductivity of bentonite–polymer composite geosynthetic clay liners. *Journal of Geotechnical and Geoenvironmental Engineering*, *145*(10), 04019071.

Von Maubeuge, K. P., & Ehrenberg, H. (2014). Investigation of bentonite mass per unit area requirements for Geosynthetic Clay Liners. *10th International Conference on Geosynthetics, ICG 2014*, *July*, 21-25

Wang, B., Xu, J., Chen, B., Dong, X., & Dou, T. (2019). Hydraulic conductivity of geosynthetic clay liners to inorganic waste leachate. *Applied Clay Science*, *168*, 244–248.

Yesiller, N., Hanson, J. L., Risken, J. L., Benson, C. H., Abichou, T., & Darius, J. B. (2019). Hydration fluid and field exposure effects on moisture-suction response of geosynthetic clay liners. *Journal of Geotechnical and Geoenvironmental Engineering*, *145*(4), 04019010.

Zhou, Z. (1995). Construction and application of clay-swelling diagrams by use of XRD methods. *JPT, Journal of Petroleum Technology*, *47*(4), 306.