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

# A STUDY ON MECHANISMS CONTROLLING THE HYDRAULIC CONDUCTIVITY OF ZEOLITE-BENTONITE AND SAND-BENTONITE MIXTURES

by Seda DURUKAN

> July, 2013 İZMİR

# A STUDY ON MECHANISMS CONTROLLING THE HYDRAULIC CONDUCTIVITY OF ZEOLITE-BENTONITE AND SAND-BENTONITE MIXTURES

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#### Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled "A STUDY ON MECHANISMS CONTROLLING THE HYDRAULIC CONDUCTIVITY OF ZEOLITE-BENTONITE AND SAND-BENTONITE MIXTURES" completed by SEDA DURUKAN under supervision of PROF. DR. ARIF ŞENGÜN KAYALAR and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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### A STUDY ON MECHANISMS CONTROLLING THE HYDRAULIC CONDUCTIVITY OF ZEOLITE-BENTONITE AND SAND-BENTONITE MIXTURES

#### **ABSTRACT**

Engineered landfill liners are used for the containment of the municipal wastes and hazardous materials. They are usually composed of compacted clayey soils and synthetic membranes. Hydraulic conductivity is the major specification for liners beneath the waste. The addition of relatively small amounts of bentonite permitted sand bentonite mixtures (SBMs) to have a required hydraulic conductivity. Similarly, zeolite bentonite mixtures were also proposed for use of a liner. Several researchers investigated zeolite bentonite mixtures (ZBMs) in terms of preliminary analysis of hydraulic conductivity. It is concluded that ZBMs had higher hydraulic conductivities when compared to SBMs even for relatively higher bentonite contents.

This dissertation deeply investigated the hydraulic conductivity behavior of ZBMs and possible reasons causing ZBMs to have higher hydraulic conductivities than SBMs. The findings of SBMs and ZBMs were compared and discussed.

A laboratory investigation on the mechanisms controlling the hydraulic conductivity of SBMs and ZBMs has been undertaken. Compaction and hydraulic conductivity characteristics were established. The influence of compaction water content on the hydraulic conductivity of SBMs and ZBMs was comprehensively studied. In addition, water content distribution of components, void ratio of bentonite and degree of saturation to bentonite in a binary mixture were investigated. Finally, a finite element analysis was conducted in order to clarify the influence of porous grains, simulating zeolite, on the hydraulic conductivity of a binary mixture. The results are presented and analyzed and recommendations for future studies are made.

**Keywords:** Zeolite bentonite mixtures, sand bentonite mixtures, hydraulic conductivity, water content distribution, bentonite void ratio, finite element method.

#### ZEOLİT-BENTONİT VE KUM-BENTONİT KARIŞIMLARININ HİDROLİK İLETKENLİĞİNİ KONTROL EDEN MEKANİZMALAR ÜZERİNE BİR ÇALIŞMA

ÖZ

Katı atık deponi alanlarının altındaki geçirimsiz tabakalar evsel atık ve tehlikeli maddelerin hapsedilmesinde kullanılmaktadırlar. Bu tabakalar genellikle sıkıştırılmış killi zeminler ve sentetik membranlardan oluşur. Hidrolik iletkenlik değeri atıkların altında yer alan bu tabakalar için öncelikli kriteri oluşturur. Kum bentonit karışımlarına (KBK) göreceli olarak az miktarda bentonit eklenmesi ile KBK'lar istenilen düzeyde hidrolik iletkenlik değerlerine kavuşmuşlardır. Benzer şekilde zeolit bentonit karışımları da (ZBK) geçirimsiz tabaka kullanımı için önerilmiştir. Bazı araştırmacılar, ZBK'ların hidrolik iletkenlik değerlerini araştırmışlardır. Sonuç olarak da yüksek bentonit içeriklerinde dahi ZBK'ların hidrolik iletkenlik değerleri KBK'larınkilerden daha yüksek olarak bulunmuştur.

Bu çalışma ZBK'larının hidrolik iletkenlik değerlerini derinlemesine incelemiş ve ZBK'ların hidrolik iletkenlik değerlerinin KBK'larınkilerden daha yüksek olmasının olası sebeplerini irdelemiştir. KBK ve ZBK'lara ait bulgular karşılaştırılmış ve tartışılmıştır. KBK ve ZBK'ların hidrolik iletkenliğini kontrol eden mekanizmalar üzerine bir laboratuvar çalışması gerçekleştirilmiştir. Kompaksiyon ve hidrolik iletkenlik karakteristikleri tanımlanmıştır. Kompaksiyon su içeriğinin KBK ve ZBK'ların hidrolik iletkenliğine olan etkisi çalışılmıştır. Bununla beraber, karışımlardaki bileşenlerin su içerikleri, bentonit boşluk oranı ve betnonit doygunluk derecesi araştırılmıştır. Son olarak zeolitin gözenekli yapısının karışımın hidrolik iletkenliğine olan etkisini araştırmak üzere bir sonlu elemanlar analizi yapılmıştır. Tüm bulgular sunulmuş ve analiz edilmiş ve gelecek çalışmalar için tavsiyelerde bulunulmuştur.

**Anahtar Sözcükler:** Zeolit bentonit karışımları, kum bentonit karışımları, hidrolik iletkenlik, su içeriği dağılımı, bentonit boşluk oranı, sonlu elemanlar metodu.

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### CHAPTER ONE INTRODUCTION

#### 1.1 Introduction

Environmental pollution rises due to the increase of population, industry and habit of consumption. The more the population and industry means the more production of wastes. Researchers have studied on prevention of the pollution especially on the subsurface contamination. Liners composed of clayey soils and synthetic membranes are used to inhibit the transition of contaminants to the groundwater. A liner is desired to contain the waste, prevent chemical attacks, act as a barrier against the hazardous materials such as heavy metals and contain leachate produced by the waste. In other words, the aim of a liner is to prevent the transient flow of the waste materials, contaminants to the groundwater systems such as aquifers, wells. In order to prevent dangerous leakage, a liner should have the required hydraulic conductivity which is less than or equal to  $10^{-9}$  m/s.

Low hydraulic conductivity and high adsorption capacity are the most desired parameters for landfill liner materials. In addition, it should also be resistant to temperature and moisture content fluctuations and have physical and chemical stability. Compacted clay liners (CCLs) are preferred because of low hydraulic conductivity. However, CCLs are not resistant to freeze-thaw and/or shrinkage-swelling cycles which results in large increases in hydraulic conductivity due to the cracks formed during the cycles (Chamberlain et al., 1990; Benson & Othman, 1993; Othman & Benson, 1993; Othman et al., 1994; Chamberlain et al., 1995; Albrecht & Benson, 2001). Formation of the cracks due to the variation of temperature and water content are prevented by using coarser particles, such as sand, with appreciable amounts of bentonite (Kleppe & Olson, 1985). Sand-bentonite mixtures (SBMs) are the most known bentonitic mixture that have widely been investigated by many researchers (Kenney et al., 1992; Mollins et al., 1996; Stern & Shackelford, 1998; Komine, 2004). A bentonite content of 10% was found to be sufficient in order to have a desirable hydraulic conductivity also avoiding volumetric shrinkage.

However, the lacking of adsorption capacity of sand let researchers to suggest other alternatives for a liner. An alternative material for clay liners is geo-synthetic clay liner (GCL) (Lin & Benson, 2000) but GCLs have not been preferred because of their high cost in our country. Besides, Meer & Benson (2007) showed that GCLs had large increases in hydraulic conductivity after long service periods.

Lately, compacted zeolite bentonite mixtures (ZBMs) have been proposed as an alternative material to SBMs prior to the adsorption capacity and volumetric shrinkage advantages (Kayabalı, 1997; Kayabalı & Kezer, 1998; Güney & Koyuncu, 2002; Kaya & Durukan, 2004; Ören, 2011). Zeolite is known as a micro-porous material which has many interconnected pores and channels in its structure. These pores do not permit the passage of larger molecules while allowing smaller molecules. Based on this case, zeolite is referred to as "molecular sieve" (Breck, 1974; Mumpton, 1999). Zeolite structure remains rigid during the transition of molecules. When water freely moves in and out, the zeolite structure has no volume change and stands rigid. ZBMs are mostly compared with SBMs. However, compacted ZBMs have dry densities and optimum water content values that are far from those of compacted SBMs. Besides, zeolites are known as "porous" materials which can affect the hydraulic conductivity behavior as well. Regardless of the material, hydraulic conductivity is the basic parameter that should be considered during landfill liner and cover design. Thus, the factors controlling the hydraulic conductivity of bentonitic mixtures should be known prior to their application.

Compaction water content is one of the parameters that has a significant influence on the hydraulic conductivity. The hydraulic conductivity of clayey soils compacted on dry of optimum water content ( $w_{opt}$ ) is almost three orders of magnitude greater than the hydraulic conductivity of the samples compacted on wet of optimum (Lambe, 1958). Although many attempts have been put forward to determine the effect of compaction water content on the hydraulic conductivity of SBMs (Haug & Wong, 1992; Kenney et al., 1992; Abichou et al., 2002), there is no reported information about the influence of compaction water content on the hydraulic conductivity of ZBMs. This uncertain point may become a challenge for the

engineers that should be cleared up and it deserves more attention to detail the alternative use in geotechnical engineering applications.

Since no studies have been conducted on the relation between molding water content and hydraulic conductivity, the researchers studied the hydraulic conductivity of ZBMs, investigated them regarding the compaction criteria of SBMs. So, it is necessary to investigate the influence of molding water content on hydraulic conductivity of compacted ZBMs and compare the behavior with that of SBMs. In addition, as a micro-porous material, zeolite structure would contain some water unlike sand. Thus, zeolite and bentonite is expected to be in a competition for water uptake.

Based on the limited discussion, this doctoral dissertation mainly aims to put insight to the hydraulic conductivity behavior of ZBMs. For this purpose, this study initially presents and discusses the impact of compaction water content on the hydraulic conductivity of ZBMs. Consequently, investigates the water contents of constituents, the sufficiency of bentonite amount in ZBMs and SBMs. In addition, it is also aimed to investigate the influence of porous structure of zeolite grains on the hydraulic conductivity of a bentonitic mixture using finite element method.

#### 1.2 Objective and Scope of the Thesis

The objective of this study is to investigate the behavior of hydraulic conductivities of ZBMs and compare the results with those of SBMs. For this purpose, along with basic geotechnical properties; compaction characteristics, hydraulic conductivities for varying compaction water contents, bentonite void ratio, and sufficiency of bentonite amounts present in the mixtures were investigated for both ZBMs and SBMs. The bentonite content (by weight) of the mixtures was limited to 10% and 20% due to the reported literature data which were satisfactory for use of a liner.

An extensive literature search had been conducted on SBMs and ZBMs. Most of the research contents were about the influence of compaction water content on the hydraulic conductivity of SBMs, bentonite void ratio of SBMs. These facts for ZBMs were not defined in literature. Also many studies about the ZBMs including preliminary analysis of hydraulic conductivity and adsorption capacity were extensively searched. The experimental work in this study was focused on understanding the behavior of hydraulic conductivity of ZBMs. A brief explanation of the content is given in the organization of the dissertation section below.

#### 1.3 Organization of the Dissertation

This dissertation consists of seven chapters.

Chapter Two gives an extensive literature review on hydraulic conductivity results and bentonite void ratios of SBMs and ZBMs. Finally, a brief summary of materials used and tests conducted in the ZBM researches of are given as tables.

Chapter Three describes the geotechnical properties of the materials used in the experiments, gives the compaction characteristics and designates the main experimental program.

Chapter Four gives the hydraulic conductivity results of zeolite blocks, ZBMs and SBMs having 10% and 20% bentonite contents. Also discusses the influence of water content on the hydraulic conductivities of ZBMs and SBMs. Finally summarizes the results, compares with each other and also with the previous results.

Chapter Five investigates the water content distribution to components and compares the bentonite void ratio of SBMs and ZBMs. A new definition is made and named as the degree of saturation to bentonite. This new concept is determined for 20% ZBM and SBM and compared.

Chapter Six presents a modeling study using the finite element method. This model compares effect of the hydraulic conductivity of porous grains -simulating zeolite- and non-porous grains -simulating sand- embedded in fine matrix -simulating swollen bentonite- and also compares the findings with the data in literature and in this study.

Chapter Seven discusses the research program, lines up the conclusions and draws the recommendations for the future work.

#### CHAPTER TWO LITERATURE REVIEW

The selected research papers on the hydraulic conductivity behavior of sand-bentonite mixtures (SBMs) and zeolite-bentonite mixtures (ZBMs) are presented in this chapter. The studies related with the effect of water content on the hydraulic conductivity of SBMs were published in early 90's even though the SBMs had been proposed as a liner material in early 80's. Afterwards, researchers continued on swelling behavior, effect of freeze-thaw cycles, adsorption processes, pore size distributions and modeling of SBMs. The studies concerning ZBMs were published first in the late 90's and most of the following studies are governed by the adsorption processes. However, the effect of water content on the hydraulic conductivity had never been the main research topic. Moreover, the hydraulic conductivity behavior of ZBMs was accepted to be the same as SBMs.

#### 2.1 Sand-Bentonite Mixtures

SBMs have been offered for landfill liner applications in 1980s as an alternative to compacted clay liners (CCLs) which may have great shrinkage problems. In order to reduce the adverse effects of cracks and to increase strength, volume stability and bring down the construction costs; bentonite is blended with coarser particles, such as sand, for use of a liner (Kleppe & Olson, 1985). Most researchers investigated the convenience of these materials on landfill liner applications by means of hydraulic conductivity, chemical stability, adsorption processes and the effects of temperature and moisture fluctuations etc. (e.g., Kenney et al., 1992; Haug & Wong, 1992; Villar & Rivas, 1994; Kraus et al., 1997; Stewart et al., 1999; Sivapullaiah et al., 2000; Tay et al., 2001; Abichou et al., 2002; Stewart et al., 2003; Komine, 2004). Among many criteria, determining the hydraulic conductivity still plays an active role for decision of a reasonable landfill liner material. Typically, a liner is required to have a hydraulic conductivity less than or equal to 1x10<sup>-9</sup> m/s. It is known that for sandy clays the lowest hydraulic conductivity value is reached at their 4% wet of optimum water content (Lambe, 1958). The decrease in the hydraulic conductivity from dry of

optimum to wet of optimum is explained by the swelling phenomena and the orientation of clay particles i.e. flocculated to dispersed (Holtz & Kovacks, 1981). According to Daniel & Benson (1990), the soil must be compacted to a minimum dry unit weight equal to 95% of the maximum dry unit weight and the water content must be 0-4% points of optimum water content of standard proctor compaction.

Kenney et al. (1992) ran fourteen tests on a consolidation cell used for permeability tests either with distilled water or salt water on SBMs having up to 22% bentonite content (B/S = bentonite/sand by dry mass). Uniform graded sand (under No.10 sieve) was blended with Na-bentonite which had a liquid limit of 500% and a plastic limit of 40%. The dry density of SBM increased while bentonite content increased where the optimum water content remained the same.

For 8% and 12% samples they found that the hydraulic conductivity values decrease as much as a three orders of magnitude from dry of optimum molding water content to the wet of optimum molding water content and then, followed an increase while the water content increases. Nevertheless, for 4%, 16% and 22% samples, no significant change in hydraulic conductivities was determined. It is clear that the 4% bentonite content was insufficient to reach the desired hydraulic conductivity and the swollen bentonite in the mixture did not fully fill the voids and led preferential flow paths. The 16% and 22% samples had bentonite volume which was more than the voids volume and the hydraulic conductivity behavior of the mixture was always governed by bentonite for both samples. The effect of the orientation of bentonite particles and the swelling of bentonite, depending on the water content, can be seen from the decrease in hydraulic conductivity of 8% and 12% samples.

Due to the very small water holding capacity of sand when compared to bentonite, the authors suggested that in a SBM, the mixture is composed of dry sand and wet bentonite and accepted that the mixture's water content concerns bentonite alone. Depending on this criterion, the water content of bentonite and bentonite void ratio for varying B/S proportions among with the volume proportions of air, water, bentonite and sand in a SBM was determined.

Haug & Wong (1992) investigated the impact of molding water content on the hydraulic conductivity of compacted SBMs by using a triaxial permeameter testing equipment. Wyoming Bentonite was used having a liquid limit of 533% and a plastic limit of 33%. Tests were conducted on nine samples of 8% bentonite content by weight, having a molding water content variation of 6 to 19% under standard Proctor energy. Finally it is shown that hydraulic conductivity of SBMs showed a very slight decrease while the molding water content increases up to the wet of optimum molding water content value and then start to increase again. Authors mentioned that, molding water content was not a design criterion for SBMs for use of a liner. They also determined that the bentonite void ratio varied between 6 and 7.5.

Kraus et al. (1997) investigated the effect of freeze-thaw cycling on the hydraulic conductivity of bentonitic barriers (SBMs and geosynthetic liners) both in laboratory and in field. The SBM mixture was prepared from the field application. Poorly graded sand of which 90% passing No.30 sieve and less than 5% passing No.200 sieve was used. The bentonite was CG-50, a granular Na-bentonite with no polymer additives. The atterberg limits of the bentonite were not stated in the paper. Initially, the authors reported the compaction curve and hydraulic conductivity results of the 12% SBMs with tap water (Figure 2.1). The authors concluded that the hydraulic conductivity was almost insensitive to the molding water content but sensitive to compactive effort. It is also reported that, freezing and thawing did not result in an increase in hydraulic conductivity for both materials used in the study.

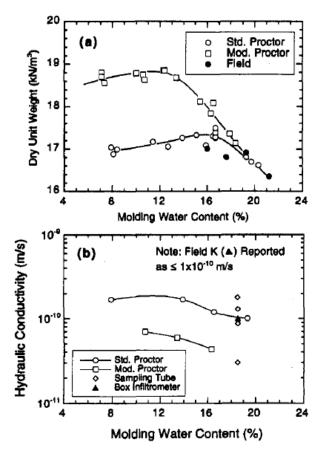


Figure 2.1 The compaction curves and hydraulic conductivities for 12% sand-bentonite mixtures (Kraus et al., 1997)

Tay et al. (2001) essentially investigated the shrinkage and desiccation cracking in bentonite sand mixtures. The shrinkages and hydraulic conductivities of 10% and 20% SBMs (bentonite/total by dry weights) were reported. SPV200 Wyoming Bentonite with a liquid limit of 354% and a plastic limit of 27% was used. It is found that shrinkage was insensitive to the compactive effort. It only had minor cracking when they compacted at their wet of optimum points (optimum+5% and optimum+10%). In Figure 2.2, the hydraulic conductivity data show that 10% SBMs reach their minimum hydraulic conductivity at the wet of optimum point and then starts to increase where the optimum water content is 12%. However, a similar trend cannot be seen for 20% SBMs, due to the lack of data.

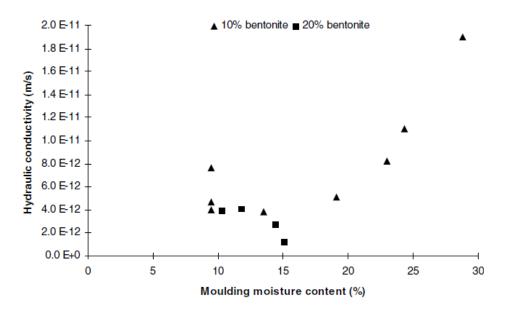


Figure 2.2 The hydraulic conductivities for 10% and 20% sand-bentonite mixtures (Tay et al., 2001)

Cho et al. (2002) determined the hydraulic conductivities of soil and bentonite (including 60% quartz, 70% montmorillonite, respectively) mixtures having various dry densities. The bentonite was a calcium bentonite which had a cation exchange capacity of 58 meq/100 g. The mixtures had 0, 5, 10, 15 and 20% bentonite contents by weight and the dry densities for each mixture varied in the interval of 1.4 – 1.8 Mg/m³. The hydraulic conductivities for each mixture are presented in Figure 2.3. For soils having 1.4 and 1.5 Mg/m³ dry densities hydraulic conductivity did not significantly decrease when the bentonite content reached up to 20%. However, for the samples having dry densities of 1.6 and 1.8 Mg/m³, hydraulic conductivity values rapidly decreased even at lower bentonite contents such as 5%.

Bentonite void ratios for each mixture and the swelling of bentonite in mixtures were also investigated. The change of void ratio of bentonite with increasing bentonite content for dry densities of 1.6 and 1.8 Mg/m³ were plotted in Figure 2.4. According to the authors, the void ratio of bentonite decreases rapidly when the bentonite content is lower than 10%, due to the lacking of the continuity of the bentonite matrix at lower bentonite contents.

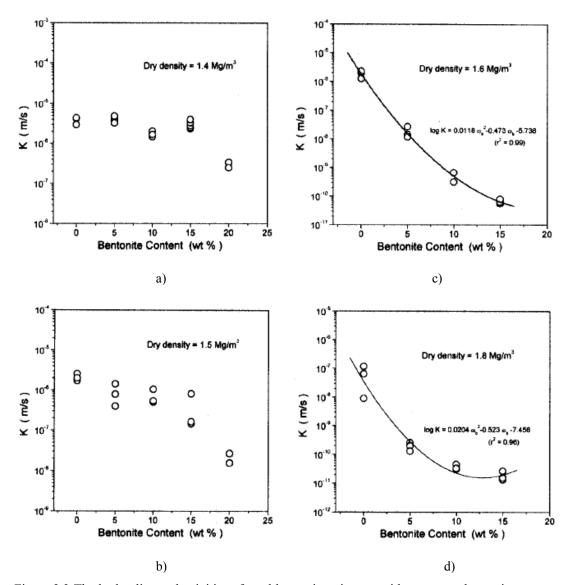


Figure 2.3 The hydraulic conductivities of sand-bentonite mixtures with respect to bentonite contents where the dry densities are a)  $1.4 \text{ Mg/m}^3$ , b)  $1.5 \text{ Mg/m}^3$ , c)  $1.6 \text{ Mg/m}^3$ , and d)  $1.8 \text{ Mg/m}^3$  (Cho et al., 2002)

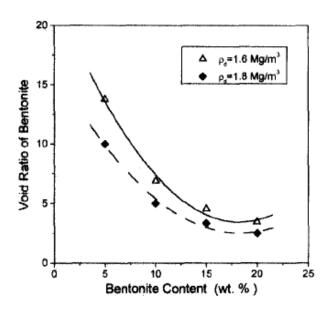


Figure 2.4 The void ratio of bentonite with respect to bentonite contents where the dry densities are 1.6 Mg/m³ and 1.8 Mg/m³ (Cho et al., 2002)

Komine (2004) discussed the bentonite content in a SBM regarding the swelling potential of bentonite to fully fill the voids in the mixture. Hydraulic conductivity tests for different bentonite contents at different dry densities were conducted. Furthermore, Komine (2004) proposed a simplified evaluation for hydraulic conductivity by using the swelling volumetric strain of montmorillonite which was previously proposed by Komine & Ogata (1999). A Japanese bentonite: Kunigel-V1 was used which had a liquid limit of 474% and a plastic limit of 27%. In addition, the bentonite had a montmorillonite content of 48%. The study covered bentonite contents of 5, 10, 20, 30 and 50%. The hydraulic conductivities for different bentonite contents at different dry densities are given in Figure 2.5. The author emphasized the proper amount of bentonite in order to fill all the voids.

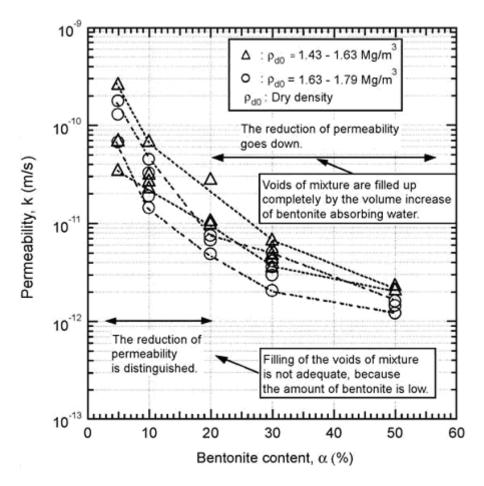


Figure 2.5 The permeability, bentonite content, dry density relationship for sand-bentonite mixtures (Komine, 2004)

The author also concludes that swelling phenomena of SBMs was directly related to the montmorillonite percentage, and in the study, the swelling of montmorillonite was denoted by swelling volumetric strain of montmorillonite ( $\varepsilon_{sv}^*$ , %). The equation of  $\varepsilon_{sv}^*$  (%) can be seen in Equation 2.1, the detailed derivation of  $\varepsilon_{sv}^*$  (%) is given in Ogata et al. (1999). The  $e_0$  and  $\rho_{solid}$  used in Equation 2.1 are given in Equations 2.2 and 2.3 respectively.

Permeability versus  $\varepsilon_{sv}^*$  (%) and regression equation are given in Figure 2.6. The author stated that the regression relation between the permeability and the  $\varepsilon_{sv}^*$  (%) is regardless of the bentonite content in a SBM. However, the author mentioned that this relation was valid when the bentonite was Na-bentonite and the permeant was distilled water.

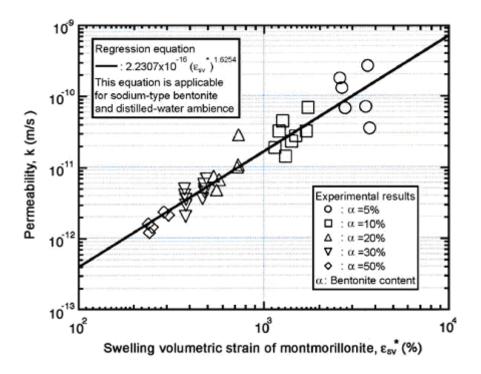


Figure 2.6 The permeability as a function of swelling volumetric strain of montmorillonite for sandbentonite mixtures having varying BCs (Komine, 2004)

$$\varepsilon_{sv}^* = \left(e_0 + \frac{\varepsilon_{s \max}}{100} \left(e_0 + 1\right)\right) \left(1 + \left(\frac{100}{C_m} - 1\right) \frac{\rho_m}{\rho_{nm}} + \left(\frac{100}{\alpha} - 1\right) \frac{100}{C_m} \frac{\rho_m}{\rho_{sand}}\right) 100 \tag{2.1}$$

$$e_0 = \frac{\rho_{solid}}{\rho_{d0}} - 1 \tag{2.2}$$

$$\rho_{solid} = \frac{\frac{100}{C_m} \frac{100}{\alpha} \rho_m}{\left(1 + \left(\frac{100}{C_m} - 1\right) \frac{\rho_m}{\rho_{nm}} + \left(\frac{100}{\alpha} - 1\right) \frac{100}{C_m} \frac{\rho_m}{\rho_{sand}}\right)}$$
(2.3)

Where;

 $\epsilon_{s\;max}$  = the maximum swelling strain ( $\epsilon_{s\;max}$  was equal to 0% in the study)

 $e_o$  = the void ratio

 $C_m$  = the montmorillonite content of bentonite (%)

 $\alpha$  = the bentonite content (%)

```
\begin{split} &\rho_m = \text{the particle density of montmorillonite (Mg/m}^3) \\ &\rho_{nm} = \text{the particle density of minerals including montmorillonite (Mg/m}^3) \\ &\rho_{sand} = \text{the particle density of sand (Mg/m}^3) \\ &\rho_{d0} = \text{the dry density (Mg/m}^3) \end{split}
```

Sun et al. (2009) investigated the swelling of SBMs and the bentonite void ratio in SBMs. They used Kunigel- $V_1$ - $Na^+$ -Bentonite and Toyoura Sand. The bentonite was of 48% montmorillonite and had a liquid limit of 474% and a plastic limit of 27% which is the same soil used in Komine (2004) used. In this study, swelling was defined in terms of bentonite void ratio. Also, the pure montmorillonite fraction of bentonite was used in order to determine the bentonite void ratio ( $e_b$ ) and named as montmorillonite void ratio ( $e_m$ ). For this purpose, an equation (Equation 2.4) was derived to determine the  $e_m$ .

$$e_m = e_2 \frac{\rho_m}{\rho_s \alpha \beta} 10^4 \tag{2.4}$$

Where;

 $e_2$  = the final void ratio  $ho_s$  = the density of mixture (Mg/m³)  $ho_m$  = the density of montmorillonite (Mg/m³)  $ho_m$  = the bentonite content (%)  $ho_m$  = the montmorillonite content of bentonite (%)

Sun et al. (2009) showed that the logarithm of montmorillonite void ratio was related to the logarithm of effective stress ( $\sigma'_v$ ) and atmospheric pressure (Pa) and insensitive to the bentonite content in a mixture (Figure 2.7). The authors also mentioned that this line may be determined from results of two swelling deformation tests for varying effective vertical stresses and one can pretend the volumetric strain from the initial state to the saturated state for a given vertical stress regardless of bentonite content.

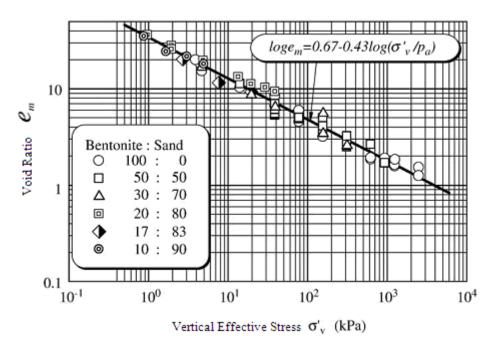


Figure 2.7 The void ratio vertical effective stress relationship of sand-bentonite mixtures for varying bentonite contents (Sun et al., 2009)

Akgün (2010) performed laboratory tests in order to investigate the performance of the bentonite/sand mixtures for sealing of underground waste repositories. A natural and non-treated Na-bentonite from Karakaya Bentonite Co. was used which contained at least 90% montmorillonite and named as KAR-BEN. The bentonite had a liquid limit of 450% and a plastic limit of 35%. The standard compaction procedure was followed. The compaction characteristics of the mixtures and the hydraulic conductivities as a function of BC are plotted in Figures 2.8 & 2.9 respectively.

The mixtures were placed in a rigid-wall permeameter. Distilled and de-aired water was used in the tests. The hydraulic conductivity tests were run on the samples which are at their 2% wet of optimum water contents. Tests lasted at least the outlet was obtained and the author emphasized that each test lasted for 1.5 to 2 months, and concluded that this was the approximate time which was needed for the samples to attain full saturation.

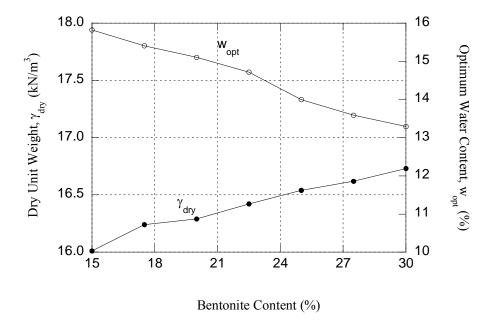


Figure 2.8 The compaction characteristics for varying bentonite contents of sand-bentonite mixtures (Akgün, 2010)

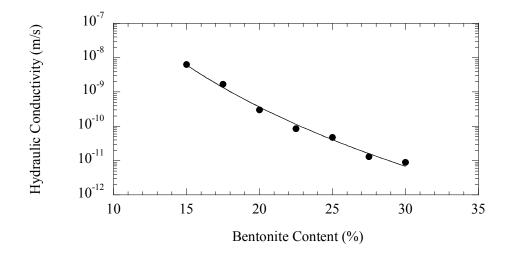


Figure 2.9 The hydraulic conductivities for varying bentonite contents of sand-bentonite mixtures (Akgün, 2010)

#### 2.2 Zeolite-Bentonite Mixtures

Kayabalı (1997) investigated the properties of zeolite-bentonite mixtures for use of liner applications. The liquid and the plastic limits of the bentonite used in the study were 320% and 50% respectively. The author conducted hydraulic

conductivity and strength tests on compacted mixtures having various bentonite (B) to zeolite (Z) ratios (B/Z) by dry weights at their optimum or slightly wet of optimum water contents. Compaction was done by a vibration hammer instead of standard procedure. The author used a falling head testing equipment with test durations of 10 to 15 days. B/Z ratios varied between 0.05 and 0.4 and the average hydraulic conductivity of the mixtures determined in the range of  $2 - 4x10^{-10}$  m/s averages. The compaction characteristics and the hydraulic conductivities of the samples are given in Figure 2.10 and Figure 2.11, respectively.

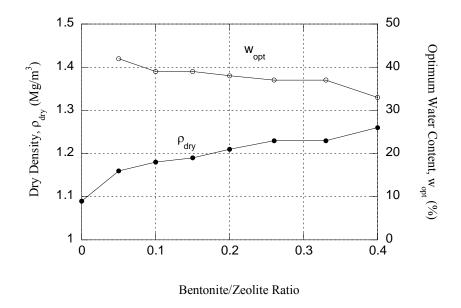


Figure 2.10 The compaction characteristics for varying bentonite contents of zeolite-bentonite mixtures (Kayabalı, 1997)

Kayabalı (1997) also obtained the bentonite water content and volumes of air, water, zeolite and bentonite in proportion to total volume related to the bentonite content of the mixtures. The bentonite water content for varying bentonite contents can be seen in Figure 2.12. The author calculated bentonite water contents based on the criteria of Kenney et al. (1992) which assumes sand is dry. Regarding the study of Kenney et al. (1992), Kayabalı (1997) also assumed that zeolite water content was equal to zero either. So, Kayabalı (1997) divided the water of the mixtures by the bentonite ingredient and called it as bentonite water content. However, zeolite is

known with its water uptake affinity and it is not reasonable to assume zeolite to have no water content in a mixture.

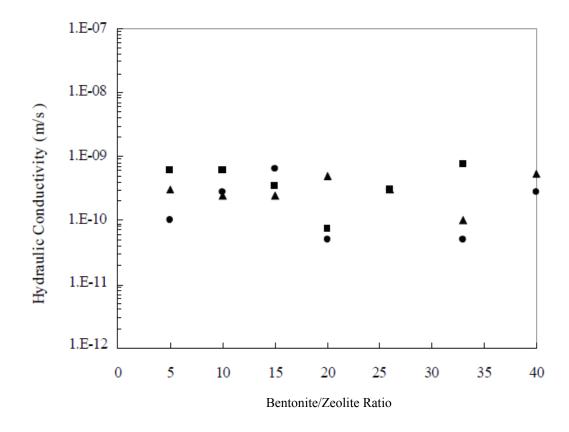


Figure 2.11 The hydraulic conductivities for varying bentonite contents of zeolite-bentonite mixtures (Kayabalı, 1997)

Kayabalı & Kezer (1998) investigated the removal of heavy metals from liquid waste. Zeolite, powdered bentonite and conventional hazardous solid waste as leachate including Cu<sup>2+</sup>, Fe<sup>2+</sup>, Pb<sup>2+</sup>, Mg<sup>2+</sup>, Se<sup>2+</sup>, As<sup>3+</sup>, Ca<sup>2+</sup>, K<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup>P, etc. were used during the experiments. Depending on the previous study of Kayabalı (1997), B/Z ratio of 0.04 was selected for tests. Tests were conducted by attaching falling head permeameters to the compaction molds. The authors reported no significant change in hydraulic conductivity of B/Z= 0.04 samples for varying molding water contents (Figure 2.13) when the tests were concluded with tap water.

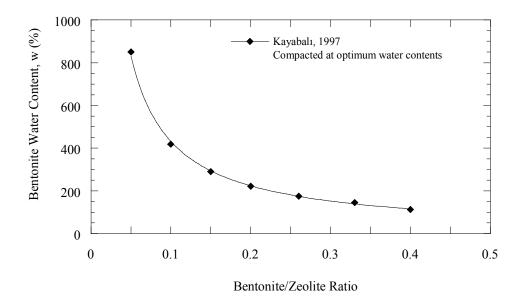


Figure 2.12 The bentonite water contents for varying bentonite contents of zeolite-bentonite mixtures (Kayabalı, 1997)

The optimum water content for B/Z=0.04 sample was not given. Instead, the optimum water content of B/Z=0.05 sample was given as 42%. Assuming that the optimum water contents of B/Z=0.04 and 0.05 samples to be close, it is clear that the reported hydraulic conductivities are at the dry side of the optimum water content.

Some of the results of the effluent fluid with respect to the influent are as follows;

- Ca increased up to 30 times.
- Na content reduced about 10%.
- Greater than 95% of K was removed.
- Mg concentration was up to 2-3 times greater
- Greater than 90% of Pb, Zn, Cu and ΣCr were removed at the end of 20 days.
   After 20 days, an increase in Pb, Zn, and Cr was observed whereas Cu stayed still.
- A tremendous increase in ΣFe was dramatically observed. The concentration was 40 times greater than the initial solution.

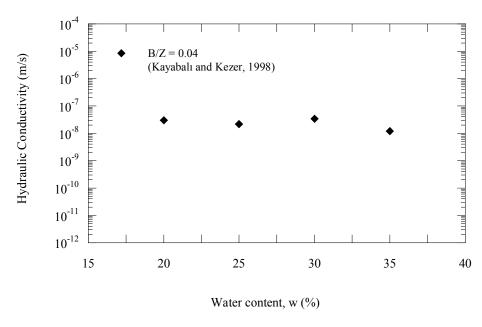


Figure 2.13 The hydraulic conductivities of 4% zeolite-bentonite mixtures at varying water contents (Kayabalı & Kezer, 1998)

Kayabalı & Mollamahmutoğlu (2000) investigated the influence of hazardous liquid waste on the permeability of earthen liners. The word "earthen liners" corresponds to sand-bentonite, zeolite-bentonite, sand-microcement and zeolite-microcement mixtures in their study. The cation exchange capacity (CEC) of zeolite and bentonite is given as 100 meq/100g and 60 meq/100g, respectively. The authors determined the hydraulic conductivities of each mixture with five permeants which are of solutions simulating effluents of fertilizer production (Solution 1), glass manufacturing industry (Solution 2), silver and gold mining (Solution 3), wastewater from a leather processing facility and leachate from a municipal solid waste (MSW) disposal site. Six mixtures were prepared which are 5%, 10% and 15 % SBMs; 10% ZBM and 10% Sand-Microcement and 10% Zeolite-Microcement Mixtures.

The authors used a falling head polyurethane compaction mold permeameter during the hydraulic conductivity tests with a gradient of about 20. In the study of Kayabalı & Mollamahmutoğlu (2000) hydraulic conductivity tests were run on samples which are at their optimum water contents and repeated the tests three times. Among the mixtures tested, 15% SBM and 10% ZBM were found to be more resistant against highly acidic solutions.

Kayabalı & Mollamahmutoğlu (2000) also mentioned that, these mixtures performed well against the other solutions as well. It is also concluded that, bases did not have considerable effect on the permeability of all mixtures. After the three repetition for each sample with each solution, the reported average hydraulic conductivity values of B/Z = 0.1 sample were summarized in Table 2.1.

Table 2.1 Hydraulic conductivity values of B/Z = 0.1 subjected to varying solutions

Solutions	Hydraulic conductivity (m/s)
Solution 1	1x10 <sup>-9</sup>
Solution 2	$5x10^{-9}$
Solution 3	$6x10^{-9}$
Leather waste water	$3x10^{-10}$
MSW leachate	$8x10^{-10}$

For comparison purposes tests results of 10% SBMs and 10% ZBMs are presented in Figures 2.14 & 2.15, respectively.

Another study was conducted on zeolite-bentonite mixtures by Güney & Koyuncu (2002). A B/Z = 0.1 mixture was used, the CEC of bentonite and zeolite reported as 90 meq/100g and 165 meq/100g respectively. The leachate used in the experiments was composed of high concentrations of NaCl, MgCl<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, CrCl<sub>2</sub>.6H<sub>2</sub>O, KCl, ZnCl<sub>2</sub> and a mixture of all. The results of the hydraulic conductivity tests are given in Table 2.2. It should be noted that the hydraulic conductivity tests were run on samples which are at their optimum water contents. No significant change on hydraulic conductivity of bentonite zeolite mixtures were observed when permeated with non-standard liquids.

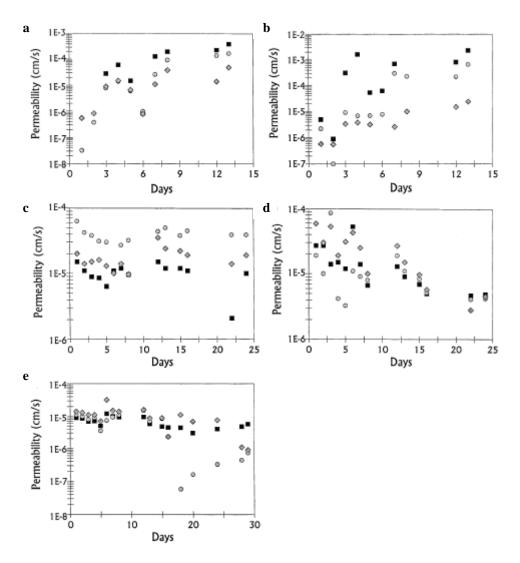


Figure 2.14 The hydraulic conductivities of 10% sand-bentonite mixture subjected to solutions of a) solution 1, b) solution 2, c) solution 3, d) leather leachate and e) landfill leachate (Kayabalı & Mollamahmutoğlu, 2000)

Table 2.2 Hydraulic conductivity test results on B/Z = 0.1 samples (Güney & Koyuncu, 2002)

Permeant Liquid		Hydraulic Conductivity (m/s)	
Тар	Water	2.5 x 10 <sup>-9</sup>	
	MgCl <sub>2</sub>	1.2 x 10 <sup>-9</sup>	
Salts	NaCl	$8.2 \times 10^{-10}$	
	KCl	8.8 x 10 <sup>-10</sup>	
	CrCl <sub>3</sub>	2.1 x 10 <sup>-9</sup>	
Metals	$ZnCl_2$	1.8 x 10 <sup>-9</sup>	
CuCl <sub>2</sub>		$1.1 \times 10^{-9}$	
Mixture of above		1.4 x 10 <sup>-9</sup>	

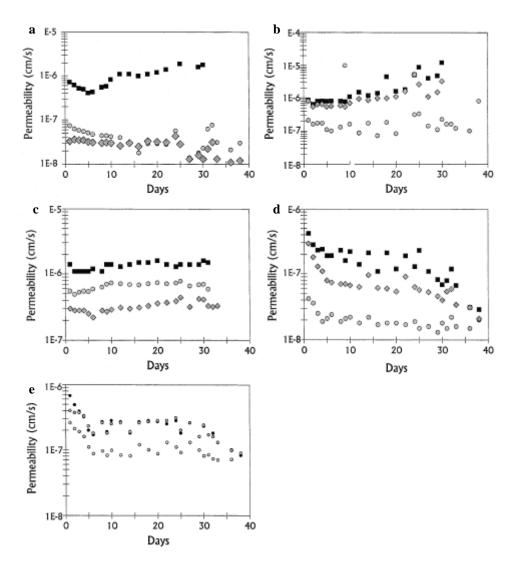


Figure 2.15 The hydraulic conductivities of 10% zeolite-bentonite mixture subjected to solutions of a) solution 1, b) solution 2, c) solution 3, d) leather leachate and e) landfill leachate (Kayabalı & Mollamahmutoğlu, 2000)

Tuncan et al. (2003) conducted triaxial permeability tests on B/Z = 0.1 sample at its optimum water content. The liquid limit of bentonite was 447% and the plastic limit was 60%. The cell pressure and the back pressure were reported as 98 kPa and 7 kPa, respectively. The authors also reported the hydraulic head as 14 kPa where the samples had a diameter of 11.5 cm and a height of 10 cm. Distilled water, sanitary leachate, Pb, Cu, Cr, Zn at various PH values were used as permeants. The effluent for each test was collected and it is reported that zeolite-bentonite mixtures acted like

an efficient chemical filter (Table 2.3). Finally, average hydraulic conductivities were found to be varying between  $1x10^{-10}$  and  $5x10^{-10}$  m/s. The authors offered zeolite-bentonite mixtures as a useful chemical filter layer when it is in direct contact with municipal solid wastes.

Table 2.3 Electrical conductivity and pH values of heavy metals used in study of Tuncan et al. (2003)

		Pb	Cr	Ni	Zn	Cu
Before test	рН	4.70	2.88	6.67	6.04	5.28
Before test	EC* (mS/cm)	0.46	2.52	0.27	3.08	2.08
After test	рН	7.86	8.20	7.81	7.56	8.20
Titter test	EC* (mS/cm)	0.64	2.13	0.96	0.84	1.26
Metal concentration	Fresh	63.3	1.1	15.0	66.3	13.1
(mg/kg)	7 days	40.5	0.1	5.7	26.0	2.9

\*EC: Electrical conductivity

Kaya & Durukan (2004), (related to Durukan, 2002) conducted hydraulic conductivity tests on zeolite bentonite and sand-bentonite mixtures - named as BEZ and BES, respectively - of 10% and 20% bentonite contents (dry bentonite weight over the total weight). The liquid limit of bentonite was 210% and the plastic limit was 92%. Durukan (2002) used oedometers to determine the hydraulic conductivities of the samples which were at their optimum water contents. The final hydraulic conductivity values of 10% and 20% BEZ were found to be 2.1x10<sup>-10</sup> and 1.4x10<sup>-10</sup> m/s respectively and 4.81x10<sup>-9</sup> m/s for 20% BES as seen in Figure 2.16 with respect to the void ratio. The authors also concluded that BEZ had very small volumetric strain when compared to BES.

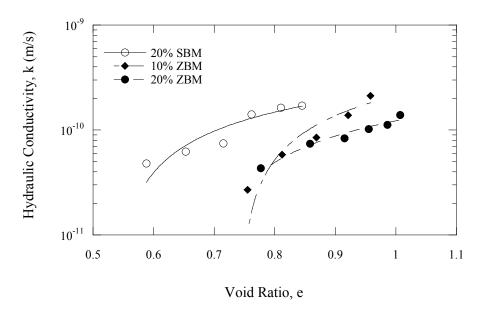


Figure 2.16 The hydraulic conductivities of 10% and 20% zeolite-bentonite and sand-bentonite mixtures as a function of void ratio (Durukan, 2002)

Kaya & Durukan (2004) also investigated the  $Pb^{+2}$  adsorption capacity of zeolite in comparison with bentonite. The authors plotted the  $Pb^{+2}$  adsorption of Nabentonite, Ca-bentonite and zeolite in Figure 2.17. The amount of metal ion removed by zeolite at equilibrium ( $q_e$ , ml/g) was calculated from the following equation;

$$q_e = (C_i - C_e) / S$$
 (2.5)

where;  $C_i$  = initial metal ion concentration (mg/l)

 $C_{\rm e}$  = equilibrium metal ion concentration (mg/l)

S = slurry concentration (g/l)

The equilibrium removal of metal ions,  $q_e$ , can be written in terms of adsorption isoterms. Adsorption isoterm data are commonly fitted to Equation (2.6). When this model is rearranged to the linear form, then Equation (2.7) was written as follows;

$$q_e = K_L C_e / (1 + aC_e)$$
 (2.6)

$$C_e / q_e = (1 / K_L) + (a / K_L) C_e$$
 (2.7)

The authors concluded that, even though zeolite had the lowest adsorption capacity when compared to bentonite samples; it is still advantageous to sand which has no adsorption capacity.

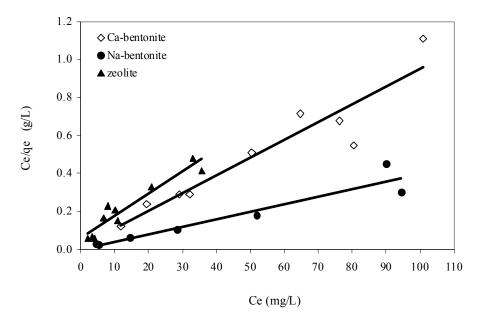


Figure 2.17 Isoterm of Na-bentonite, Ca-bentonite and zeolite with Pb(NO<sub>3</sub>)<sub>2</sub> (Kaya & Durukan, 2004)

Akpınar (2005) investigated the possible use of sepiolite (S) (a clay mineral mostly occurring in Eskişehir, Turkey) and zeolite (Z) mixture in the design of the hazardous landfill waste area. The mixture was prepared to have a proportion of S/Z = 0.3 (30%). The geotechnical and physico-chemical properties of the mixtures were investigated. Besides, a miniature landfill tank was designed to obtain the closest results of in-situ applications (Figure 2.18). As permeants, Cu and Cr solutions were used. Akpınar (2005) had conducted 3 tests using flexible-wall permeameter, both with constant and falling head methods with varying cell pressures. The results which give hope to use zeolite as an alternative landfill liner material can be seen in Table 2.4.

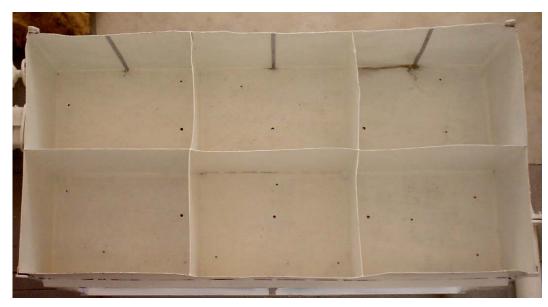


Figure 2.18 The top view of miniature landfill tank (Akpınar, 2005)

Table 2.4 Results of hydraulic conductivity tests by Akpınar, 2005

Comple	Hydraulic	Cell Pressure,	Testing Type
Sample	Conductivity, k (m/s)	σ <sub>3</sub> (kPa)	(rigid wall)
S/Z (30%)	0.75 x 10 <sup>-10</sup>	0	Falling Head
S/Z (30%)	1.17 x 10 <sup>-10</sup>	70	_
Miniature landfill tank sample (Cu solution)	3.5 x 10 <sup>-10</sup>	42	Constant Head

Turan & Ergun (2009) studied the removal of Cu from leachate by using bentonite zeolite mixture (called as BNZ in the study) for use of a landfill liner. The hydraulic conductivity values were also determined for varying bentonite contents. The zeolite was Gördes zeolite and bentonite was of montmorillonite mineral. However, the physical geotechnical parameters i.e. grain size, porosity, compaction criterion etc. of both materials were absent in the paper. The mixtures were announced to have 0, 5, 10, 20, 30 and 40% zeolite by dry weight, which were named in the study as BNZ1, BNZ2, BNZ3, BNZ4, BNZ5, and BNZ6, respectively.

The authors constructed six prototype landfill systems and each system was made using an open-ended plastic tank with a volume of 25L (20cm×25cm×50cm). During each test, 12 kg of copper flotation waste was placed onto the liner materials. It is mentioned that the uptake of the metal was very fast in the first 20 days, then kept

increasing gradually until the equilibrium was reached and remained constant. Efficiency of the Cu sorption for different BNZ mixtures are given in Figure 2.19.

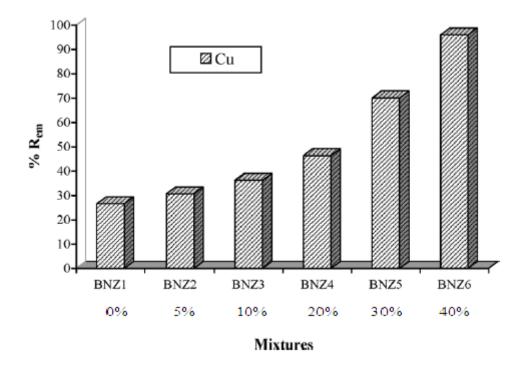


Figure 2.19 Efficiency of the copper sorption for bentonite zeolite mixtures (Turan & Ergun, 2009)

Shaqour et al. (2011) investigated 10 different mixtures including Rmah zeolite (RZ), Rmah tuff (RT), marl, kaolinite (Kt), sand and bentonite (Bt) with varying ratios (Table 2.5). Rmah is a quarry located in Jordan. Shaqour et al. (2011) found that optimum moisture contents of the mixtures increased with an increase in zeolite proportion (Figure 2.20). The authors explained the situation related to the high absorption capacity of the zeolite minerals. Also it is concluded that, much of the water went into the structure of zeolite framework before water started to liquefy the material.

Among ten mixtures, Shaqour et al. (2011) selected the two which had the maximum dry densities at their optimum water contents to run hydraulic conductivity test (1 and 9). A fixed ring consolidometer apparatus was used with a ring of 75 mm in diameter and having a height of 20 mm. The hydraulic conductivity values of the mixtures were determined to be  $1.2 \times 10^{-9}$  and  $1 \times 10^{-9}$  m/s.

Table 2.5 Mixture design of the study (Shaqour et al., 2011)

	Mixture Components					Proctor	Values	
Mix	RZ	RT	Marl	Kt	Sand	Bt	MDD	OWC
no.	(%)	(%)	(%)	(%)	(%)	(%)	$(Mg/m^3)$	(%)
1	30	20	20	30	0	0	1.71	0.17
2	40	40	10	10	0	0	1.65	0.19
3	30	20	20	0	0	30	1.64	0.19
4	50	0	30	0	10	10	1.68	1.87
5	70	0	10	0	10	10	1.5	0.25
6	60	0	30	0	0	10	1.56	0.22
7	40	0	20	0	20	20	1.66	0.19
8	50	0	30	0	15	5	1.65	0.19
9	30	0	50	0	5	15	1.75	0.16
10	70	0	5	0	20	5	1.5	0.245

MDD = Maximum dry density

OWC = Optimum water content

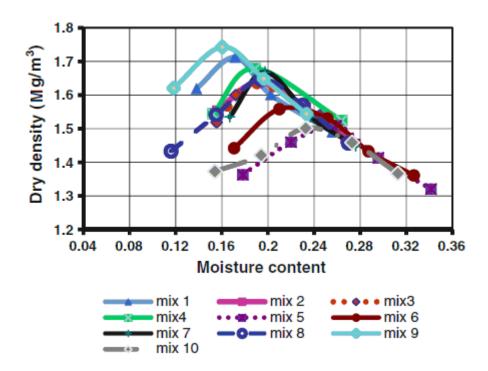


Figure 2.20 The compaction characteristics of the mixtures (Shaqour et al., 2011)

Ören et al. (2011) investigated the hydraulic conductivity of ZBMs and SBMs and also the zeolite's grain size effect on ZBMs and compared ZBM and SBM in terms of hydraulic conductivity and water content of bentonite in each mixture. Na-

bentonite from Süd-Chemie Co. and Gördes zeolite were used. The liquid limit of bentonite was 244% and the plastic limit was 49%. The mixtures included 10%, 20% and 30% ZBMs; 10% and 20% SBMs and 10% ZSBM where the percentages represented the bentonite weight to the overall weight.

During the hydraulic conductivity tests, ASTM D5084 procedure was followed and a backpressure of 350 kPa was applied. The cell pressure was 370 kPa. Hydraulic gradient of the tests varied between 10 and 120. Test samples were prepared at their 2-5% wet of optimum water contents. The hydraulic conductivities of ZBMs and SBMs are presented in Figure 2.21 along with some selected literature data. Moreover, the hydraulic conductivities with respect to the pore volumes of flow for each mixture are given in Figure 2.22.

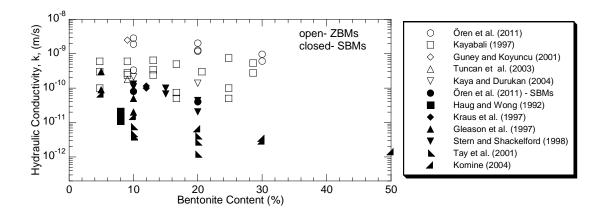


Figure 2.21 The hydraulic conductivity data of Ören et al. (2011) along with some selected literature data

The authors determined that ZBM samples, even the 30% ZBM, have higher hydraulic conductivities at least one order of magnitude when compared to that of SBMs. Consequently, the situation was contributed to the porous structure and water uptake potential of zeolites. The authors suggested that there might have occurred flow paths when zeolite grains were in contact named as zeolite network in the paper.

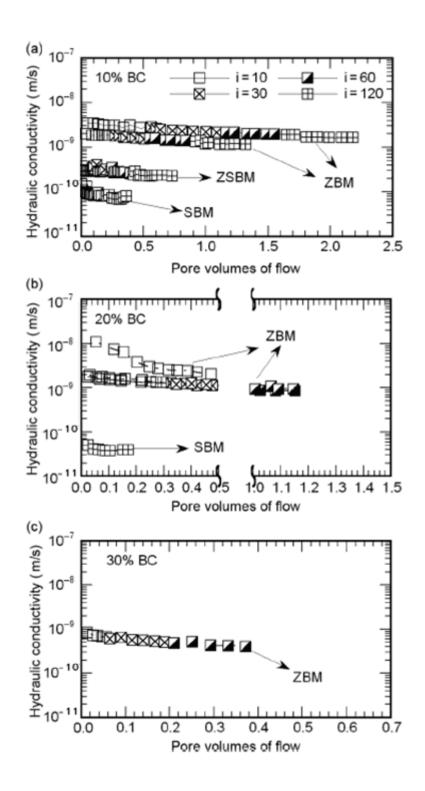


Figure 2.22 The hydraulic conductivity of the mixtures related to their pore volumes of flow of zeolite-bentonite sand-bentonite mixtures a) 10% bentonite content b) 20% bentonite content c) 30% bentonite content (Ören et al., 2011)

Ören et al. (2011) also investigated the water content of bentonite in ZBMs and SBMs. In order to determine the bentonite's water content in a ZBM, they proposed a modified analytical model for ZBMs which originally proposed by Kenney et al. (1992) for SBMs and which was also used by Kayabalı (1997). In SBMs it is accepted that bentonite had all water in the mixture and sand had no water content. Based on the criteria Kenney et al. (1992) proposed a model to calculate the water content of bentonite in a SBM. However, zeolite is known for its water uptake affinity. Ören et al. (2011) mentioned that due to the water uptake of zeolite the water content distribution of components in a ZBM would differ than that of in a SBM and analytically investigated the situation and recalculated Kenney's model. The model results are given in Figure 2.23 and they found that the bentonite in a ZBM would have less water content than it would have in a SBM where sand particles had no water content or had a water content of 2.8%.

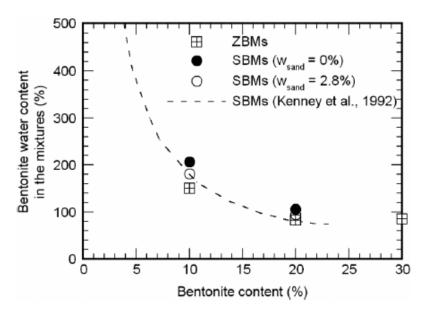


Figure 2.23 The bentonite water content variation with bentonite content in bentonitic mixtures (Ören et al., 2011)

Hong et al. (2012) investigated whether a zeolite (chabazite and clinoptilolite) addition would affect the consolidation and hydraulic conductivity parameters of soil-bentonitic backfills. However, zeolite had very little proportions (2%, 5%, and 10 %) in the mixtures. Fixed ring oedometers and flexible wall permeation tests were conducted. The mixtures contained 5.8% Na-bentonite and the rest was sand. It was

found that zeolite addition had little impact on the hydraulic conductivity values and did not alter the compression index as well. However it should be noted that zeolite addition was as small as 2% to 10%. The mixture without zeolite was reported to have a hydraulic conductivity of  $2.4 \times 10^{-10}$  m/s where that of zeolite added samples varied between  $1.2 \times 10^{-10}$  and  $3.9 \times 10^{-10}$  m/s.

# 2.3 Brief Summary of Testing Environment of ZBMs in Literature

When comparing the results given in literature, it is important to be aware which material was tested with what type of test method. However, it may be complicated to track the basic properties of the materials or test methods used in each study. In order to make it better comparable and less complicated, the characteristics of ZBMs which are mentioned above are compiled and presented in Tables 2.6 & 2.7. Some basic material properties of the studies are given in Table 2.6. Also, a brief summary of testing environment of these studies is presented in Table 2.7.

Table 2.6 Some basic characteristics of materials used in related studies

		Ö	A 1	Güney &	Kaya &	Kayabalı
		Ören,	Akpınar,	Koyuncu,	Durukan,	& Kezer
		2007	2005	2002#	2004	1998*
	Bentonite	2.76	-	2.63	2.71	2.25
×	Zeolite	2.28	2.37	2.60	2.39	2.22
Ğ	Sepiolite	-	2.68	-	-	-
	Sand				2.61	
0g)	Bentonite	67.1	-	90	104.4	60
CEC (meq/100g)	Zeolite	69.3	In a range	165	40	95
(me	Sepiolite	-	of 55 – 64	-	-	-
	Bentonite	244.4	-	447	210	320
$w_{L}\left(\%\right)$	Zeolite	63	-	-	42	-
≱	S/Z = 30%	-	68	-	-	-
	Bentonite	49.4	-	60	52	50
W <sub>P</sub> (%)	Zeolite	NP	-	NP	NP	NP
M <sub>I</sub>	S/Z = 30%	-	45	-	-	-
	10% BEZ	40.6–	-	_	36 – 1.25	_
	10,0222	1.115			20 1.20	
	20% BEZ	37. 9-	-	_	37-1.23	_
dry		1.123				
$\frac{w_{opt} - \rho_{dry}}{(\% - g/cm^3)}$	10% BES	18.6-	_	_	15-1.76	_
		1.642				
	20% BES	19-1.594	-	-	16-1.72	-
	S/Z = 30%	-	36.5 – 1.21	-	-	-
	B/Z = 0.1	-	-	39 – 1.63	-	39 – 1.18

<sup>\*</sup> The data are also valid for the study of Kayabalı and Mollamahmutoğlu, 2000.

 $<sup>^{\</sup>sharp}$  The data are also valid for the study of Tuncan et al., 2003.

Table 2.7 Hydraulic conductivity related characteristics of materials used in related studies

		Ören, 2007	Akpınar, 2005	Güney & Koyuncu, 2002 #	Durukan, 2002	*
Materials		10% - 20%-30% BEZ (fine & granular)	S/Z = 30%	B/Z = 10%	10% - 20% BEZ 20% BES	B/Z=0.05- 0.10-0.15- 0.20-0.26- 0.33-0.40
Methods		Flexible wall permeameter / standard proctor compaction / Falling head	Flexible wall permeameter / standard proctor compaction / Falling & constant head	Flexible wall permeameter / Standard proctor compaction	Consolidation test / Standard proctor compaction	Polyurethane compaction mold permeameter / Standard vibratory compaction / Falling head
k (m/s)	Tap water	0.4-2.84x10 <sup>-9</sup> 10%BEZ(3x4) 20%BEZ(2x3+1) 30%BEZ(1x4+1x3) (related to varying "i")	Falling head $(\sigma_3=0 \text{ psi})$ $0.75 \times 10^{-10}$ Constant head $(\sigma_3=10 \text{ psi})$ $1.17 \times 10^{-10}$	2.5x10 <sup>-9</sup>	BEZ= 2.5-4.5x10 <sup>-11</sup> BES= 4.8x10 <sup>-11</sup>	2-4x10 <sup>-10</sup>
	Salts	•	-	8-12x10 <sup>-10</sup>		(mixture)
	Metals	-	$(\sigma_3 = 6 \text{ psi})$ 3.5x10 <sup>-10</sup>	1-2x10 <sup>-9</sup>	-	For only B/Z=0.04
	Landfill leachate	-	-	-		10 <sup>-8</sup>
Hydra gradie		10, 30, 60, 120	unknown	14	-	20
Test (range	duration	2-12 weeks	unknown	unknown	24-48 hrs	2-8 weeks
Number of tests		30 tap water	2 tap water 1 metal (Cu)	1 tap water 3 salts 3 metals 1 mixture	7 tap water	18 tap water 4 chemical mixture

<sup>\*</sup> Kayabalı & Kezer, 1998; Kayabalı & Mollamahmutoğlu, 2000.

 $<sup>^{\</sup>it \#}$  The data are also valid for the study of Tuncan et al., 2003.

#### **CHAPTER THREE**

#### MATERIALS AND EXPERIMENTAL METHODS

This chapter presents the basic characterization of the materials used in this study and covers the standards and details of the experiments run during the research. Most properties were obtained via experiments throughout the study and a few were collected from the literature and/or related cooperations. The experimental study focused on understanding the hydraulic conductivity behavior of bentonitic mixtures which were made of zeolite-bentonite and sand-bentonite. Both mixtures were investigated by several researchers for various criteria such as adsorption characteristics, preliminary analysis of hydraulic conductivity, the effect of grain size, compaction effort, hydraulic gradient, smearing, desiccation etc. (Kayabalı, 1997; Kayabalı & Kezer, 1998; Güney & Koyuncu, 2002; Kaya & Durukan, 2004; Ören, 2011). Based on the criteria, the experimental program was set on the comparison of the hydraulic conductivity behavior of two bentonitic mixtures namely ZBMs and SBMs. The mechanisms controlling the hydraulic conductivity of these binary mixtures were investigated in terms of;

- i) Void ratio (initial and final).
- ii) Water contents of components in the mixtures.
- iii) The effect of zeolite as porous grains in the mixture.

In addition to the hydraulic conductivity laboratory tests, a modeling study has also been made as described in detail in Chapter 6.

# 3.1 Materials

Commercial natural zeolite, sand and powdered Na-bentonite were used in the tests. Two binary mixtures namely sand-bentonite mixtures (SBMs) and zeolite-bentonite mixtures (ZBMs) were prepared. Mixture ratio denotes the bentonite percentage in the mixture (e.g. 10% SBM means that, the ratio of bentonite weight to the mixture weight is 0.1 in a sand-bentonite mixture).

Natural sand was obtained from Aydınlar Co. (Turgutlu/Manisa-Turkey), whereas

zeolite was supplied by Rota Madencilik Co. (Gördes/Manisa-Turkey). Natural

Gördes Zeolite was composed of clinoptilolite minerals. Unlike sand, zeolite has a

negatively charged surface and is known as molecular sieve on account of its porous

structure. The natural Na-bentonite is comprised of montmorillonite minerals and

ordered from Karakaya Bentonit Co., (Ankara-Turkey).

Zeolites are similar to clays but they exhibit no sensible volume change when

exposed to water, due to their rigid structure. They differ in their crystalline

structure. Zeolites have interconnected cages and tunnels inside which let them to

confine minerals and let water to get in and out freely. The zeolite framework

contains voids or pores, which are generally filled with water, cations and/or other

molecular species (Jacobs & Förstner, 1999). For this reason zeolites are often called

microporous materials.

Many clays have a layered crystalline structure, similar to a deck of cards, and are

subjected to shrinking and swelling, when exposed to water. In contrast, zeolites

have a rigid, 3-dimensional crystalline structure, similar to a honeycomb (Figure

3.1), having a network of interconnected tunnels and cages. This network is

generated by the framework structures built from corner sharing TO<sub>4</sub> tetrahedra (T =

Si<sup>4+</sup>, Al<sup>3+</sup>) (O'Keeffe & Yaghi, 1999). The general formulization of zeolite and the

formulization for clinoptilolite type zeolite used in this study are as follows,

respectively;

General: M<sub>2/n</sub>O.Al<sub>2</sub>O<sub>3</sub>.xSiO<sub>2</sub>.yH<sub>2</sub>O

Clinoptilolite: (Ca, K<sub>2</sub>, Na<sub>2</sub>, Mg)<sub>4</sub>.Al<sub>8</sub>Si<sub>40</sub>O<sub>96</sub>.24H<sub>2</sub>O

Natural zeolites occur in different geological settings as rock-forming minerals in

many locations in the world. Turkey has large and rich zeolite reserves in many parts

of Anatolia like Bigadiç and Gördes (Baysal et al., 1986). The other reserves are

Ankara Polatlı Mülk Oğlakçı Area, Şaphane, Gediz and Emet (Ataman, 1977).

Characterization of BET isotherm of Gördes natural zeolite (clinoptilolite) was

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investigated by Özkırım & Yörükoğulları (2005). The specific gravities, specific surface areas, average pore diameters of the natural zeolite and ion exchanged modified forms of zeolite were determined by nitrogen adsorption method. Some selected results from the study of Özkırım & Yörükoğulları (2005) are presented in Table 3.1. From Table 3.1, the porous structure of zeolite and the effect on the specific gravity can be seen. When comparing these results it also should be noted that no volume change occurs in zeolite structure.

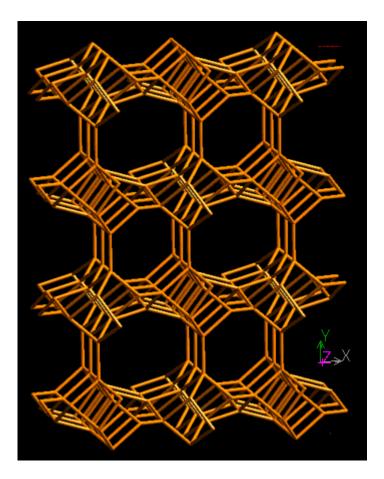


Figure 3.1 The framework model of zeolite-clinoptilolite (Database of zeolite structures)

Table 3.1 Summary of the variation of BET characteristics of Gördes zeolite due to ion exchange (Özkırım & Yörükoğulları, 2005)

Sample	Specific Gravity	BET Surface	Average pore
Sample	Specific Gravity	Area (m <sup>2</sup> /g)	diameter (°A)
Natural zeolite	2.20	52.369	32.79
0.1N Na <sup>+</sup>	2.49	51.710	22.85
0.5N Na <sup>+</sup>	2.59	51.572	21.50
1N Na <sup>+</sup>	2.67	51.905	20.31
0.1N Ca <sup>+2</sup>	2.39	34.354	34.55
0.5N Ca <sup>+2</sup>	2.47	36.836	32.34
1N Ca <sup>+2</sup>	2.50	34.699	30.12
0.5N K <sup>+</sup>	2.77	51.601	24.58
0.5N Mg <sup>+2</sup>	2.65	32.904	21.36

## 3.2 Physical Characteristics and Index Properties

Grain size distributions and the Atterberg limits (the liquid limit and the plastic limit) of the materials used in this study were performed according to ASTM D422 and ASTM D4318, respectively. The specific gravity values of each material were obtained based on ASTM D854. Basic characteristics of the materials used in hydraulic conductivity tests are presented in Table 3.2 and the grain size distribution of these materials are given in Figure 3.2. The mineralogy data of Na-bentonite is determined by Tubitak using Schimadzu X-ray diffractometer XRD-6000 equipment. Zeolite mineralogy data are directly obtained from Rota Madencilik Co. product information.

For the purpose of comparison, sand and zeolite materials were prepared to have similar grain size distributions. Two different groups were tested for different purposes:

- i) Fine zeolite or sand (between No.16 and No.200) + powdered bentonite.
- ii) Coarse zeolite or sand (3/4'' 3/8'') + powdered bentonite.

Fine grains are used in compaction tests and hydraulic conductivity tests whereas coarse grains are used to obtain the water contents of the mixture components.

Table 3.2 Summary of basic material characteristics

Properties	Bentonite	Zeolite	Sand
Mineralogy	Montmorillonite Kristabolite Quartz	Clinoptilolite (88-95 %) Feldispat Montmorillonite	Quartz
Particle size distribution			
Gravel	0%	0%	0%
Sand	4%	98%	100%
Silt	23%	2%	0%
Clay	73%	0%	0%
Montmorillonite Content*	80-90 %	2-5 %	0%
Atterberg limits Liquid limit Plastic limit Plasticity index	405% 57% 348%	58% 54% 4%	NA
Specific gravity	2.71	2.31	2.65

<sup>\*</sup>Based on the product informations

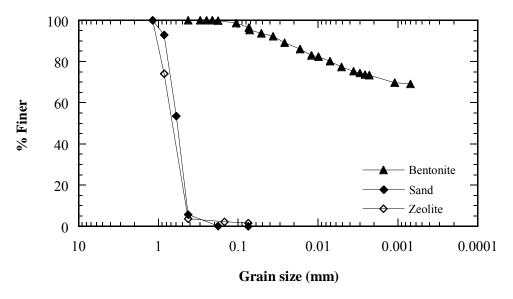


Figure 3.2 Grain size distribution of materials used in hydraulic conductivity tests

# 3.3 Specimen Preparation and Experimental Methods

#### 3.3.1 Compaction Tests

Proctor compaction and hydraulic conductivity tests were conducted at 10% and 20% bentonite contents (BCs) for both ZBMs and SBMs. All mixtures were prepared in their air dried state. Then, water was added with a spray bottle and the mixtures were blended thoroughly without allowing formation of any clods. The moist specimens were sealed in a plastic bag and left 24h for curing. Then, compaction tests were conducted applying standard Proctor compactive effort at various water contents as specified in ASTM D 698.

Standard compaction characteristics of the mixtures are presented in Figure 3.3a-f. Compaction curves of zeolite, 10% and 20% ZBM are presented in Figures 3.3a, b & c, respectively. The compaction curves of 10% and 20% SBM are presented in Figures 3.3d & e, respectively. The compaction curves of all mixtures are also presented in Figure 3.3f.

The differences between the optimum water contents ( $w_{opt}$ ) and the maximum dry densities ( $\rho_{dry-max}$ ) of ZBMs and SBMs are obvious in Figure 3.3f. The optimum water content of ZBMs is almost 2.5 times higher than that of SBMs and the maximum dry density of SBMs is almost 1.5 times higher than that of ZBMs for both 10% and 20% mixtures. The difference between the compaction characteristics is due to the low specific gravity, high porous structure and high water uptake potential of zeolite when compared to sand.

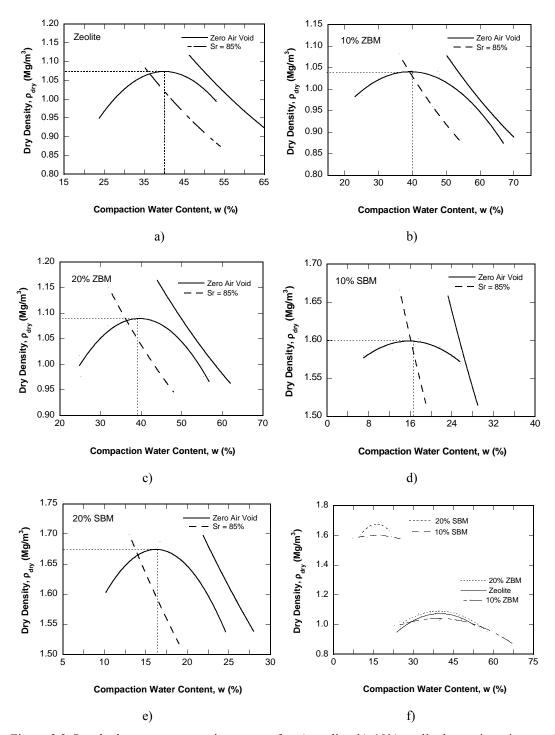


Figure 3.3 Standard proctor compaction curves for a) zeolite, b) 10% zeolite-bentonite mixture, c) 20% zeolite-bentonite mixture, d) 10% sand-bentonite mixture, e) 20% sand-bentonite mixture, f) All samples

Due to the difference between the specific gravity values of zeolite and sand, the compaction curves are also presented in normalized form in Figure 3.4. All compaction curves are normalized by a specific gravity value of 2.65 as

recommended by Sridharan et al. (2001) in order to allow a better comparison. The formulations used in normalization process are given in Equations 3.1 & 3.2. Sridharan et al. (2001) suggest that 2.65 can be selected for the standard value of specific gravity, because it represents the specific gravity of most soils.

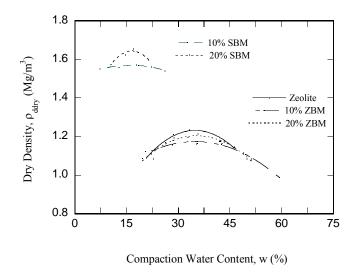


Figure 3.4 Standard proctor compaction curves for all samples normalized by a specific gravity of 2.65 recommended by Sridharan et al. (2001)

Normalised dry density: 
$$\rho_{dn} = \rho_{dm} \left( \frac{G_{std}}{G_m} \right)$$
 (3.1)

Normalised water content: 
$$w_n = w_m \left( \frac{G_m}{G_{std}} \right)$$
 (3.2)

Where;  $\rho_{dm}$  = the dry density of the given material

 $w_m$  = the water content corresponding to  $\rho_{dm}$ 

 $G_m$  = the specific gravity of the given material

 $G_{std}$  = the standard value of specific gravity

Figure 3.4 shows the compaction behavior of ZBMs and SBMs in terms of normalized dry density and normalized water content. The compaction curves resembles to the curves shown in Figure 3.3f. The only difference is that the

compaction curves for ZBMs (Figure 3.4) shifted upwards, when compared to the compaction curves of ZBMs in Figure 3.3f. However, the compaction densities of ZBMs are still less than those of SBMs even influence of specific gravity is eliminated. The compaction characteristics of the mixtures are also presented in Table 3.3. For both ZBMs and SBMs it is observed that, when the bentonite content increases from 10% to 20%, the optimum water content decreases whereas the dry density increases.

Table 3.3 Compaction characteristics of the mixtures

	ZB	M	SBM	
Bentonite content per total weight (%)	10	20	10	20
Optimum water content (%)	40.0	39.0	17.5	16.5
Dry density (Mg/m³)	1.035	1.095	1.600	1.670

The studies reported in the literature about the compaction behavior of ZBMs and SBMs were gathered and plotted as function of  $\rho_{dry-max}$  and  $w_{opt}$  in Figure 3.5.

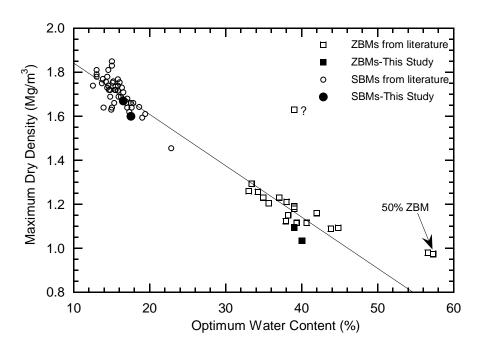


Figure 3.5 Comparison of the compaction parameters of zeolite-bentonite and sand-bentonite mixture

Figure 3.5 indicates the compaction parameters of ZBMs and SBMs, including the findings of this study. It is clear that the data obtained from this study is in agreement with the data reported in the literature. Moreover, ZBMs and SBMs data were evaluated together and a linear relationship between  $\rho_{dry-max}$  and  $w_{opt}$  has been found (Figure 3.5). That is,  $\rho_{dry-max}$  linearly decreased as the  $w_{opt}$  increased. There is only one data (Tuncan et al., 2003) scattered from this trend. It may be due to the specific gravity of natural zeolite that was used in their study. They reported 2.63 for the specific gravity of zeolite which is relatively high and out of the range of specific gravities reported in the literature (i.e. 2.0-2.4). It is also important to note that the data for 50% ZBM slightly deviates from the linear trend. It is because of high bentonite percentage in the mixture. The swollen bentonite particles start to dislocate the coarse grains from each other. Thus, the compaction behaviour is predominantly governed by bentonite particles when bentonite content in the mixture is appreciably high (Ören & Kaya, 2013).

# 3.3.2 Hydraulic Conductivity Tests

## 3.3.2.1 Compacted Samples

Once the compaction curves were obtained, fresh compacted samples were prepared at various water contents for the hydraulic conductivity tests. The specimens were extruded from the compaction mold and placed in the triaxial permeameter cell. The dimensions of the test specimens were 150 mm in diameter and 115 mm in height. The hydraulic conductivity tests were performed with flexible wall permeameters using tap water as the permeant (ASTM D5084). The specimens were tested under a confining pressure of 35 kPa and an average hydraulic gradient of 12. Backpressure was not applied during the experiments. The specimens were prehydrated with tap water for 24 hours before the start of permeation.

Permeameters were connected to each other and fed from a common water reservoir which is elevated at 3.65 m above from the base line of the experimental system. The schematic form of the permeation set is presented in Figure 3.6. The permeameter cells can be seen in Figures 3.7, 3.8 & 3.9.

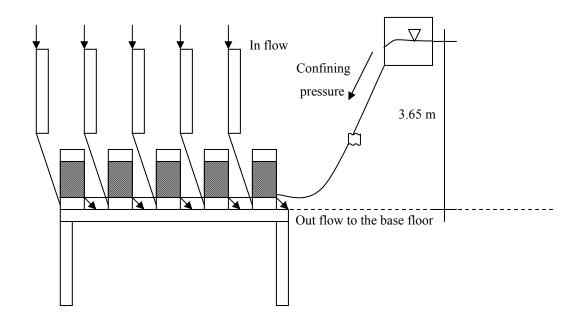


Figure 3.6 Schematic view of the permeation set



Figure 3.7 Tube connections and flexible wall permeameters through which permeation continues



Figure 3.8 A view of the top and bottom plexiglass caps and the tube connections

The permeations lasted at least seven months for specimens with low hydraulic conductivity i.e.  $\leq 10^{-9}$  m/s and in addition, until at least one pore volume of flow had been collected for specimens with relatively high hydraulic conductivity i.e.  $> 10^{-9}$  m/s. The tests were terminated, when inflow and outflow rate was not changed for at least three consecutive hydraulic conductivity determinations.



Figure 3.9 A view of the flexible wall permeameters

Scatter of hydraulic conductivity test samples for ZBMs and SBMs are shown in the compaction diagrams of each mixture in Figure 3.10, indicating how many samples were tested. For 10% ZBMs and 20% ZBMs, nine tets and six tests were conducted, respectively. For SBM samples, three and four tests were conducted on 10% and 20% SBMs, respectively. Each mixture had at least 1 test at its dry of optimum, optimum and wet of optimum water contents.

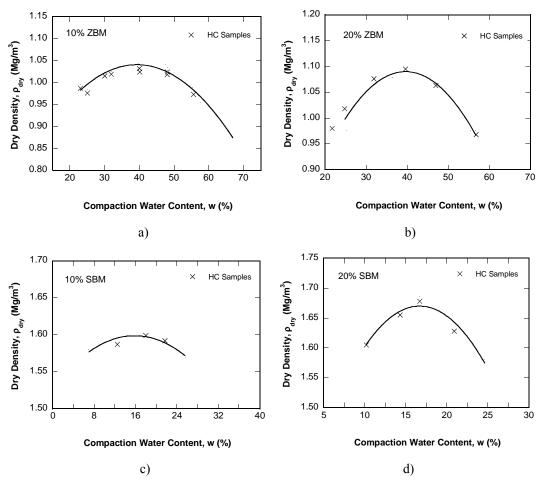


Figure 3.10 Scatter of hydraulic conductivity test samples conducted on a) 10% zeolite-bentonite mixture, b) 20% zeolite-bentonite mixture, c) 10% sand-bentonite mixture, and d) 20% sand-bentonite mixture compaction diagrams

## 3.3.2.2 Zeolite Blocks

The hydraulic conductivity tests of zeolite blocks were also conducted. The blocks were 5 cm in diameter. The sampling stage of the blocks can be seen in Figure 3.11. For the assessment of anisotropy, zeolite block samples were collected from orthogonal directions (Figure 3.11). The large pores in the zeolite section can be seen in Figure 3.12. In addition, the zeolite blocks to be subjected to permeation tests are also presented in Figure 3.13.



Figure 3.11 Sampling stage of zeolite blocks from different directions



Figure 3.12 Large pores in zeolite block section

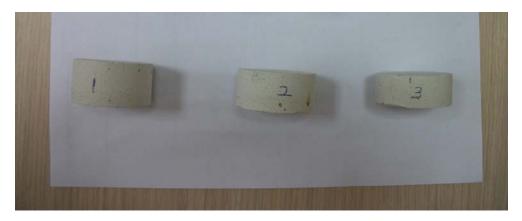


Figure 3.13 Zeolite blocks used in the hydraulic conductivity tests

In order to avoid trapped air and also to speed up the permeation process, carbon dioxide (CO<sub>2</sub>) percolation through the samples was recommended before the start of permeation. To reach full saturation quicker and easier, it is convenient to use a gas which can dissolve in water better. As Henry's Constant for CO<sub>2</sub> is much larger than it is for air, it is easier to reach full saturation when CO<sub>2</sub> is percolated through the sample (Carroll et al., 1991). In other words, by percolating CO<sub>2</sub>, water permeation would be easier just because that CO<sub>2</sub> would dissolve in water easier when compared to air.

For instance, Mulilis et al. (1975) percolated CO<sub>2</sub> through sand samples for about 15 minutes. Afterwards, the samples were subjected to water permeation. In addition, the permeation measurements began when outflow had no bubbles which meant that there were no CO<sub>2</sub> left in the sample.

Similarly, in order to avoid formation of the trapped air bubbles in the zeolite block sample, CO<sub>2</sub> percolation was applied as seen in Figure 3.14. After the CO<sub>2</sub> percolation process, each flexible wall cell was attached to the falling head permeation system.

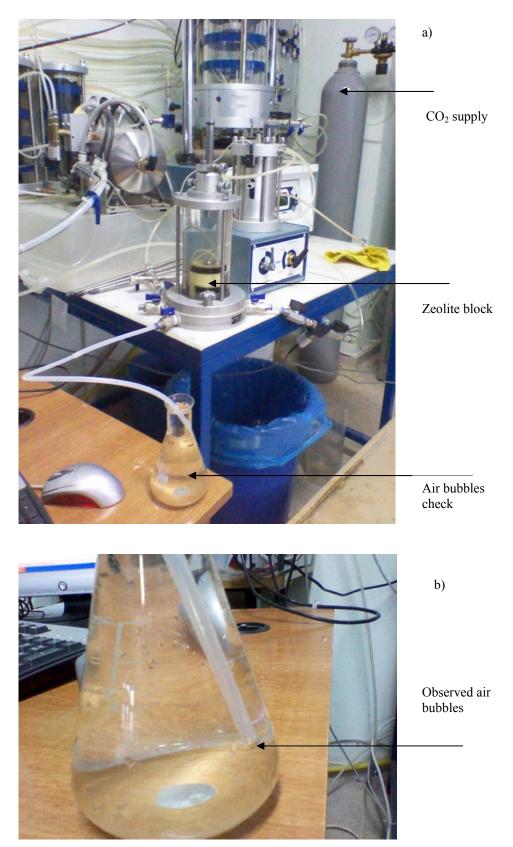


Figure 3.14 CO<sub>2</sub> percolation a) zeolite block under process, b) observed air bubbles in outflow

#### **CHAPTER FOUR**

## HYDRAULIC CONDUCTIVITIES OF ZBMS, SBMS & ZEOLITE BLOCKS

Hydraulic conductivity tests were conducted on ZBMs and SBMs for 10% and 20% BCs at various compaction water contents (w) for comparison purposes. The pore volumes of flow (PVF) of the samples which had low hydraulic conductivities i.e.  $\leq 10^{-9}$  m/s, were limited because of the long testing periods i.e.  $\geq 7$  months. For the rest of the samples having relatively high hydraulic conductivities, the tests were terminated where the samples had at least one PVF. In addition, the hydraulic conductivities of zeolite blocks were also determined.

# 4.1 Hydraulic Conductivity of ZBMs

Nine tests were conducted on 10% ZBMs and six were conducted on 20% ZBMs. The hydraulic conductivity test was doubled at optimum and tripled at wet of  $w_{opt}$  for 10% ZBMs. For 20% ZBMs only one sample was compacted at  $w_{opt}$  and run for the hydraulic conductivity test. At the dry side of optimum three samples, and at the wet side of optimum two samples were prepared by compaction and subjected to hydraulic conductivity tests.

The hydraulic conductivities of 10% ZBMs varied between 1.3x10<sup>-6</sup> m/s and 7.4x10<sup>-11</sup> m/s of where water content changed between 23% and 55.6%. The hydraulic conductivities of 20% ZBMs varied between 9.7x10<sup>-8</sup> m/s and 2.8x10<sup>-11</sup> m/s and the water contents were 21.7% and 56.8%, respectively. Both 10% and 20% ZBMs exhibited decreasing hydraulic conductivity values as the water content increased. Samples having hydraulic conductivities lower than 10<sup>-9</sup> m/s had also PVF lower than 0.5 although they had at least 7 months of testing periods.

For easier pursuance and comparison purposes, hydraulic conductivities of ZBMs are shown together in Figure 4.1 as a function of PVF. Figure 4.1a shows that for each test, hydraulic conductivities were almost unchanged throughout the test

duration when the water contents of the samples were within the range of 23% - 40%.

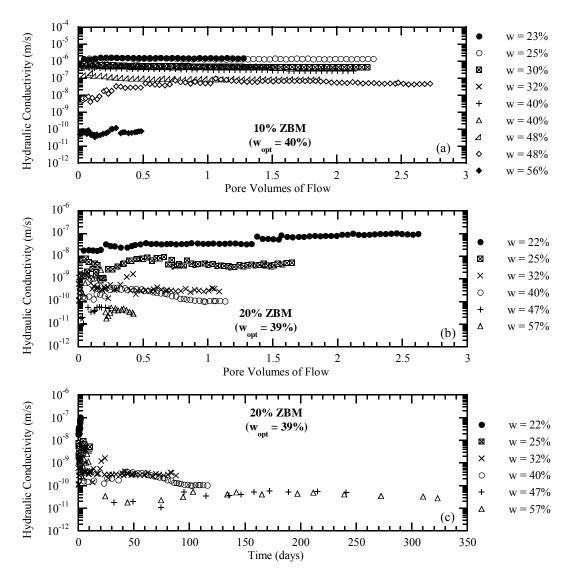


Figure 4.1 Hydraulic conductivity characteristics of zeolite-bentonite mixtures as a function of: a) pore volumes of flow for 10% bentonite content, b) pore volumes of flow and c) time for 20% bentonite content

Since an increasing trend in the hydraulic conductivity was obtained in the first test, another test was run on the sample compacted at 48% water content. In the first test, the hydraulic conductivity gradually increased and then leveled off around one PVF. The final hydraulic conductivity for this sample was  $4.6 \times 10^{-8}$  m/s. The hydraulic conductivity behavior was rather different because it was almost stable

along the test duration. The final hydraulic conductivity for this sample was  $8.4 \times 10^{-8}$  m/s (with an average of  $6.5 \times 10^{-8}$  m/s for both samples). The hydraulic conductivity tests were conducted at 56% water content as well. The results showed that the hydraulic conductivity was about 600 times less than that of sample compacted at 48% water content ( $7.4 \times 10^{-11}$  m/s). This reduction in the hydraulic conductivity is possibly due to the workability of bentonite particles at higher water contents. Since bentonite water content is high at 56% water content, bentonite particles may possibly be distributed well between zeolite grains, which may block the inter granular pores for water flow.

Figures 4.1b and 4.1c indicate the hydraulic conductivities of 20% ZBMs with respect to PVF and time, respectively. At 22% water content, hydraulic conductivity was initially  $1.8 \times 10^{-8}$  m/s and then gradually increased to  $9.7 \times 10^{-8}$  m/s. In contrast, hydraulic conductivities slightly decreased as PVF increased for the rest of the samples. There is almost three orders of magnitude hydraulic conductivity difference between the samples that had 22% and 40% water content. The hydraulic conductivity tests for the samples that had 47% and 57% water contents were terminated at 0.25 and 0.43 PVF that correspond to 240 and 325 days of permeation, respectively (Figure 4.1c). As can be seen from Figure 4.1c, hydraulic conductivities were stable with time and final hydraulic conductivity was  $2.8 \times 10^{-11}$  m/s when the water content was well above optimum (i.e. 47% and 57%).

# 4.2 Hydraulic Conductivity of SBMs

Hydraulic conductivities of 10% SBMs were determined at three different water contents regarding dry of optimum, optimum and wet of  $w_{opt}$ : i) 13%, ii) 18%, and iii) 22%. For 20% SBMs two tests were conducted at the dry side of  $w_{opt}$  (i.e. 10% and 14%). In addition to these, two other tests were also conducted. One of these tests was performed at optimum and the other test was conducted at the wet side of  $w_{opt}$ .

Test durations of SBMs are longer than those of ZBMs. However, PVF of SBMs are all lower than 0.6, although test durations were at least 8 months. The hydraulic conductivities of 10% SBMs varied between  $2.6 \times 10^{-11}$  m/s, and  $3.5 \times 10^{-12}$  m/s, and hydraulic conductivities of 20% SBMs varied between  $1.3 \times 10^{-11}$  m/s, and  $2.6 \times 10^{-12}$  m/s. When compared to the hydraulic conductivities of ZBMs, those of SBMs did not varied as much related to water content. The hydraulic conductivities 10% and 20% SBMs are plotted in Figure 4.2.

The hydraulic conductivity tests for SBMs have lasted at least 200 days. However, they correspond to a very low PVF. Thus, hydraulic conductivity behavior of SBMs is shown in Figure 4.2 as a function of PVF and time. As can be seen from Figure 4.2a and 4.2b, hydraulic conductivities of the samples with 13% and 18% water contents slightly reduced till 0.15 and 0.3 PVF (or 70 days of permeation for both), respectively. This decreasing trend in the hydraulic conductivity is possibly due to the gradual swelling of bentonite particles during permeation. Then, hydraulic conductivities became stable and almost unchanged until the end of the test. The final hydraulic conductivities for the samples of 13% and 18% water contents were  $2.6 \times 10^{-11}$  and  $1.0 \times 10^{-11}$  m/s, respectively. In contrast, the sample compacted on wet of w<sub>opt</sub> (i.e. 22%) had steady hydraulic conductivity throughout the test duration. It may be attributed to relatively high bentonite water content on account of higher compaction water content. This leads to swelling of bentonite particles, resulting obstruction of inter-granular pores. Thus, hydraulic conductivity was stable along the test and the final hydraulic conductivity was  $3.5 \times 10^{-12}$  m/s which is 7.5 times and 2.8 times less than those of the samples that had 13% and 18% water contents, respectively.

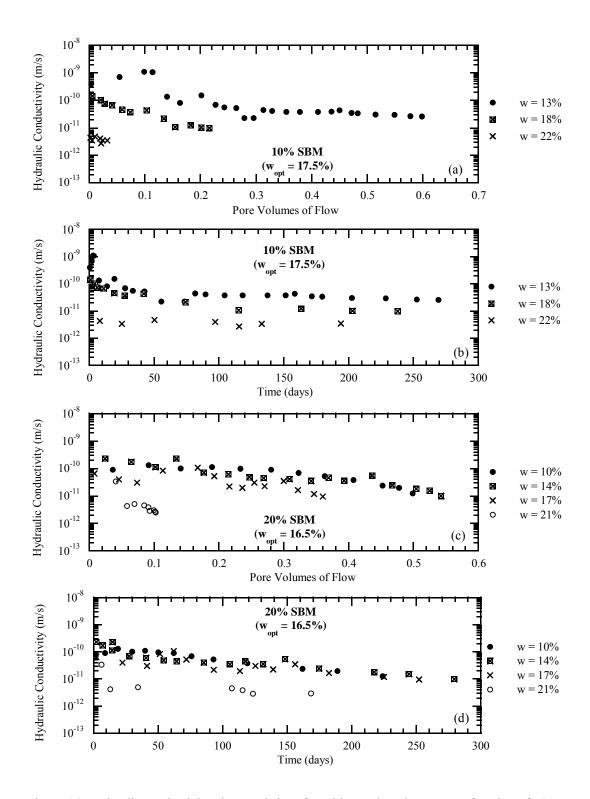


Figure 4.2 Hydraulic conductivity characteristics of sand-bentonite mixtures as a function of: a) pore volumes of flow and b) time for 10% bentonite content; c) pore volumes of flow and d) time for 20% bentonite content

The hydraulic conductivities of 20% SBM were depicted in Figure 4.2c and 4.2d as a function of PVF and time, respectively. The test duration was within the range of 225 - 280 days, depending on the water content (Figure 4.2d). The hydraulic conductivities of all samples were slightly reduced throughout the test process. The final hydraulic conductivity values at 10%, 14% and 17% water contents were almost the same with an average value of  $1.1 \times 10^{-11}$  m/s. When compaction water content was increased to 21%, the hydraulic conductivity decreased about four times with respect to the value obtained for the sample with 17% water content and reached final hydraulic conductivity of  $2.5 \times 10^{-12}$  m/s.

# 4.3 Impact of Water Content on the Hydraulic Conductivities of ZBMs and SBMs

Hydraulic conductivity results of ZBMs and SBMs are compared in terms of compaction water content in Figure 4.3a. Figure 4.3a shows that compaction water contents of ZBMs are larger than those of SBMs. That is, SBMs compacted on the wet side, still fall into the dry side of the optimum water contents for ZBMs. Thus, a direct comparison cannot be made between the hydraulic conductivities of ZBMs and SBMs when compaction water contents are considered (Figure 4.3a). For this reason, the results are compared as a function of water content relative to optimum as shown in Figure 4.3b. The water content relative to optimum can be expressed in Equation 4.1 as follows;

Water content relative to optimum = 
$$\frac{w_m - w_{opt}}{w_{opt}}$$
 (4.1)

Where,  $w_m$  is the compaction water content. The negative values in Figure 4.3b represent the water contents on dry side, whereas positive values represent the wet side of optimum.

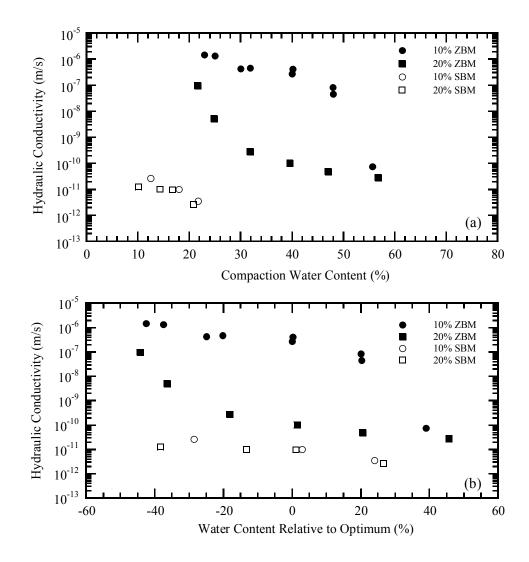


Figure 4.3 Hydraulic conductivity of zeolite-bentonite and sand-bentonite mixtures as a function of: a) water content, b) water content relative to optimum

It is clear from Figure 4.3b that the influence of compaction water content on the hydraulic conductivity of bentonitic mixtures is mostly pronounced on ZBMs. The hydraulic conductivity of 10% ZBM decreased about 20 times, when water content relative to optimum has increased from -40% to 20%. Then, hydraulic conductivity suddenly decreased from  $6.5 \times 10^{-8}$  m/s to  $7.4 \times 10^{-11}$  m/s, when water content slightly increased. The total reduction in the hydraulic conductivity within the tested water content range was more than three orders of magnitude. Similarly, the hydraulic conductivity of 20% ZBMs has reduced by 3500 times, when water content relative to optimum increased from -40% to 40%. At this time, however, a higher decrease rate took place between -40% to 0% water content relative to optimum, whereas the

reduction was by a lower decrease rate 0% to 40% water content relative to optimum. It is because of the greater amount of bentonite particles in 20% ZBMs. As compaction water content increases, bentonite particles tend to swell and block the pores progressively.

In contrast, the compaction water content had no significant influence on the hydraulic conductivity of SBMs (Figure 4.3). The hydraulic conductivity of 10% SBMs and 20% SBMs decreased about 7.5 times and 5 times, respectively, along the water content increment. This result is consistent with the findings of Haug & Wong (1992) who reported only six-fold decrease in the hydraulic conductivity relative to optimum even at lower bentonite content (i.e. B/S=8%).

Figure 4.3b also depicts that the hydraulic conductivity of SBMs are less than those of ZBMs, independent of bentonite content. The differences in the hydraulic conductivities were greater when the compaction water contents are on the dry side of optimum. On the wet side of optimum, however, the hydraulic conductivities of SBMs are one order of magnitude less than the hydraulic conductivities of ZBMs. This conclusion is also in agreement with the literature. Ören et al. (2011) reported that the hydraulic conductivity of 10% ZBM is 22 times, whereas that of 20% ZBM is 28 times greater than the hydraulic conductivities of 10% SBMs and 20% SBMs, respectively. Ören et al. (2011) also compared the hydraulic conductivities of ZBMs and SBMs that have been reported in the literature so far. They concluded that hydraulic conductivities of ZBMs were at least an order of magnitude greater than those of SBMs at the same bentonite contents. Two possible mechanisms were proposed to explain this difference in the hydraulic conductivities. It was suggested that cation exchange between zeolite and bentonite particles during permeation and zeolite network inside the bentonitic mixture may be responsible for the greater hydraulic conductivities of ZBMs relative to SBMs. Although it is difficult to determine the cation exchange between small particles of zeolite and bentonite, this mechanism was eliminated because it needs long test durations on account of low hydraulic conductivity. Indeed, Figure 4.1c shows that hydraulic conductivity of 20% ZBMs became stable at the early stages of permeation for the samples compacted at

47% and 57% water content, supporting another mechanism rather than cation exchange.

Ören et al. (2011) propounded the zeolite network model to explain the greater hydraulic conductivities for ZBMs. They reported that porous zeolite particles may form network along the specimen which facilitate water flow through this arrangement. The findings of this study also support the zeolite network model because the hydraulic conductivities of ZBMs are at least 10 times greater than SBMs.

# 4.4 Hydraulic Conductivity of Zeolite Blocks

Zeolite blocks extracted from different directions, as mentioned in Chapter 3, were tested for their hydraulic conductivities and the results are plotted in Figure 4.4. The direction of first, second and the third blocks were shown as 1, 2 and 3, respectively in Figure 4.5. It should be noted that, the original block was oriented in the direction of the third sample. The thickness of the specimens of the first, second and the third blocks were 0.98 cm, 2.25 cm and 1.16 cm, respectively. The hydraulic conductivity and porosity results of zeolite blocks and the average hydraulic conductivity are presented in Table 4.1. The hydraulic conductivity of zeolite block was not significantly influenced by the direction of sampling.

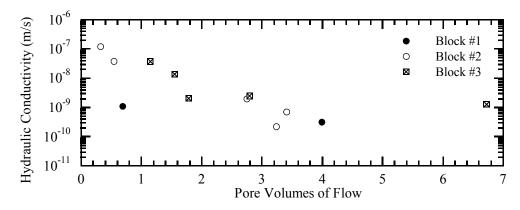


Figure 4.4 Hydraulic conductivity of zeolite blocks from different direction as a function of pore volumes of flow

Table 4.1 The hydraulic conductivities of zeolite blocks from 3 different directions

	Block #1	Block #2	Block #3	Average
Hydraulic	5.77x10 <sup>-10</sup>	1.42x10 <sup>-10</sup>	1.93x10 <sup>-9</sup>	1.31x10 <sup>-9</sup>
Conductivity (m/s)	J.//X10	1.42810	1.93810	1.51X10
Porosity	0.38	0.40	0.41	0.40

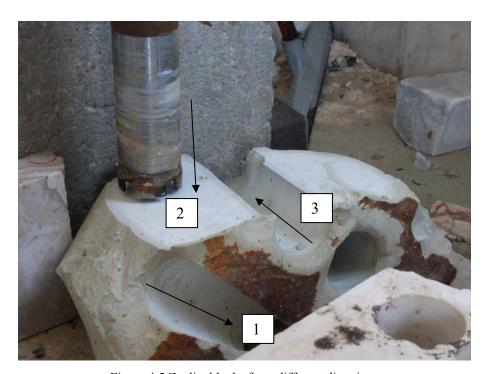


Figure 4.5 Zeolite blocks from different directions

# 4.5 Summary and Conclusions

The hydraulic conductivity of zeolite blocks was found to be 1.31x10<sup>-9</sup> m/s in average. The hydraulic conductivity behavior of ZBMs and SBMs were determined at various water contents to show whether water content has an influence on the hydraulic conductivity of these bentonitic mixtures. The study was restricted by 10% and 20% bentonite contents. This is because 20% bentonite content is high enough to seal the pores inside a granular matrix. The compacted ZBMs and SBMs which were subjected to hydraulic conductivity tests are presented in Table 4.2 in summary. The compaction characteristics, PVF and test durations of each sample along with the hydraulic conductivity values are presented in Table 4.2. The scatter of hydraulic

conductivity test samples for ZBMs and SBMs were given in the compaction diagrams of each mixture in Figure 3.10 previously.

Table 4.2 The summary of hydraulic conductivity test results conducted on zeolite-bentonite and sand-bentonite mixtures

Sample ID	$\rho_{\text{dry- max}}$ $(Mg/m^3)$	W <sub>opt</sub> (%)	$\begin{matrix} \rho_{dry} \\ (Mg/m^3) \end{matrix}$	W (%)	PVF	Test Duration (days)	Hydraulic Conductivity (m/s)
Zeolite blocks average hydraulic conductivity							1.3x10 <sup>-9</sup>
10% ZBM			0.995	23.0	1.3	*	1.3x10 <sup>-6</sup>
10% ZBM			0.985	25.0	2.3	*	$1.5 \times 10^{-6}$
10% ZBM			1.024	30.0	2.2	*	$4.0 \times 10^{-7}$
10% ZBM			1.026	31.9	1.5	*	$4.7 \times 10^{-7}$
10% ZBM	1.035	40.0	1.041	40.0	2.1	*	$2.7 \times 10^{-7}$
10% ZBM			1.033	40.1	1.5	*	$4.2 \times 10^{-7}$
10% ZBM			1.027	48.0	1.9	*	$8.4 \times 10^{-8}$
10% ZBM			1.033	48.1	2.7	*	$4.6 \times 10^{-8}$
10% ZBM			0.982	55.6	0.5	285	$7.4 \times 10^{-11}$
20% ZBM		39.0	0.980	21.7	2.6	*	9.7x10 <sup>-8</sup>
20% ZBM			1.018	24.8	1.6	*	$5.2x10^{-9}$
20% ZBM	1 005		1.076	31,9	1.1	88	$2.8 \times 10^{-10}$
20% ZBM	1.095		1.095	39.6	1.1	117	$1.0 \text{x} 10^{-10}$
20% ZBM			1.063	47.0	0.2	241	$5.0 \times 10^{-11}$
20% ZBM			0.976	56.8	0.4	324	$2.8 \times 10^{-11}$
10% SBM			1.587	12.5	0.6	270	2.6x10 <sup>-11</sup>
10% SBM	1.600	0 17.5	1.599	17.9	0.2	238	$1.0 \times 10^{-11}$
10% SBM			1.592	21.7	0.1	194	$3.5 \times 10^{-12}$
20% SBM		670 16.5	1.605	10.2	0.5	224	1.3x10 <sup>-11</sup>
20% SBM	1 (70		1.655	14.3	0.5	280	$1.0 \times 10^{-11}$
20% SBM	1.6/0		1.687	16.7	0.4	252	$9.7x10^{-12}$
20% SBM			1.628	20.9	0.1	243	$2.6 \times 10^{-12}$

<sup>\*</sup>Tests lasted shorter than 30 days.

The hydraulic conductivity behavior of ZBMs was totally different from the hydraulic conductivities of SBMs. The bentonite content and compaction water content had slight impact on the hydraulic conductivities of SBMs. However, both

factors significantly altered the hydraulic conductivities of ZBMs. The hydraulic conductivity of 10% ZBM was  $1.5 \times 10^{-6}$  m/s on dry side, whereas it was around  $6.5 \times 10^{-8}$  m/s on the wet side of  $w_{opt}$ . It is interesting to note that the distinctive reduction in the hydraulic conductivity was measured (i.e.  $7.4 \times 10^{-11}$  m/s) when the compaction water content was 56% that corresponds to the very wet side of  $w_{opt}$ . The hydraulic conductivity differences between 10% ZBM and 20% ZBM were small on either dry or wet side of optimum. However, since the hydraulic conductivity of 20% ZBMs rapidly decreased as the water content increased, the differences in the hydraulic conductivities for 10% and 20% bentonite contents were large around  $w_{opt}$ .

When the hydraulic conductivities of ZBMs and SBMs are compared, it is seen that the hydraulic conductivities of SBMs were less than those of ZBMs. The hydraulic conductivities of two bentonitic mixtures may differ up to five orders of magnitude, depending on the compaction water content. Two possible mechanisms are thought to take place to cause this difference. One of them is the possible water content distribution differences in SBMs and ZBMs. The other one is the water transition through the porous zeolite grains. The principal mechanism proposed in previous studies can be adapted to the findings of this study as well. That is, the porous zeolite network governs the hydraulic conductivity behavior of ZBMs.

#### **CHAPTER FIVE**

#### EVALUATION OF DEGREE OF SATURATION TO BENTONITE

It is very well known that, binary mixtures are identified with their bentonite contents (BCs). However, based on the specific gravity difference between zeolite and sand, the total weight of ZBMs is naturally lighter than that of SBMs for equal volumes. Thus, the bentonite weights in ZBMs are also less than those of SBMs even though they have the same BC. Based on this evaluation, it becomes necessary to investigate if the swollen bentonite in ZBMs were enough to fill the voids and had the control of hydraulic conductivity in comparison to SBMs. In addition, other than bentonite amount in ZBMs and SBMs, the water content distributions to components also differ due to the water uptake of zeolite.

In order to clarify the issues mentioned above, dry weight of bentonite filling the intergranular voids of zeolite or sand grains was investigated. The volume of intergranular voids in a compacted soil sample can be calculated and the volume of bentonite to fill these voids can also be estimated. Therefore, a series of experiments were made. Firstly, water content of bentonite in binary mixtures, and finally the dry weight or volume of bentonite to fill the voids were determined. Afterwards, the findings were compared with the amount of bentonite present in mixtures, which are subjected to hydraulic conductivity tests, in order to state whether the present bentonite was enough to fill the voids or not.

In this study, the comparison mentioned above is finally named as the degree of saturation to bentonite ( $S_B$ ) which corresponds to the ratio of present bentonite weight in the mixture to the calculated bentonite weight which is required to fill the intergranular voids of zeolite grains. Similar to degree of water saturation, when  $S_B$  has a value of unity it means that all the intergranular voids are full of swollen bentonite. However, unlike degree of water saturation,  $S_B$  may also have values more than unity due to the excessive amount of present bentonite than the required amount, to fill the present intergranular voids. When the  $S_B$  of a mixture is more than

unity it means that a volumetric increase in the total volume of the mixture will be observed related to the initial volume of that mixture.

## 5.1 Water Content Distribution in Binary Mixtures

It is assumed that, water content of sand in SBMs is negligible and bentonite adsorbs all the water in the mixture. However, in ZBMs, the condition is somewhat different, due to the water uptake potential of zeolite. Moreover, zeolite holds water physically and lets the water flow in and out freely, while bentonite constitutes chemical and electrical bonds with it. Consequently, water uptake speed of zeolite is much quicker than bentonite. This causes insufficient swelling of bentonite in early stages of hydraulic conductivity tests which may also result in preferential flow.

Zeolites are known with their tunnels and cages in their structures, which are rigid when exposed to water. Water can freely move in and out of zeolite body without any structural or volume change. This may affect the water content distribution to the constituents in zeolite bentonite mixtures. Many researchers studied on the water content of bentonite in SBMs and some tried to adapt it to ZBMs. However, these studies were theoretical (Kayabalı, 1997; Kayabalı & Kezer, 1998; Ören, 2007). Moreover, it was suggested that zeolite had no water content like sand and bentonite had all water in the mixture (Kayabalı, 1997; Kayabalı & Kezer, 1998). However, it is clear that this is not the case in reality. In this study, the water content of components in ZBMs and SBMs were determined experimentally and compared with each other.

# 5.2 Bentonite Void Ratio in Binary Mixtures, Swelling of Bentonite

In the literature, in order to impress the influence of swelling of bentonite on the hydraulic conductivity, binary mixtures are represented by the bentonite void ratio  $(e_b)$ . The values of  $e_b$  represent the final situation of bentonite in hydraulic conductivity tests. In the study of Studds et al. (1998), the effect of  $e_b$  to the hydraulic conductivity of both free swelled bentonite and compacted SBMs are

plotted in Figures 5.1 & 5.2, respectively. Figures 5.1 & 5.2 impress that the hydraulic conductivity increases with the void ratio of bentonite. However, it is seen from Figure 5.2 that at a given e<sub>b</sub> the hydraulic conductivity of 10% SBMs are lower than that of 20% SBMs and that of bentonite alone. The authors related this situation to the sand particles which were more tightly packed together in 10% SBMs and also concluded that, this situation has resulted in reduced cross-sectional area and also has increased the tortuosity for preferential flow paths.

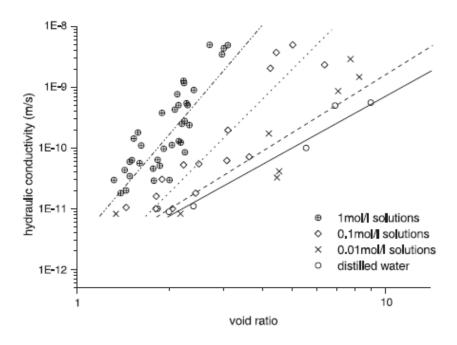


Figure 5.1 The influence of void ratio on the hydraulic conductivity of SPV-200 Bentonite when exposed to permeation with varying solutions (Studds et al., 1998)

Binary mixtures are mostly characterized by their BCs per their total weights. However, the volumetric BCs of ZBMs and SBMs differ because of the lower specific gravity of zeolite, when compared to sand. The mixtures may have different volumetric BCs, yet they have the same BC per total weight. The volumetric equivalents of BCs compared to the BC per total weight in mixtures are presented in Table 5.1. The BC per total volume in SBMs is almost 15% more than that of in ZBMs. For instance, in order to obtain a ZBM corresponding to the same volumetric BC that of 10% SBM has, at least 12% BC per total weight is required. Even though the BCs per total weight of a ZBM and a SBM are equal, the volumetric equivalents

of the mixtures differs, which may cause the lack of needed swollen bentonite to fill the voids in ZBMs. Thus, it is needed to investigate the sufficiency of bentonite amount in a mixture to swell and fill the voids and prevent preferential flow paths. For this purpose the bentonite amount needed at the beginning was estimated and compared with the present amount.

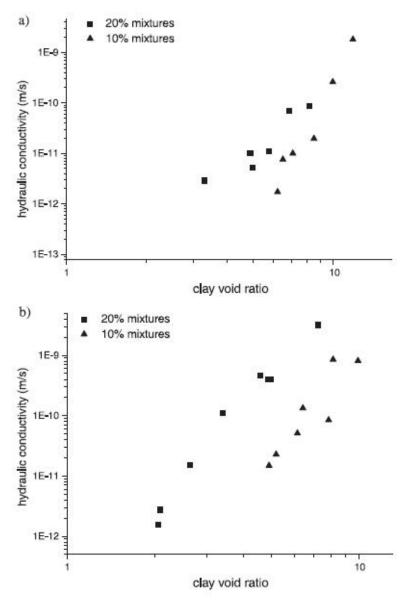


Figure 5.2 The influence of clay void ratio on the hydraulic conductivity of 10% and 20% sand-bentonite mixtures when exposed to a) distilled water b) various 0.1 mol/l chloride solutions (Studds et al., 1998)

Table 5.1 The volumetric equivalent of the bentonite content in the mixtures

	ZBM		SBM	
Bentonite content per total weight (%)	10	20	10	20
Bentonite content per total volume (%)	8.65	17.57	9.80	19.64

In this study, due to the porous structure and water uptake affinity of zeolite, along with determining the  $e_b$ , the sufficiency of present bentonite amount in mixtures to fill all the voids of the mixture was also investigated for both ZBMs and SBMs. Swelling of bentonite in binary mixtures was investigated in two different ways.

- i) By comparing the e<sub>b</sub> in SBMs and ZBMs (for the final situation)
- ii) By comparing the needed volume or weight of bentonite to fully fill the voids with the present bentonite volume or weight in SBMs and ZBMs (for the initial situation)

#### **5.3** Experimental Methods

In order to investigate the sufficiency of bentonite amount to fill the voids, a series of experiments were done as explained below. The volumes of the voids and the present bentonite in the compacted test samples were calculated. The bentonite amount, which was needed to fill the voids was estimated. In order to estimate the needed amount of bentonite;

- i) Water contents of each component in mixtures were determined
- ii) Dry bentonite volume, which free swelled to fill a glass mold having a volume of 25 cm<sup>3</sup> was determined

### 5.3.1 Water Content Distribution to Components in the Mixtures

Kenney et al. 1992, proposed a model for determining the water content distribution in SBMs as mentioned in Chapter 2. Lately, researchers managed to adapt this model to ZBMs. However, there is confusion on the water content of each

component in ZBMs. The studies done for the determination of the water content of bentonite in a ZBM were analytical because, it is hard to determine the water contents of each material in a compacted mixture sample experimentally. In this study, instant water contents of bentonite before compaction in ZBM and SBM samples were experimentally determined.

Due to the fine size of sand and zeolite used in compaction and hydraulic conductivity tests, it is almost impossible to separate bentonite from the grains of sand or zeolite. So that, coarse sand and zeolite were needed to be used. However, the grain size might have influenced the water uptake of zeolite. Thus, firstly, the grain size effect on the water content of zeolite was investigated. The zeolite samples composed of different grain sizes (–No.200, No.20 – No.200, No.10 – No.40, 3/4" – 3/8", and block sample) (Figure 5.3) were kept under water for 24 hours and their water contents were determined. The water contents of these zeolites were determined to be very close to each other. Hence it is concluded that the grain size distribution had no influence, and water content distribution tests were conducted with the grain size having a uniform distribution between 3/4" and 3/8" (Figure 5.4). This grain size interval was selected depending on the allowable maximum grain size for compaction.

In order to determine the water content distribution, ZBMs and SBMs were prepared at various water contents and left for curing for 24h in a sealed plastic bag just the same as the compaction procedure. After 24 hours, the water contents of the mixtures and bentonite in each mixture were determined. Bentonite content in 10% ZBMs was so little that it was not possible to separate bentonite even from the coarse particles. Due to this reason, water content for each component was determined for 20% and 30% ZBM and SBM samples.



Figure 5.3 Zeolite samples at different grain sizes



Figure 5.4 Coarse a) zeolite and b) sand samples used in determining the water content distribution tests

# 5.3.2 Dry Volume and/or Weight of Bentonite Filling a Glass Mold of 25 cm<sup>3</sup>

In order to evaluate whether the swollen bentonite fills the intergranular voids or not; the required dry volume or dry weight of bentonite to fill all voids was determined with respect to its initial molding water content. For this purpose, bentonite samples at various water contents were prepared and left for curing inside a sealed plastic bag for 24h. After curing, these bentonite samples were used one by one to fill a small glass mold having a volume of 25 cm<sup>3</sup> (Figure 5.5). The transparent glass mold was useful for the prevention of the formation of undesired voids. Each sample was weighed and then left for drying in oven.



Figure 5.5 Glass mold having a volume of 25 cm<sup>3</sup>

In this way, the dry weights/volumes of bentonite with respect to different bentonite water contents needed to fill the 25 cm<sup>3</sup> glass mold were determined. Afterwards, the bentonite amounts present in 20% ZBMs and SBMs (which were also subjected to hydraulic conductivity tests) were compared with the calculated amount mentioned above whether they were sufficient enough to fill the intergranular void volumes of the grains in compacted mixtures at varying water contents or not.

#### 5.4 Results

# 5.4.1 Water Content Distribution to Components in ZBMs and SBMs

The water contents of bentonite in mixtures were determined by using coarse sized zeolite and sand grains. However, due to the small amount of bentonite in 10% ZBMs, practically it was not possible to collect it. The 20% and 30% ZBMs and

SBMs were used to determine the water content of bentonite in mixtures. It should be noted that the water contents given here are instant water contents corresponding to the initial condition before the compaction process.

The bentonite water contents  $(w_b)$  of 20% and 30% SBMs and ZBMs related to the mixture water contents  $(w_{mix})$  are plotted in Figure 5.6. It is obvious from Figure 5.6 that, at a given  $w_{mix}$  the  $w_b$  of ZBMs are lower than that of SBMs due to the water uptake of zeolite.

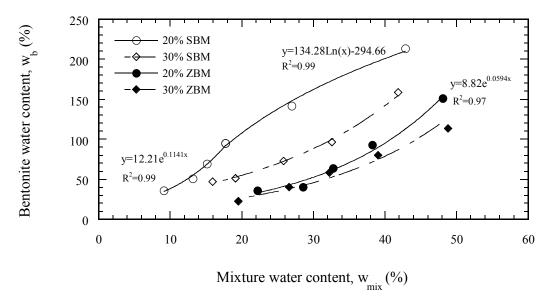


Figure 5.6 Bentonite water content of 20% and 30% zeolite-bentonite and sand-bentonite mixtures related to their mixture water contents

The relation of  $w_{mix}$  and  $w_b$  of 20% SBMs and ZBMs at their dry of optimum, optimum and wet of optimum water contents (classical  $\pm 4\%$  optimum water contents for dry and wet side of optimum water content) are plotted in Figure 5.7. When the compaction water contents of the mixtures are compared, both the  $w_{mix}$  and the  $w_b$  of ZBMs are higher than that of SBMs. However, this may be misleading when the results were not compared as relative to their optimum water contents, due to the difference between the compaction characteristics of SBMs and ZBMs. However, when the proportion of  $w_b$  to the  $w_{mix}$  is considered, it is seen that the  $w_b$  of ZBMs are lower than that of SBMs, when they are related to the  $w_{mix}$  (Table 5.2). The  $w_b$  /  $w_{mix}$  values of SBMs at their dry of optimum, optimum and wet of optimum

compaction water contents are 1.98, 1.90 and 1.67 times higher than that of ZBMs, respectively. This means that, the  $w_b$  of ZBMs does not increase as much as the  $w_{mix}$  of ZBMs, when compared to those of SBMs due to the water uptake of zeolite.

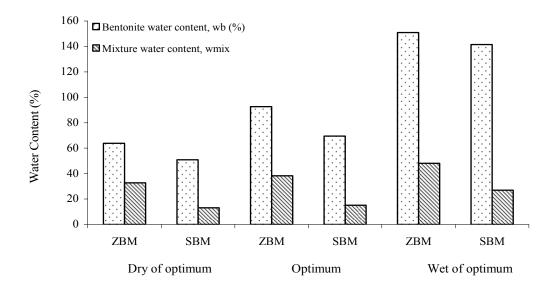


Figure 5.7 Bentonite water content and mixture water content of 20% zeolite-bentonite and sandbentonite mixture samples at their dry of optimum, optimum and wet of optimum compaction water contents

Table 5.2 Comparison of  $w_b$  related to the  $w_{mix}$  of 20% zeolite-bentonite and sand-bentonite mixtures at their dry of optimum, optimum, and wet of optimum compaction water contents

20% mixtures	Dry of optimum		Opti	mum	Wet of optimum	
	SBM	ZBM	SBM	ZBM	SBM	ZBM
$A = w_b / w_{mix}$	3.87	1.95	4.59	2.42	5.24	3.14
A <sub>SBM</sub> / A <sub>ZBM</sub>	1.98		1.90		1.67	

Kayabalı (1997) has calculated the  $w_b$  of ZBMs depending on the criteria proposed by Kenney et al. (1992), which assumes that bentonite would have all water in a binary mixture. However, in this study it is proposed that zeolite and bentonite would be in competition for water uptake. Thus, the  $w_b$  was determined experimentally and the results were found to be lower than those calculated values given in Kayabalı (1997) (Figure 5.8). In addition, according to Kayabalı (1997), the

water content of bentonite in ZBMs having a BC of lower than 13%, exceeds its liquid limit.

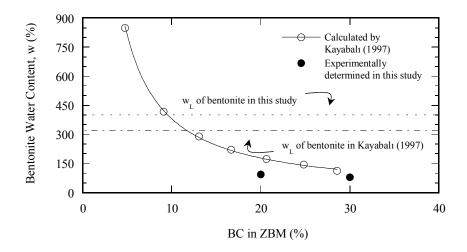


Figure 5.8 Bentonite water contents of various zeolite-bentonite mixtures at their optimum water contents calculated by Kayabalı (1997) and experimentally determined in this study

The difference between the compaction characteristics of SBMs and ZBMs were also compared by using normalized compaction water contents, as it was mentioned in Chapter 4. Similarly, the w<sub>b</sub> of SBMs and ZBMs are compared in Figure 5.9 with respect to the water content relative to the optimum compaction water contents of 20% SBM and ZBM. At -40% water content relative to its optimum compaction water content, w<sub>b</sub> of 20% SBM was slightly higher than w<sub>b</sub> of 20% ZBM. This slight difference decreases gradually and wb values of ZBMs and SBMs becomes equal while the mixture water content remains at its -20% water content relative to its optimum compaction water content. At the optimum water content, it is seen that w<sub>b</sub> of ZBM was higher than w<sub>b</sub> of SBM. While the compaction water increases, it is seen that w<sub>b</sub> of ZBM gradually increases more than w<sub>b</sub> of SBM. For instance, the w<sub>b</sub> of ZBM is 133%, where w<sub>b</sub> of SBM is 120% at 20% water content relative to optimum. Nevertheless, the w<sub>b</sub> of ZBM is 199%, where w<sub>b</sub> of SBM is 179% at 40% water content relative to optimum. The differences between the w<sub>b</sub> values of ZBM and SBM are 13% and 20% for 20% and 40% water content relative to optimum, respectively. In addition, zeolite water content (w<sub>z</sub>) was calculated and plotted in Figure 5.9. It is seen that zeolite water content increases slightly up to the optimum

water content, reaches a maximum value and then starts to decrease rapidly. It should be noted that the water content of zeolite for varying grain sizes was found to be 28% in average, after 24h soaking beneath water. The  $w_z$  of ZBMs are also found to be less than or approximately equal to 28%.

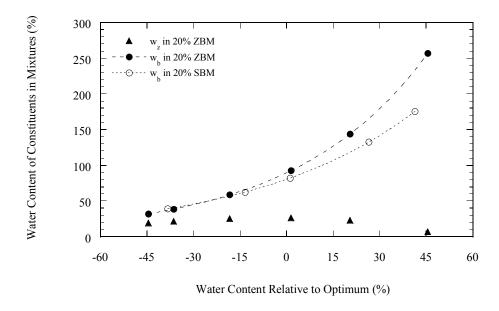


Figure 5.9 Water content of components in 20% zeolite-bentonite and sand-bentonite mixtures

As mentioned before, zeolite holds water in its structure physically, which can be explained by capillary forces, where bentonite constitutes electrical and chemical bonds with water. Thus, by inspection of the data given in Figure 5.9, it can be assumed that the bonds formed by bentonite exceed the capillary tensions in zeolite at higher water contents. It is probably because of that bentonite swelled enough to separate zeolite grains from each other and bentonite covered well each zeolite grain. When the bentonite confines the zeolite grains, the contact of the bentonite to the surface of zeolite grain maximizes which may cause the bentonite to absorb the water holded physically by suctions in zeolite grains. The findings of this study supports this imaginary argument, however, validation of this argument needs more intensive investigation including the suctions in zeolites, bentonite water uptake potential, suction characteristics of both zeolite and bentonite and comparison of these for varying water contents which are out of the scope of this study. However, the case will be strongly suggested as a future study. Because, the water content of zeolite may be responsible of high hydraulic conductivity values at dry of optimum water

contents where the grains also may be in contact to each other which may form a network of porous grains along with the preferential flow paths.

#### 5.4.2 Bentonite Void Ratio

In literature, the response of bentonite is mostly denoted by the bentonite void ratio (e<sub>b</sub>), which is usually defined as the ratio of the volume of water over the volume of dry bentonite. In chapter 2, such approaches for e<sub>b</sub> were mentioned. Some of the researches used the classical definition and some others defined more detailed equations. An instance, Cho et al. (2002) defined e<sub>b</sub> as the ratio of total void volume to the volume occupied by bentonite in mixture. However, Cho et al. (2002) reported relatively smaller e<sub>b</sub> values when compared to other researchs. Komine (2004) derived a swelling volumetric strain equation other than e<sub>b</sub> (Equation 2.1), whereas Sun et al. (2009) derived an e<sub>b</sub> equation regarding the bentonite content and the density of the mixture (Equation 2.2). However, it should be noted that, the equations derived for determining the e<sub>b</sub> give results more or less the same. In this study, the equation derived by Sun et al. (2009) was used and the findings were plotted in Figure 5.10.

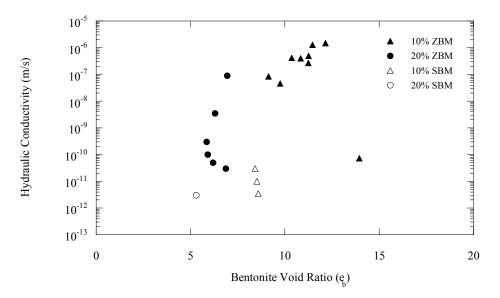


Figure 5.10 Hydraulic conductivities of 10% and 20% zeolite-bentonite and sand-bentonite mixtures related to their bentonite void ratios

The e<sub>b</sub> of SBMs were found to be in aggrement to the findings of Studds et al. (1998), which were given in Figure 5.2. In their analysis, the authors used one of the classical approaches, which was mentioned as the ratio of the volume of water over the volume of dry bentonite. The results were similar to the findings of this study even though the calculation methods were different. The e<sub>b</sub> of ZBMs were found to be higher than those of SBMs. Bentonite volume in ZBMs were found to be less than that of SBMs and, this is the reason that the e<sub>b</sub> of ZBMs were higher. For 20% ZBMs, they had e<sub>b</sub> values between 10% and 20% SBMs However, the former's hydraulic conductivity values were still higher than both 10% and 20% SBMs. In addition, Studds et al. (1998) found that the tightly package of 10% SBMs was effective on the hydraulic conductivity values even they had higher void ratio values. It also may be concluded that for both 10% and 20% SBMs were more tightly packed than 20% ZBMs which were resulted in lower hydraulic conductivities.

For comparison purposes, the corresponding water contents of bentonite for each  $e_b$  were calculated assuming that they were saturated and the results are plotted in Figure 5.11. Figure 5.11 shows that most  $w_b$  values of 10% ZBMs are around their liquid limit, moreover, even some of them exceeded it.

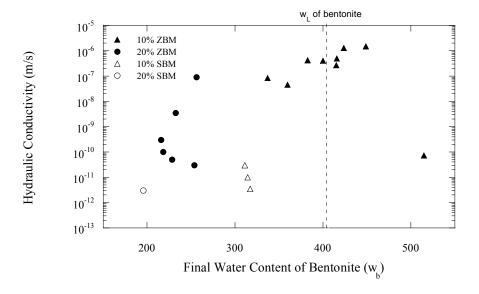


Figure 5.11 Hydraulic conductivities of 10% and 20% zeolite-bentonite and sand-bentonite mixtures related to their bentonite water contents

In the study of Nagaraj et al. (1990) the hydraulic conductivity values of different soils including brown soil, black cotton soil, SBM, and bentonite at their liquid limit state were tested and their hydraulic conductivities were found to be so close to each other having an average of  $2.3 \times 10^{-9}$  m/s even they had void ratios very far from each other. The hydraulic conductivity values of the soils at their liquid limit state were found to be almost the same, even though they had seven-fold variation in terms of void ratio. However, the hydraulic conductivity values of 10% ZBMs were found to be far from  $10^{-9}$  m/s, which is also the critical hydraulic conductivity required for a liner. This shows that, bentonite did not have the controlling of hydraulic conductivity for 10% ZBMs. If the bentonite had filled the voids in 10% ZBMs, then it would have the controlling of hydraulic conductivity and thus, hydraulic conductivities of 10% ZBMs would have approached to the values given in Nagaraj et al. (1990). This also shows that, actually swollen bentonite was not enough to fill the intergranular voids and the discontinuity of the bentonite caused such preferential flow paths when the ZBMs had a BC of 10%.

# 5.4.3 Assessment for Degree of Saturation to Bentonite in ZBMs and SBMs

Abichou et al. (2004) modeled SBMs in three different ways regarding the packing type to predict the hydraulic conductivity. The quantity of bentonite in the network is denoted by "bentonation" (B) which is the volume of swollen bentonite divided by the intergranular void volume, based on the microstructure visualizing techniques other than experimental or derivated methods. Bentonation values varied between 0 and 1. The authors concluded that, theoretically the hydraulic conductivity values slightly decreased when the B was less than 0.5. When B increased from 0.5 to 0.8, the hydraulic conductivity decreased in almost three orders of magnitudes. Moreover, when B was more than 0.8 the continuous path ways were found to be prevented. It should be noted that the study of Abichou et al. (2004) investigated the microstructure by using visualizing techniques, which gave the final situation of the swollen bentonite.

In this study, the degree of saturation to bentonite was defined and calculated based on the initial intergranular void volume. This definition preference was due to determine the sufficiency of bentonite at the beginning of the hydraulic conductivity tests. Because, most of the ZBM samples in this study had relatively higher hydraulic conductivities even from the early stages of the tests (Chapter 4). Consequently, in order to assess the degree of saturation to bentonite (S<sub>B</sub>) firstly, the dry weight and dry volume of bentonite which can fill a volume of 25 cm<sup>3</sup> at various water contents are determined and results are plotted in Figure 5.12.

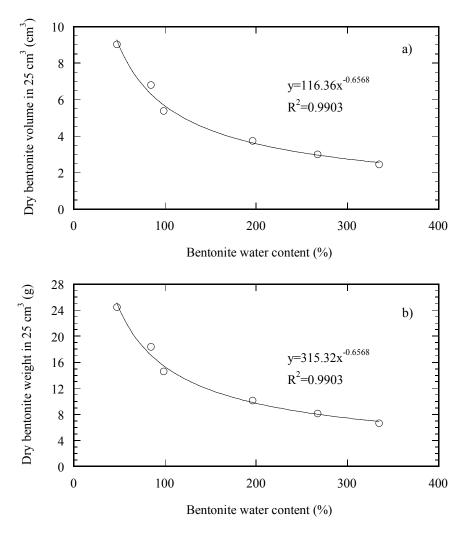


Figure 5.12 a) Dry bentonite volume which can fill a 25cm<sup>3</sup> volume at different water contents b) Dry bentonite weight which can fill a 25cm<sup>3</sup> volume at different water contents

The dry volume or weight measurement of bentonite for a volume of 25 cm<sup>3</sup> in varying water contents was used to evaluate degree of saturation to bentonite in binary mixtures. The water content of bentonite in a binary mixture can be calculated (Figure 5.6). Consequently, the dry volume or weight of bentonite at the calculated water content can be determined by using Figure 5.12. It should be noted that, this amount was calculated for 25 cm<sup>3</sup>. However, the concern is the intergranular void volume. Then, by proportioning 25 cm<sup>3</sup> and intergranular void volume, the needed bentonite amount can be found.

Due to the porous structure of zeolite grains a part of the total void volume in ZBMs belongs to the rigid structure of zeolite, which is named as intragranular voids ( $V_{v-intra}$ ). In order to determine the sufficiency of bentonite filling the intergranular voids of skeleton of zeolite grains, the volume of zeolite ( $V_{s-zeo} + V_{v-intra}$ ) should be subtracted from the total volume. The porosity of zeolite ( $n_{zeo}$ ) can be used to compute the  $V_{v-intra}$  ( $V_{v-intra} = n_{zeo} \times V_{s-zeo}$ ). The average porosity of zeolite blocks was found to be 0.40. Consequently, intragranular voids have been eliminated and the intergranular void volumes, which were to be filled by swollen bentonite have been determined. In SBMs, the void volume corresponds directly to the intergranular void volume. Finally, the needed amount of bentonite can be found by proportioning the amount previously determined for 25 cm<sup>3</sup> and this calculated volume.

A step-by-step explanation of the determination of the degree of saturation to bentonite of ZBMs and SBMs is given below. The calculations are presented in Table 5.3 and findings were plotted in Figure 5.13 for 20% ZBMs and SBMs.

- 1) Determination of bentonite water content in a binary mixture for a certain initial water content of the mixture from Figure 5.6.
- 2) Determination of dry bentonite weight from Figure 5.12 for 25cm<sup>3</sup> for the above water content.
- 3) Determination of void volume of dry zeolite ( $V_{s-zeo}$ ) and intragranular void volume of zeolite ( $V_{v-intra} = n \times V_{s-zeo}$ ).
- 4) Determination of intergranular void volume  $(V_{v-inter} = V_{initial} (V_{s-zeo} + V_{v-intra}))$ .

- 5) Determination of the needed dry bentonite weight for intergranular void volume.
- 6) Determination of present dry bentonite weight used in the mixture.
- 7) Determination of the degree of saturation to bentonite.

Table 5.3 The assessment of degree of saturation to bentonite in a) 20% zeolite-bentonite mixtures and b) 20% sand-bentonite mixtures

a)	20% ZBM					
W <sub>mix</sub> (%)	21.66	24.82	31.87	39.57	47	56.75
W <sub>B</sub> (%)	31.93	38.52	58.55	92.51	143.84	256.68
W <sub>b</sub> in 25cm <sup>3</sup> (g)	32.42	28.66	21.77	16.12	12.06	8.25
V <sub>total</sub> (cm <sup>3</sup> )	2022.39	1893.69	2059.16	2132.70	2132.70	2132.70
$V_{s-zeo}$ (cm <sup>3</sup> )	695.06	688.83	780.09	808.48	779.22	729.00
V <sub>v-intra</sub> (cm <sup>3</sup> )	278.03	275.53	312.03	323.39	311.69	291.60
V <sub>v-inter</sub> (cm <sup>3</sup> )	1049.30	929.33	967.04	1000.82	1041.79	1112.09
$W_{B-needed}(g)$	1396.39	1114.25	872.63	657.89	513.99	378.51
W <sub>B-present</sub> (g)	401.40	397.80	450.50	466.90	450.00	421.00
S <sub>B</sub> (%)	29	37	54	72	90	115

b)	20% SBM						
W <sub>mix</sub> (%)	10.18	14.29	16.70	20.90			
w <sub>B</sub> (%)	39.01	62.35	82.08	132.55			
W <sub>b</sub> in 25cm <sup>3</sup> (g)	28.42	20.89	17.44	12.73			
V <sub>total</sub> (cm <sup>3</sup> )	2132.70	2132.70	2132.70	2132.70			
V <sub>s-sand</sub> (cm <sup>3</sup> )	1033.10	1065.58	1074.43	1027.77			
V <sub>v-inter</sub> (cm <sup>3</sup> )	1099.60	1067.12	1058.27	1104.93			
W <sub>B-needed</sub> (g)	1250.17	891.62	738.12	562.56			
W <sub>B-present</sub> (g)	680.00	700.00	683.00	705.00			
S <sub>B</sub> (%)	54	79	93	125			

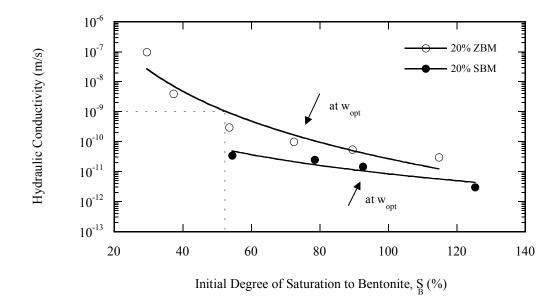


Figure 5.13 Hydraulic conductivity values of 20% zeolite-bentonite and sand-bentonite mixtures related to their initial degree of saturation to bentonite values

In the study of Abichou et al. (2004) hydraulic conductivity of SBMs were found to decrease in three orders of magnitude within a variation of 0.5 and 0.8 in B values (the volume of swollen bentonite divided by the intergranular void volume) depending on the photomicrographs. In addition, a B of 0.5 was also found to be satisfactory in terms of a hydraulic conductivity of a liner.

In this study, S<sub>B</sub> was experimentally found to be at least 53%, in order to reach the desired hydraulic conductivity for use of a liner for 20% ZBMs. All of the 20% SBMs were found to have higher S<sub>B</sub> values than this specified value of 53%. However, for 20% ZBMs, the samples at their dry of optimum water contents had lower S<sub>B</sub> values than 53% or at most equal to it. A rapid decrease in hydraulic conductivity was determined in mixtures having S<sub>B</sub> values between 30% and 53%. All of these mixtures belonge to 20% ZBMs. The S<sub>B</sub> value of 20% ZBM at its optimum water content was even less than the S<sub>B</sub> value of 20% SBM at its dry of optimum water content. It is clear that ZBMs contain less bentonite than SBMs. Moreover, the present bentonite in some 20% ZBMs, which are less than 53% S<sub>B</sub> was not enough to prevent the preferential flow paths and could not have the control of hydraulic conductivity.

The present bentonite in 20% SBMs was enough to fill the voids and prevented the formation of continuous pores. Thus, the variation of hydraulic conductivity in 20% SBMs was found to be very much less than that of 20% ZBMs due to the orientation of clay particles and not related to the bentonite amount. This finding also supports the findings of Haug & Wong (1992) and Kenney et al. (1992). However, the hydraulic conductivity values of 20% ZBMs varied almost three orders of magnitude for S<sub>B</sub> values lower than 53%, due to the lack of bentonite amount. In addition, hydraulic conductivity of 20% ZBM samples having S<sub>B</sub> values higher than 53% varied similar to 20% SBMs. This can again be explained by the orientation of clay particles.

The insufficiency of bentonite amount in ZBMs is critical, when studying with ZBM as a liner. The final bentonite void ratio and initial S<sub>B</sub> in ZBMs and SBMs were calculated and seen that at the beginning of the hydraulic conductivity test the bentonite in 10% ZBMs and the 20% ZBMs at its dry of optimum water content were not enough to prevent the preferential flow paths. When at least one flow path occurs then the hydraulic conductivity tests are quitted due to the high hydraulic conductivity values. The present bentonite would not work and have the controlling of hydraulic conductivity even it tends to swell because of that the test will be ended (1 to 4 hours) before bentonite has time to swell.

This study showed that ZBMs have completely different behavior in terms of hydraulic conductivity when compared to that of SBMs. The bentonite contents previously determined for SBMs cannot be suggested for ZBMs as well. In this study, it has been clearly shown that 10% ZBMs were not satisfactory for use of a liner. Even, the 20% ZBM samples at their dry of optimum compaction water contents were also not recommended for use of a liner.

#### **CHAPTER SIX**

#### MODELING OF ZBMS AND SBMS USING FINITE ELEMENT METHOD

There are limited modeling studies investigating the hydraulic conductivity of binary mixtures in the literature. Most of these studies are related to the modeling of the hydraulic conductivity of SBMs. However, it is believed that hydraulic conductivity of bentonitic mixtures, including both non-porous and porous granules, such as SBMs and ZBMs, has not been modeled so far.

In this chapter, it is aimed to make an assessment of ranges of the saturated hydraulic conductivity values of different types of bentonitic mixtures using finite element method (FEM). The hydraulic conductivity of a barrier material is determined from laboratory tests before application. However, these tests are time consuming which may last from several months to years, depending on the value of hydraulic conductivity. Thus, in addition to laboratory investigations, the hydraulic conductivity needs to be modeled as well. The modeling can help:

- i. Rapid assessment of the most suitable barrier material before laboratory tests,
- ii. Prediction of the long term hydraulic conductivity behavior of the selected material.
- iii. Determination of the parametric sensitivity of hydraulic conductivity.

Laboratory test results present in the literature and obtained in this study revealed that ZBMs have higher hydraulic conductivity values than SBMs. This finding is tied to two possible reasons: 1) water content distribution of components in the mixtures 2) water movement through zeolite grains. Water transition through the zeolite grains covers the content of this chapter. Hydraulic conductivity behavior is modeled with Plaxflow Version 1.5, a modeling software using FEM, and the results are compared with the laboratory hydraulic conductivity test results.

For comparison purposes with the test results, two different mixtures are modeled which represent SBMs and ZBMs. Sand grains are represented as impervious grains with zero hydraulic conductivity. In contrast, zeolite grains are represented with pervious particles. A range of hydraulic conductivity values are selected to study how the pervious grains affect the hydraulic conductivity of the mixture. The grain shape effect on hydraulic conductivity of binary mixtures was also investigated. Afterwards, the specific hydraulic conductivity value obtained from laboratory tests is selected to represent the zeolite grains in this modeling study. Finally, comparison of the laboratory and modeling results for SBMs and ZBMs are made and presented.

# **6.1** Background: Modeling of Binary Mixtures

The hydraulic conductivity of compacted clays is generally predicted by statistical models. There are numerous studies that estimate the hydraulic conductivity from correlation analysis which use basic soil index parameters (i.e. consistency limits, activity, clay content) as the independent variables (Benson et al., 1994; Benson & Trast, 1995). In contrast, modeling the hydraulic conductivity of SBMs is rather complex. This is because the amount of bentonite is relatively less than the amount of sand in the SBMs. Therefore, the hydraulic conductivity may be high or low depending on the bentonite content. In the case of low bentonite content, the hydrated bentonite particles are not evenly distributed within the pores, resulting preferential flow path along the inter-granular pores. On the other hand, bentonite starts to govern the hydraulic conductivity when BC is high enough in the mixture. In this case, the inter-granular pores are blocked by bentonite particles and sand grains are started to dislocate from each other. Hence, the flow occurs between small pores of bentonite particles. Based on above explanation, it is clear that the pore network of the mixture is strongly dependent on bentonite property which directly influences the porosity and void ratio of SBMs. Thus, most of the studies reported in the literature consider these two parameters while modeling the hydraulic conductivity of SBMs (Chapuis, 1990; Kenney et al., 1992; Mollins et al., 1996; Sivapullaiah et al., 2000).

Chapuis (1990) reports hydraulic conductivity test results for 45 SBMs, having various bentonite contents. The obtained hydraulic conductivity is poorly correlated to porosity alone. However, his predictive model suggests a good relationship between hydraulic conductivity and "efficient porosity" of the mixture, where pore space is available for fast-moving water between bentonite particles.

Kenney et al. (1992) investigated hydraulic conductivity characteristics of SBMs in terms of void ratio. In their model, it is assumed that all water is associated with bentonite particles; sand is dry and act as impervious matrix in the mixture; and the fabric of bentonite is unaffected from sand grains. They stated that the hydraulic conductivity of SBMs is a function of bentonite void ratio and thus, bentonite hydraulic conductivity.

Sivapullaiah et al. (2000) performed hydraulic conductivity tests on bentonite and SBMs. They applied regression analysis to the obtained results. Based on regression analysis, high correlation was obtained when the hydraulic conductivity is predicted from void ratio and liquid limit of the mixture.

Abichou et al. (2004) suggested three pore network models; namely grain coating model (GCM), tube blocking model (TBM) and junction blocking model (JBM), to interpret the laboratory hydraulic conductivity results of SBMs. In the case of GCM, the pore tube diameters decrease as the thickness of the bentonite coating on the sand grains increases, resulting decrease in the hydraulic conductivity. They report similar trends for TBM and JBM. However, Abichou et al. states that the favorable comparisons with respect to hydraulic conductivity are obtained with GCM and JBM.

#### **6.2** FEM Modeling of Binary Mixtures

Plaxflow Version 1.5 was used while computing the modeled binary mixtures. Plaxis is a range of finite element programs which are used worldwide for geotechnical engineering and design. Plaxflow is one of the Plaxis products and is a

package intended for two-dimensional transient and steady-state analysis of saturated and unsaturated groundwater flow problems in geotechnical engineering and hydrology. Plaxflow 1.5 is the stand-alone version of this groundwater flow program including steady state flow, transient flow, unsaturated behavior and time-dependent boundary conditions. It allows for automatic generation of unstructured 2D finite element meshes composed of 3-node triangular elements with options for global and local mesh refinement. For compatibility with the Plaxis deformation program, 6-node and 15-node elements can also be chosen. Mesh coarseness can be selected as "very coarse, coarse, medium, fine and very fine". Boundary heads can also have "user-defined" values (Manuals of Plaxflow). Plaxflow is equipped with features to deal with various aspects of complex geotechnical flow problems such as the simulation of the unsaturated, time-dependent and anisotropic behavior of soils.

# **6.3** Designation of Binary Mixtures

The binary soil mixture has two components: the coarse grains and the fine particles. Coarse grains indicate either non-porous granule such as sand or porous granule such as zeolite, whereas fine particles denote only clays, especially bentonites. Coarse grains (C) and fine-matrix (F) mixture (M) will be denoted by CFM corresponding to the universal representation of SBM (sand-bentonite mixture) and ZBM (zeolite-bentonite mixture). The mixture percentage in binary mixtures is generally interpreted in terms of weight ratio. However, in Plaxflow, the mixture percentage can only be defined in terms of area ratio. Therefore, the area ratio, expressed as the ratio of fine-matrix area to the total sample area, is converted to the weight ratio by multiplying the unit width and the respective unit weights of materials. The value given by CFM indicates the fine matrix percentage in mixture. For example, 20% CFM means that 20% of the mixture by weight is fine matrix.

To begin with Plaxflow, the model geometry should be defined first and then binary mixture components should be symbolized. Since permeameters used in hydraulic conductivity tests, have nearly 1:1 dimension on account of 10.16 cm

diameter and 11.64 cm height, the aspect ratio (i.e. the length of vertical axis to the horizontal axis) of the model was set unity to get a symmetric geometry.

The analysis were run for two different configurations of coarse grains. In the first configuration, "grains which are not in contact" case was first considered and analyzed. This represents the case where coarse grains are dislocated from each other, because of high fine-matrix content (FC). For this purpose, all coarse grains were surrounded by fine matrix in the model (Figure 6.5). Fine-matrix is located only in the intergranular void spaces of mixture. In the next configuration, the case of "grains which are in contact" was held and analyzed. This case considers the condition of low FC in the mixture. Note that the inter-granular void spaces are filled with fine matrix and there are no air spaces between the grains.

The Plaxflow analysis was initially run for the case of "grains which are not in contact" model (Figure 6.1). In order to investigate the influence of the grain shape in a binary mixture, regular and/or irregular shapes were drawn inside the model geometry, simulating the coarse grains embedded in fine matrix in a binary mixture (Figure 6.1). The coarse grains were initially represented by regular and irregular elements as shown in Figures 6.1a-d and Figure 6.1e, respectively.

The obtained hydraulic conductivity had to be controlled by hand calculation. To this end, a simple geometry was defined using single grain but the same FC as in Figure 6.1a (Figure 6.1f). The analysis was run on Figure 6.1f again and the hydraulic conductivities of both representations were compared. The results showed that the hydraulic conductivities computed from Figure 6.1a and Figure 6.1f were the same. Thus, hand-calculation was made on Figure 6.1f on account of its simplicity.

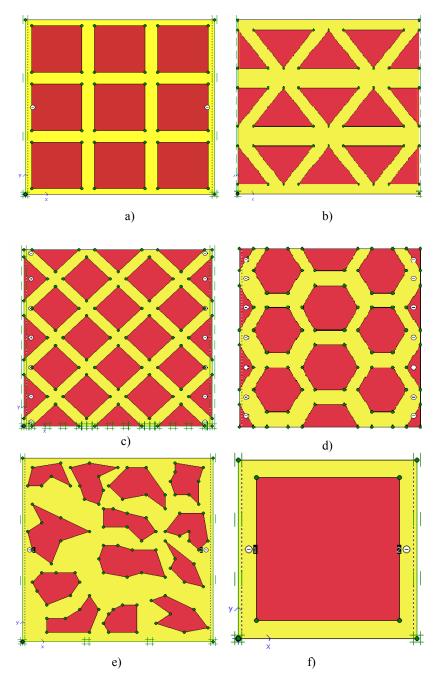


Figure 6.1 Representation of coarse grains by regular shapes a) square, b) triangle, c) diamond, d) hexagon, e) irregular, f) representative unit model of square grains

The grains can also be in contact with each other. For this case, the contacted grains form a network along the cross section. Since contacted grains have higher hydraulic conductivity than that of fine-matrix, then the preferential flow paths occur through the granule network. In this case, the flow path through granules can either be single or multiple as shown with arrows in Figure 6.2. The upper limit of this

network configuration can be modeled with a tube of coarse grain embedded in less conductive fine matrix at various FCs (Figure 6.3). Note that thin and thick tubes were drawn at the minimum and maximum allowable limits of grid spacing that was defined by user before, respectively. The analysis were run for different FCs by changing the tube width. This will lead the upper boundary for the hydraulic conductivity of binary mixtures.

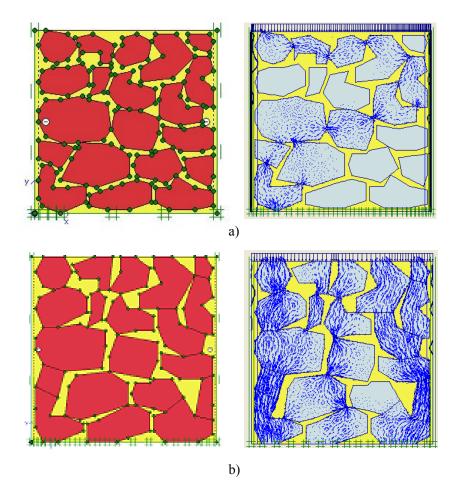


Figure 6.2 Two examples for the case of "grains which are in contact": visualization of a) single flow path and b) multiple flow paths, in analysis

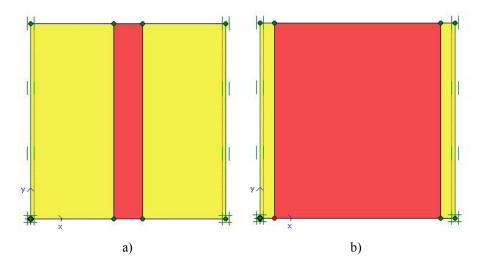


Figure 6.3 Representation of connected coarse grains with: a) Thin (high fine content) and b) thick (low fine content) tubes. Note that dark and light regions in the models represent coarse grains and fine matrix, respectively

When the binary mixture has low BCs (i.e. lower than 8%), it is probable that voids may occur due to the insufficient swelling of bentonite. These voids would result in preferential flow paths which would cause higher hydraulic conductivities. In order to simulate this condition, a very thin column was defined as a preferential flow path in the model (Figure 6.4) and the mixtures were run in Plaxflow. The model presented in Figure 6.4 had a BC and flow path percentages of 6.5% and 3.5%, respectively. Coarse grain percentage of the model was 90%.

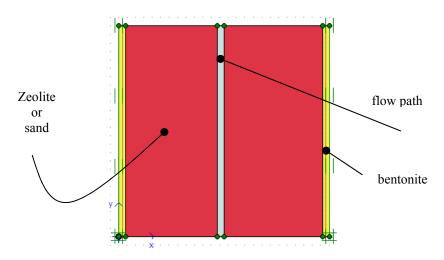


Figure 6.4 Representation of binary mixture with a preferential flow path

In a hydraulic conductivity test, the preferential flow rate is limited by the hydraulic conductivity of porous stones used at the up and bottom of the test specimen. In this study instead of porous stones, geotextile was used. The hydraulic conductivity of geotextiles is reported to be in a range of  $2x10^{-3}$  and  $10^{-5}$  m/s. Thus, it is reasonable to use the average of these reported results ( $10^{-4}$  m/s) to represent the preferential flow in the model.

## 6.4 Analysis Steps

The numerical analysis solution was initiated by assigning the material properties to coarse grains and fine matrix. Note that, all analysis were run for the case of saturated condition. Finally, mesh generation was made before running the finite element analysis.

The flow direction in the hydraulic conductivity tests are usually selected from bottom towards up, in order to squeeze entrapped air out of the specimen. Thus, upward flow was generated in the analysis by assigning different heads to the top and bottom boundaries. The flow is selected to be upwards based on the criteria that the laboratory flow is also applied upwards, due to avoiding trapped air formations in the specimen. The boundary heads were attained by using "user defined head" option. The water table was defined for both upper and lower boundaries. The left and right sides are defined to be impervious by using "closed head boundary" option, in order not to let water out of the specimen laterally (Figure 6.5).

Plaxflow calculates the flow rate (total discharge in m³/day/m-for the unit width) instead of hydraulic conductivity. Thus, the hydraulic conductivity was obtained by dividing the flow rate by the cross-section area and hydraulic gradient as in the following equation;

$$k = \frac{q}{i \cdot A} \tag{6.1}$$

Where,

q = flow rate

i = the hydraulic gradient of the system

A = the cross-section area of the model geometry.

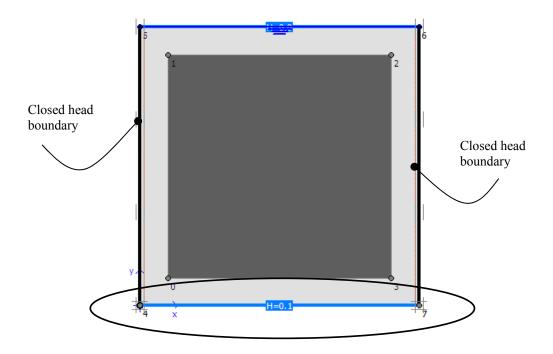
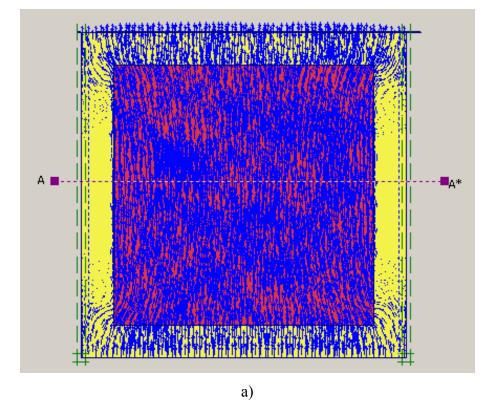
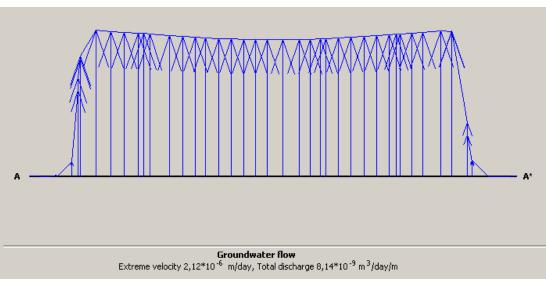


Figure 6.5 Head definition to the model boundaries

The output may be obtained in different ways. In this study, the focus is on obtaining the hydraulic conductivity. Thus, the "total discharge" of the model is needed as hydraulic conductivity can be calculated by using the total discharge. The "total discharge" is obtained via using the "cross section" option (Figure 6.6a) when the output file is viewed as "flow field". Finally the total discharge given for the related cross section has been calculated by the computer program (Figure 6.6b).





b)
Figure 6.6 a) Upwards flow and placement of section A-A' b) Total discharge at section A-A'

# 6.5 Verification Calculation

For a verification calculation, an analytical solution was done on the model as seen in Figure 6.1f. The hand calculation was considered for isotropic and horizontally stratified soil layers (Figure 6.7). The thicknesses of these layers are H<sub>1</sub>

and  $H_2$  and the respective hydraulic conductivities are  $k_1$  and  $k_2$ . Based on the horizontal and vertical direction of flow (Figure 6.7a-b), the equivalent hydraulic conductivities can be formulated as follows (Craig, 2004):

$$k_{x} = \frac{H_{1}.k_{1} + H_{2}.k_{2}}{H_{1} + H_{2}} \tag{6.2}$$

$$k_z = \frac{H_1 + H_2}{\left(\frac{H_1}{k_1} + \frac{H_2}{k_2}\right)} \tag{6.3}$$

Where; x and z denotes the horizontal and vertical axes, respectively.

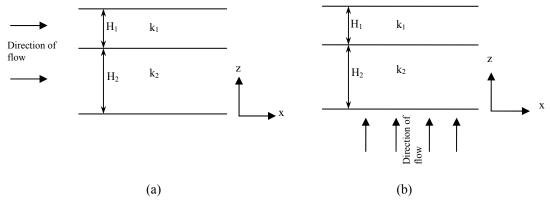


Figure 6.7 Direction of flow on horizontally stratified soil layer: a) horizontal flow and b) vertical flow

In a similar manner, the hydraulic conductivity of the binary mixture can be computed using Equations (6.2) and (6.3). Figure 6.8a schematically represents the coarse grain-fine matrix mixture at any FC. The upward flow direction is shown on Figure 6.8 as well. The dashed lines given in Figure 6.8b divide the mixture into different portions as PI, PII, and PIII. PI and PIII are composed of one single layer (i.e. fine matrix). However, there are three layers in PII which resembles the horizontal soil layers given in Figure 6.7. Hence, the equivalent hydraulic conductivity in PII can be calculated similar to Equation (6.3):

$$k_{FC,eq} = \frac{H_1 + H_2 + H_1}{\frac{H_1}{k_E} + \frac{H_2}{k_C} + \frac{H_1}{k_E}} = \frac{2H_1 + H_2}{\frac{2H_1}{k_E} + \frac{H_2}{k_C}}$$
(6.4)

Where,  $k_{FC,eq}$  is the equivalent hydraulic conductivity,  $k_F$  and  $k_C$  are the hydraulic conductivities of fine matrix and coarse grains, respectively;  $H_1$  and  $H_2$  are the layer thicknesses of fine matrix and coarse grain, respectively.

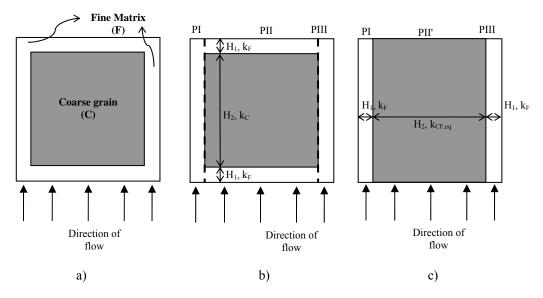


Figure 6.8 Schematic representation of the calculation of equivalent hydraulic conductivity: a) binary mixture soil model (initial condition), b) dividing the mixture along the coarse grain edges to obtain layers, c) final condition of binary mixture

Now, PII turned to a single layer which is shown as PII' in Figure 6.8c. Then, the equivalent hydraulic conductivity for the binary mixtures can be calculated using Equation (6.2):

$$k_{z,eq} = \frac{H_1 k_F + H_2 k_{CF,eq} + H_1 k_F}{H_1 + H_2 + H_1} = \frac{2H_1 k_F + H_2 k_{CF,eq}}{2H_1 + H_2}$$
(6.5)

Where,  $k_{z,eq}$  is the equivalent hydraulic conductivity of binary mixture.

The verification calculation was not only made on Figure 6.8, but also made at various FCs. The obtained results from hand calculation showed that Plaxflow analysis successfully estimates the hydraulic conductivity of binary mixture. Since the results of the analysis and hand calculation converged for square coarse grain model, then the Plaxflow analysis were confidently applied on regular and irregular shapes of coarse grains and configurations of mixture.

## 6.6 FEM Analysis

# 6.6.1 Grain Shape Effect

The Plaxflow analysis were run for each shape of coarse grains and at various FCs. The analysis results are depicted in Figure 6.9 as a function of FC. The lowest hydraulic conductivity values were obtained when coarse grains had triangular shape. However, the hydraulic conductivities of all mixtures slightly differed from each other and are independent of the shape of coarse grains. Figure 6.9 also shows a slight decrease in the hydraulic conductivity as the FC is increased, indicating that the fine matrix controls the hydraulic conductivity behavior of the mixture.

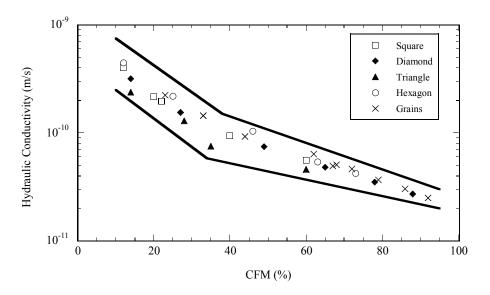


Figure 6.9 Change in hydraulic conductivity of mixtures depending on the shape of coarse grains as a function of fine content

### 6.6.2 CFM with Porous Grain

The effect of porous grains to the hydraulic conductivity of the mixture is the main question of this study. For this purpose, a range of hydraulic conductivity values were given to the elements to notice its impact on the binary mixture's hydraulic conductivity. The model was the square grains embedded in fine matrix. Three FCs were used, they were 41%, 22% and 12%.

Two approximations were considered, one was changing the hydraulic conductivity of coarse soil, while the fine matrix's stayed constant and the other was the opposite. The mixture hydraulic conductivity  $(k_{MIX})$  was determined related to the changes of fine matrix hydraulic conductivity  $(k_F)$  and coarse grain hydraulic conductivity  $(k_C)$ . The effect of  $k_F$  and  $k_C$  on  $k_{MIX}$  was plotted in Figure 6.10. Figure 6.10 presents the variation of mixture hydraulic conductivity related to fine matrix hydraulic conductivity  $(k_{MIX}/k_F)$  and the variation of mixture hydraulic conductivity related to coarse grains hydraulic conductivity  $(k_{MIX}/k_C)$  as a function of  $k_C/k_F$ .

It is seen from Figure 6.10 that,  $k_C/k_F$  varied in a very large interval such as  $10^{-5}$  and  $10^{5}$ . The plotted results indicate that  $k_{MIX}/k_C$  decreased from  $10^{4}$  to  $10^{-4}$  while  $k_C/k_F$  increased from  $10^{-5}$  to  $10^{5}$ . In other words, while the  $k_C/k_F$  increased, there are at most four magnitudes of difference between  $k_{MIX}$  and  $k_C$  values. This finding shows that,  $k_{MIX}$  had values far from  $k_C$  had, which also shows that coarse grains did not have the control of the hydraulic conductivity behavior. However, while the  $k_C/k_F$  increased from  $10^{-5}$  to  $10^{5}$ , there is at most 20 times difference between  $k_{MIX}$  and  $k_F$  values which shows that  $k_{MIX}$  had close values to  $k_F$ . Based on Figure 6.10 it can be said that fine matrix have the control of the hydraulic conductivity behavior of a binary mixture and the coarse grains embedded in the fine matrix can be said to increase the hydraulic conductivity of a binary mixture at most 20 times. It should be noted that the grains do not contact each other in this model.

An another presentation is given in Figure 6.11 which shows  $k_{MIX}/k_F$  as a function of CFM (%) having different  $k_C/k_F$  values. It is seen from Figure 6.11 that while the

fine matrix percentage decreased the  $k_{MIX}/k_F$  in other words  $k_{MIX}$  increased. Besides,  $k_{MIX}/k_F$  also increased while  $k_C/k_F$  increased. However, this increase gradually decreased while  $k_C/k_F$  increased and stabilized when  $k_C/k_F$  was over 1000. Depending on the modeling results; it can be said that, when  $k_C/k_F$  exceeds three orders of magnitude, the overall hydraulic conductivity value held constant. Besides,  $k_{MIX}$  became stable around 5, 10 and 20 times of  $k_F$  for CFMs of 41, 22 and 12% respectively.

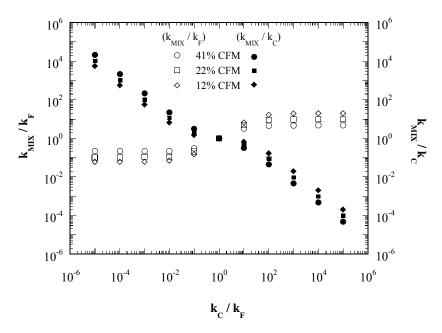


Figure 6.10 Variation of  $k_{MIX}/k_F$  and the  $k_{MIX}/k_C$  as a function of  $k_C/k_F$  at three different fine contents (41, 22 and 12%)

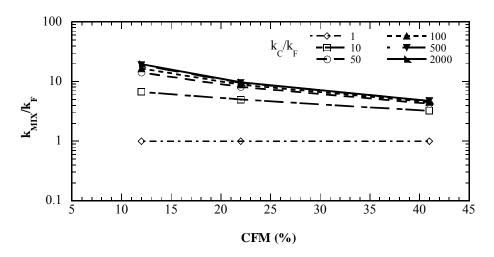


Figure 6.11 Variation of  $k_{MIX}/k_F$  as a function of fine content for different  $k_C/k_F$  values

## 6.6.3 CFM with Porous Grain Simulating ZBMs

The hydraulic conductivity of the zeolite blocks was found to be  $1.31 \times 10^{-9}$  m/s in average, as mentioned in Chapter 4. Similarly Ören (2011) performed hydraulic conductivity tests on zeolite blocks, having various thicknesses. He showed an increasing trend with decreasing thickness of zeolite block and reports  $10^{-9}$  m/s hydraulic conductivity for the specimen having 1 cm thickness. Therefore, the saturated hydraulic conductivity of porous granules was attained  $1 \times 10^{-9}$  m/s when analysis was conducted on ZBMs simulating porous grains-bentonite mixtures. The saturated hydraulic conductivity of fine-matrix is selected as  $2 \times 10^{-11}$  m/s, which is typical hydraulic conductivity of Na-bentonite (Chapuis, 1990; Kenney et al., 1992; Sivapullaiah et al., 2000). Finally, mesh generation was made before running the finite element analysis.

### 6.6.4 CFM with Non-Porous Grain Simulating SBMs

The same model geometries were used as previously formed for CFM with porous grains. Non-porous grains are selected to be simulating sand grains. In contrast to zeolite, hydraulic conductivity value was attained as "0" (zero) to sand. The analysis were run initially for "grains which are not in contact" case. The analysis results showed that there are three orders of magnitude less hydraulic conductivity with respect to CFM with porous grain obtained at low FCs, when non-porous coarse grain was used in the mixture. The hydraulic conductivity difference for CFM constituted both porous and non-porous grains converge at 100% FC. All results for both porous and non-porous mixtures are presented in Figure 6.12.

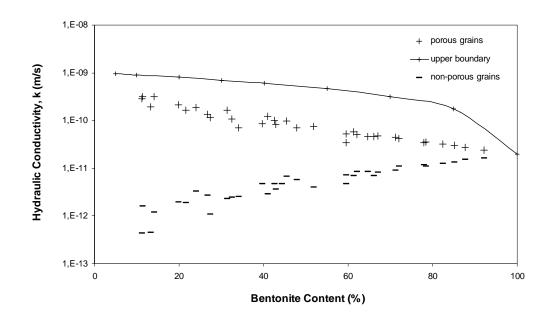


Figure 6.12 Modeling results of porous and non-porous grains in binary mixtures

## 6.6.5 CFM with Voids Simulating Preferential Flow Paths

In literature, BCs more than 10% were considered as not likely to have preferential flow paths for SBMs (Cho et al., 2002; Yong et al., 1986). However, from the SEM photomicrographs of SBMs Abichou et al. (2002) showed that even 10% SBMs had voids. In addition, from several hydraulic conductivity tests, it is seen that BC of SBMs lower than 8% had relatively higher hydraulic conductivities showing that there were certain preferential flow paths (Kenney et al., 1992; Abichou et al., 2002). However the findings of this study showed that 10% ZBMs had preferential flow paths. Moreover, it is also shown that the volumetric BC of ZBMs and SBMs are not the same even though the BC by weight of them was the same. Thus, the 8% and 10% SBM equivalents of ZBM, BC by weight should be determined considering the volumetric equality. Consequently, depending on the literature results, 9% and 12% BCs were calculated as ZBM BCs by weight corresponding to 8% and 10% BCs for SBMs. In other words, to have the same volumetric BCs with the 8% and 10% SBMs, the ZBMs should have 9% and 12% values respectively. Thus, between 9% and 12% BCs, there should be a transition between the model results having flow paths and upper limit for ZBMs which was defined above.

### 6.7 Results & Conclusions

The hydraulic conductivity results of this study (including data between -20% and 40% water content related to optimum compaction water content) and the data reported in the literature (including data reported as optimum and wet of optimum compaction water contents) for ZBMs are plotted as a function of BC in Figure 6.13 were compared with modeling results. Similarly SBMs are plotted in Figure 6.14. Finally both results of ZBMs and SBMs are combined in Figure 6.15. As seen in Figure 6.15, literature data clearly fits into the modeling results.

Laboratory data fits very well to the model supporting the findings of Chapter 4 & 5. The ZBM data are in harmony with the assumption of that porous zeolite grains formed a network, when they were in contact to each other. On the other hand, some of the laboratory data of 10% ZBMs fall into the model boundary, which had preferential flows. In Chapter 5 it is also concluded that bentonite amount in 10% ZBMs were insufficient regarding the bentonite void ratio and final bentonite water content. ZBMs were found to have at least 12% BC by weight in order to have the same volumetric BC with 10% SBMs, which were found to be sufficient enough to be a liner. ZBMs having 10% BC cannot be used as a liner. In addition, ZBM samples at their dry of optimums were found to have hydraulic conductivities higher than that of required for a liner unlike SBM samples even they had BCs by weight as much as 20%. Inspection of the findings mentioned in Chapter 4, 5 & 6 ZBMs were found to have higher hydraulic conductivities than SBMs even they had the same BC by weight due to influence of the porous structure of zeolite, water content distribution to the constituents and insufficient bentonite amount.

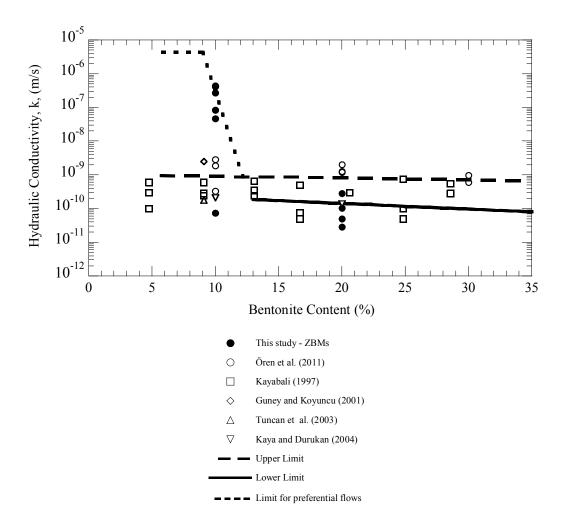


Figure 6.13 Hydraulic conductivity test results of this study and test data present in the literature fitted in modeling results for porous grains

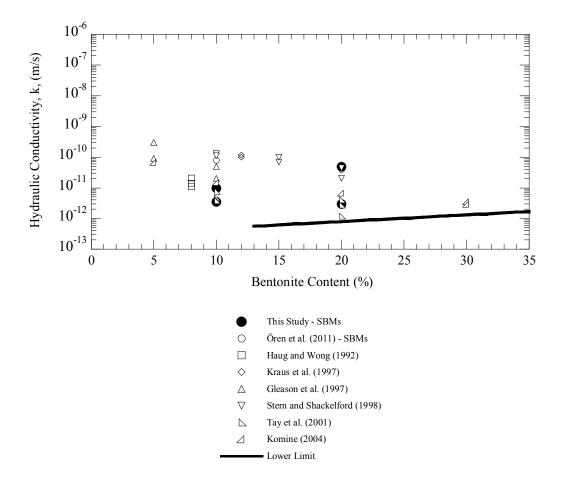


Figure 6.14 Hydraulic conductivity test results of this study and test data present in the literature fitted in modeling results for non-porous grains

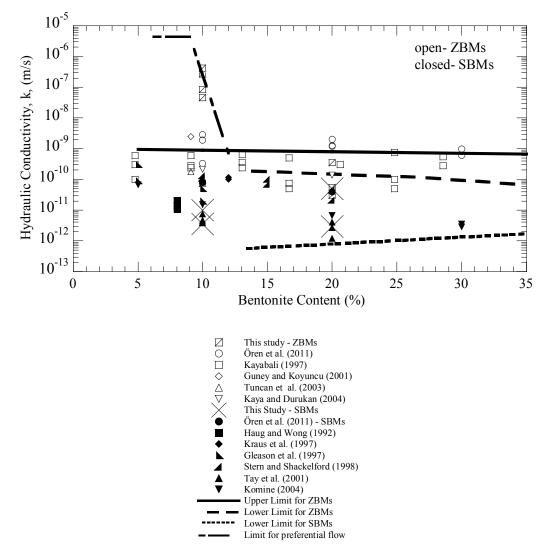


Figure 6.15 Hydraulic conductivity test results of this study and in the literature fitted in modeling results for both porous and non-porous grains

# CHAPTER SEVEN CONCLUSIONS AND RECOMMENDATIONS

#### 7.1 Conclusions

An experimental and modeling study had been conducted on understanding the mechanisms controlling the hydraulic conductivity of ZBMs in comparison to SBMs. The basic geotechnical characteristics of the materials, compaction characteristics and hydraulic conductivities of the mixtures were determined. In addition to conventional tests done, water content distribution of each element in the mixtures were experimentally determined and swollen bentonite amount to fill the voids were investigated. The modeling study investigated the zeolite in ZBMs and sand in SBMs as porous and non-porous grains respectively. Based on the obtained results in this study, the conclusions are drawn as the following;

# 7.1.1 Compaction Characteristics

The optimum water content of ZBMs is almost 2.5 times higher than that of SBMs and the maximum dry density of SBMs is almost 1.5 times higher than that of ZBMs for both 10% and 20% mixtures.

The difference between the compaction characteristics is due to the low specific gravity, porous structure and high water uptake potential of zeolite when compared to sand.

ZBMs and SBMs data were evaluated together and a linear relationship between  $\rho_{dry-max}$  and  $w_{opt}$  has been found.

The compaction densities of ZBMs were still less than those of SBMs, even influence of specific gravity is eliminated by normalizing with a specific gravity value of 2.65 in order to allow a better comparison.

# 7.1.2 Hydraulic Conductivity Tests

The hydraulic conductivity of zeolite blocks was found to be 1.31x10<sup>-9</sup> m/s in average.

The hydraulic conductivity behavior of ZBMs was totally different from the hydraulic conductivities of SBMs.

The influence of compaction water content on the hydraulic conductivity of bentonitic mixtures is mostly pronounced on ZBMs. In contrast, the compaction water content had no significant influence on the hydraulic conductivity of SBMs.

The hydraulic conductivity of 10% ZBM has decreased by about 20 times, when water content relative to optimum has increased from -40% to 20% water content relative to optimum.

The hydraulic conductivity of 20% ZBMs has reduced by about 3500 times, when water content relative to optimum has increased from -40% to 40% water content relative to optimum.

The hydraulic conductivity of 10% SBMs and 20% SBMs decreased about 7.5 times and 5 times, respectively, along the water content increment.

The hydraulic conductivity of SBMs was less in value than those of ZBMs independent of bentonite content. The differences in the hydraulic conductivities were greater, when the compaction water contents are on the dry side of the optimum. On the wet side of the optimum, however, the hydraulic conductivities of SBMs are one order of magnitude less than the hydraulic conductivities of ZBMs.

Two possible mechanisms were proposed to explain these differences in the hydraulic conductivities. One of them is the possible water content distribution differences in SBMs and ZBMs. The other one is the water transition through the porous zeolite grains.

## 7.1.3 Water Content Distribution to Components in Binary Mixtures

The volumetric BCs of SBMs and ZBMs differed, even though they had the same BC by weight, due to the specific gravity differences between sand and zeolite grains. It's found that the volume of bentonite in ZBMs was remarkably lower than that of SBMs at the same BC by weight.

Water content in ZBMs was determined experimentally and the results were found to be lower than those calculated values given in Kayabalı (1997).

At -45% water content related to its optimum compaction water content,  $w_b$  of 20% SBM was slightly higher than  $w_b$  of 20% ZBM. The difference decreases gradually and  $w_b$  values of ZBMs and SBMs becomes equal, while the mixture water content remains to its -20% water content related to its optimum compaction water content. While the compaction water increases, it's seen that  $w_b$  of ZBM gradually increases more than  $w_b$  of SBM.

Zeolite grains were found to have appreciable water content in ZBMs. It's seen that zeolite water content increases slightly upto the optimum water contents to reach a maximum and then starts to decrease rapidly. The saturated water content limit for water uptake of zeolite was determined to be 28%.

The decrease in water content of zeolites in ZBMs at relatively higher mixture water contents was related to the competition between capillary tensions in zeolite and electrical and chemical bonds of bentonite.

# 7.1.4 Degree of Saturation to Bentonite

The BC per total volume in SBMs is almost 15% more than that of in ZBMs. Even though the BC per total weight of a ZBM and a SBM is equal, the volumetric equivalents of the mixtures differs which may cause the lack of needed swollen bentonite to fill the voids in ZBMs. In order to obtain a ZBM corresponding to the same volumetric BC that 10% SBM has, at least 12% BC per total weight is required.

The e<sub>b</sub> of ZBMs were found to be higher than those of SBMs. For 20% ZBMs, they had e<sub>b</sub> values between 10% and 20% SBMs. Bentonite volume in ZBMs were found to be less than that of SBMs and, this is the reason that the e<sub>b</sub> of ZBMs were more.

Most w<sub>b</sub> values of 10% ZBMs were around their liquid limit. Moreover, even some of them exceeded it. Nagaraj et al. (1990) found that the hydraulic conductivity values of the soils at their liquid limit state were found to be almost the same. If the bentonite filled the voids in 10% ZBMs, then it should have had the controlling of hydraulic conductivity and thus, hydraulic conductivities of 10% ZBMs should have approached to the values given in Nagaraj et al. (1990).

Swollen bentonite was not enough to fill all the intergranular voids and the deterioration of the continuity of the bentonite caused such preferential flow paths to form when the ZBMs had a BC of 10%.

This has caused to introduce a new approach degree of saturation to bentonite (S<sub>B</sub>), in order to investigate the sufficiency of present bentonite amount in binary mixtures.

 $S_B$  was experimentally found to be at least 53% in order to reach the desired hydraulic conductivity for use of a liner for 20% ZBMs. A rapid decrease in hydraulic conductivity was determined in mixtures having  $S_B$  values between 30% and 53%. The hydraulic conductivity values of 20% ZBMs varied almost three

orders of magnitude for  $S_B$  values lower than 53%, due to the lacking of bentonite amount.

The present bentonite in 20% SBMs was found to be enough to fill the voids and prevented the formation of continuous pores. However, for 20% ZBMs, the samples at their dry of optimum water contents had lower S<sub>B</sub> values than 53% or at most equal to it.

This study showed that ZBMs have completely different behavior in hydraulic conductivity when compared to that of SBMs. The bentonite contents previously determined for SBMs cannot be suggested for ZBMs as well.

# 7.1.5 Modeling of Binary Mixtures

When the ratio of the hydraulic conductivity of the components in a binary mixture (which were not in contact to each other) exceeded three orders of magnitude, the mixture hydraulic conductivity value held constant, as it was and did not change anymore.

The grain shape did not have a notable effect on the hydraulic conductivity of binary mixtures. They differed at most by 4 times.

For porous grains embedded in fine matrix, it's concluded that the contact of the grains to each other had a significant influence on the hydraulic conductivity of binary mixtures. The situation was attributed to the environments, where bentonite did not swell enough and couldn't separate the grains as well.

ZBMs and SBMs data clearly fit the model formed by porous and non-porous grains which corresponded to zeolite and sand respectively.

ZBM results were in a good harmony with the models that had porous grains. Some of the laboratory data of 10% ZBMs fall into the model boundary which had

preferential flows, showing that 10% ZBMs were insufficient for use of a liner. As it was previously concluded in this study that bentonite amount in 10% ZBMs were also shown to be insufficient, regarding the bentonite void ratio and final bentonite water content.

ZBMs were found to have higher hydraulic conductivities than SBMs even they had the same BC by weight due to the influence of the porous structure of zeolite, water content distribution to the constituents and insufficient bentonite amount.

### 7.2 Recommendations For Future Studies

Each study is naturally limited and gives clues for the following studies. This study mostly focused on the experimental findings on understanding the mechanisms controlling the hydraulic conductivity of ZBMs and SBMs. These findings were followed by a modeling study by using FEM. Depending on the conclusions drawn above; some suggestions are drawn below for future investigations in order to complete the absent data on the ZBMs.

The investigations on the hydraulic conductivity of ZBMs should be widen including the usage of original waste water. The hydraulic conductivity range may change, when subjected to chemical solutions. The chemical compatibility of ZBMs hadn't been investigated by means of hydraulic conductivity testing yet. The water from inflow and outflow should be investigated in comparison to terms of cation contents, such as heavy metals, alkali earthen elements and pH degree.

Tomographic visualizing investigations may be conducted on compacted samples. The MR techniques may be helpful understanding the intergranular void formation in compacted ZBMs. The numerical analysis can also be done by using the imaging techniques. There are such computer programs which can convert the images to 3D computational models. The researchers may model the compacted binary mixtures by using the imaging techniques and the converted 3D equivalents.

It would be useful to investigate the micro-structure of ZBMs by environmental scanning electron microscope (ESEM). ESEM allows the investigation of the hydrated specimens unlike SEM, where SEM permits seeing only the freeze-dried samples. The photomicrographs at varying moisture contents would be helpful to understand the swelling of bentonite in ZBMs. In addition, the swelling of bentonite can also be observed in consecutive photomicrographs by increasing the relative humidity of the environment.

The findings of this study strongly suggested a comprehensive investigation on the suctions in zeolites, bentonite water uptake potential and the relation between them regarding the variation in zeolite water content in ZBMs.

Regarding the fact that the compacted liners are naturally unsaturated, the suction characteristics (matric, osmotic and total suction) also should be determined. The soil water characteristic curve (SWCC) or water retention curves of ZBMs can be determined in comparison to that of SBMs. These curves are key to understand the unsaturated behavior of the binary mixtures.

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