AN EXPERIMENTAL INVESTIGATION OF NANOPARTICLES ASSIMILATED HYDRO-MECHANICAL BEHAVIOUR OF BENTONITE SAND BUFFER

by

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Abstract

Disposal of high toxic radioactive waste is one of the alarming concerns of these days. Until now, the best accepted disposal method of such hazardous materials is placing into an underground containment system known as deep geological repository (DGR). DGR systems have risk of contaminating underground geosphere. Water may intrude into the DGR and intrusion mainly takes place as a form of advection. At present, the multiple barrier system is proposed around the hazardous waste containing cylinders known as clay barrier system. Bentonite sand buffer (BSB) is one of the main components of the multiple clay barrier system. Literature indicates extensive studies have been carried out with the existing BSB material. These researches emphasize to improve the hydraulic and mechanical behaviour of the BSB. To achieve the improved hydraulic and mechanical behaviour, it was intended to conduct laboratory test based study on the material, with integrated bentonite nanoparticles in saturated condition. Nanoparticles of bentonite were prepared using the ball milling process. Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (XEDS) and X-Ray Diffraction (XRD) analysis were adopted to characterize the size, elements and crystal structures of bentonite nanoparticles. Several laboratory tests such as the atterberg limit test, compaction test, unconfined compression test and onedimensional consolidation test were conducted to examine the mechanical and hydraulic behaviour of the BSB, with varying proportion of nanoparticles.

This is a new concept to capture the performance of BSB material after introducing nanoparticles. Fewer literatures directly relate to the problem and provide less evidence towards the achieved laboratory data. Furthermore, the obtained laboratory results illustrate significant improvement in the hydro-mechanical behaviour of the BSB material.

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Preface

An individual research is presented in this thesis, which presents a novel and unique experimental work to improve barrier material. The experiments and the analysis of the results were performed by me. It consists of six chapters. None of the text is directly taken from earlier published articles. Early stage of the research methodology development was assisted by Siddiqua S. I have been preparing a manuscript about preparation of bentonite nanoparticles, based on chapter 4 and the conjunct results presented in chapter 5, while collaboration was made with Sarkar G. and Siddiqua S. Nevertheless, Siddiqua S. has been assisting to prepare the manuscript based on the laboratory test results, presented chapter 5, which contains the hydro-mechanical improved behaviour of the buffer material.

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List of Symbols

e ₀	Initial Void Ratio
e ₁ , e ₂	Void Ratio corresponding to first and second load phase
è	Void Ratio at earlier loading stage
Δe	Change in void ratio
Gs	Specific gravity
k	Hydraulic conductivity of Soil, m/s
σ_{v1}	Stress corresponding to void ratio e1, kPa
σ_{v2}	Stress corresponding to void ratio e2, kPa
q _u	Unconfined compressive strength, kPa
γ_{w}	Unit Weight of Water, 9.81 kN/m ³
γ	Bulk unit weight, kN/m ³
γd	Dry unit weight, kN/m ³
3	Strain, %
Н	Initial specimen height, m
H _s	Height of solid, m
H_v	Height of void, m
ΔΗ	Change in height, m
ΔΡ	Change in stress, kPa
C _c	Compression Index, kPa ⁻¹
Cs	Swelling index, kPa ⁻¹
C _v	Coefficient of consolidation, m ² /sec
m _v	Coefficient of volume compressibility, m ² /kN

a	Coefficient of compressibility, m ² /kN
E	One-dimensional modulus, kPa
A	Area, m ²
M _s	Mass of solid, g
$ ho_{ m w}$	Density of water, 1000 Kg/m ³
C _u	Uniformity coefficient
D ₁₀	Particle Size of the 10% sample distribution, %
D ₃₀	Particle Size of the 30% sample distribution, %
D ₆₀	Particle Size of the 60% sample distribution, %
η	Viscosity, cP
w	Water content, %
Μ	Mass, g
M_1	Mass of wet sample, g
M ₂	Mass of dry sample, g
V	Volume, cc
V_1	Volume of sample with wax coat, cc
V_2	Volume of wax coat, cc
W	Weight, g
ΔL	Change in length, mm
L ₀	Initial length, mm
Т	Temperature, K

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To my parents

Chapter 1: Introduction

1.1 Problem statement

At this state of prosperity and escalating energy demand, an abundant source of energy is essential. One of the alternative energy sources is nuclear fuel, which is abundant and highly efficient. Compared to fossil fuel it releases less carbon dioxide to the atmosphere. However, the spent nuclear fuel leaves hazardous radioactive waste. The radioactive waste from the spent nuclear fuel is so harmful that it can pose a risk of extinction to the living beings.

At present nuclear fuel is utilized by many developed countries around the world to meet the power crisis. There are 436 nuclear reactors and 72 are under construction (World Statistics, 2014). The nuclear reactors generate about 2000-2300 metric tons of hazardous waste each year. It takes at least 100 years to dissipate the heat from the spent fuel and decades for the radiation. Previously, radioactive waste was disposed under the deep sea. Disposal of the waste under water had a high risk of affecting underwater environment. As a result, the waste is now disposed into underground deep geological repository, an underground containment system for hazardous waste. Band of barrier material around the waste container are constructed to seal the system with rigidity. Again, dumping the hazardous waste into the underground repository, pose serious risk to the ground water that intrudes into the containment zone. However, at present the deep geological repository is the safest disposal method of the waste, compared to the previous placement methods. Necessary initiatives must be taken to reduce contamination of underground water that intrudes into the hazardous waste facility.

One of the ways of reducing the contamination process is, by improving the barrier material. Generally, clay based material such as bentonite is used alone and sometimes used with the sand, as a barrier material. The literature shows that, use of nanoparticles has a great effect on the engineering properties of clays. Literatures also reflect that, nanoparticles can improve the concrete strength by using in a small percentage. Being small in size nanoparticles fill the pores between the larger particles and help to interlock the grains and block the drainage path. These properties can improve the hydraulic and mechanical behaviour of the clay barrier system. Therefore, higher strength of the material can be expected and intrusion of water can be minimized. Laboratory-based research can be demonstrated for the investigation of hydraulic and mechanical improved behaviour, of the barrier material with additional nanoparticles.

In summary, disposal of hazardous waste, which is generated from the nuclear reactors, is one of the main concerns to address. Safe disposal of the waste is required due the radiation threat to the ecosystem. In this study, an idea has been developed to improve, the barrier material that can reduce the level of contamination from the present state.

1.2 Background

Deep geological repository is constructed below the ground surface. In order to emplace hazardous spent fuel into deep underground hard rock strata, excavation is carried out. The excavated area is sometimes called excavated damaged zone (EDZ). Waste is transported using motor vehicles through the tracks after cooling down in a controlled chamber. Mild slope is constructed in several stories for safest transportation of the hazardous waste to the underground facility.

1.3 Deep geological repository

Highly radioactive waste is disposed in a remote underground facility known as deep geological repository (DGR) situated at 200 m – 1000 m below (fig. 1.1) the ground surface (Guo, 2010). Previously, several methods were undertaken such as cooling the nuclear waste for long period in controlled environment and isolating under sea. However, the volume of the waste is increasing day by day. Previous disposal methods required large facility, massive finance and constant monitoring to keep waste secured. Therefore, deep geological repository is the suitable solution for long-term safe disposal. Many concepts are available throughout the world for disposing highly radioactive nuclear waste in the deep geological repositories. The disposal methods are almost similar. However, different country has developed their suitable concept depending on the formation of geology and availability of the materials. Canada has developed their concept for hazardous waste disposal too, which is most suited for the geological formation near Ontario. Canadian shied holds supreme quality for emplacing the hazardous waste. Atomic Energy of Canada Ltd (AECL) has been developing the containment facility to dispose radioactive waste near the Chalk River in Quebec.



Figure 1.1 Deep geological facility (after Baumgartner, 2006)

The DGR consists of several components like clay barrier system or engineered barrier system, canister and backfill materials, discussed in the following sections.

1.3.1 Engineered Barrier system (EBS)

Radioactive waste is emplaced in a secured geological formation. It is essential that the waste be placed into the hard rock strata. It is necessary to choose suitable bedrock and favorable geology to contain the waste safely for a long period. Generally, clay type material is emplaced in between the nuclear waste containing cylinder and host rocks, which is known as clay barrier. Clay barrier surrounding the canister regulate the ground water infiltration into the DGR. It encircles the canisters with impermeable layers around it. It also acts as a medium for transferring heat. Bentonite is a special type of clay having large swelling property. This behaviour permits bentonite to seal itself. Now-a-days engineered barrier system concept uses bentonite materials in form of multiple barriers (fig. 1.2) around the repositories (NUKEM, 2003; Siddiqua et al. 2011). Recent concept of repository design in multiple barriers includes various type of bentonite clay layer to be constructed in several layers. The multiple barriers consists of bentonite sand buffer (BSB), highly compacted bentonite (HCB), light backfill (LBF) and dense backfill (DBF). Most of these barrier materials are composed of bentonite and bentonite clay composite of varied density. Bentonite sand buffer is the bentonite and sand composite. It exhibits high strength and high temperature gradient compared to other barrier materials due to the sand fraction.



Figure 1.2 Multiple barrier system (after Siddiqua et al., 2011)

1.3.2 Canisters

The canister encapsulates the spent nuclear waste within it (fig. 1.3). The canisters are the most important barrier for isolating the waste. Within the canisters waste are kept in fuel bundles. The canister is generally made of metal alloy such as nonabrasive zirconium. The height of the canisters is generally 0.5 m and these canisters are kept into the 4 m long cylinders stacking in circular array (fig. 1.4). The canisters keep the waste apart from the geology and provide utmost rigidity against rupture.



Figure 1.3 Canister placement (after Baumgartner, 2006)



Figure 1.4 Waste-containing canister (after Baumgartner, 2006)

There are two main emplacement methods (fig. 1.5 and fig. 1.6) for the nuclear waste canisters in the repositories such as in-floor emplacement system and in-room emplacement system (Hobbs et al., 2005). In an in-floor system, the canisters are placed horizontally while the canisters are kept vertically in an in-room system. The in-room placement method is convenient for the Canadian repository concept.



Figure 1.5 In-room placement system (modified from: Baumgartner, 2006)



Figure 1.6 In-floor placement system (modified from: Baumgartner, 2006)

1.3.3 Backfill

Function of backfill is to stabilize the disposal tunnel. It keeps the clay barrier system in place and prevents water intake. Backfill is emplaced after emplacing the waste cylinders into the DGR. The plugs are installed at the end of the tunnel in order to prevent extrusion of the buffer and the backfill material into another tunnel.

1.4 Objectives

The study was performed in the laboratory with the BSB material and small proportionate mixture of bentonite nanoparticles. The goal of this study was investigating the properties of the bentonite sand buffer with integrated nanoparticle with an intension to achieve lower hydraulic conductivity. The specific objectives of this study are also enlisted as follows:

- Preparation of nanoparticles of bentonite.
- Confirmation of the microstructure, chemical composition and crystal structure of the prepared nanoparticles.
- Determination of the hydraulic conductivity (k) of the BSB material after introducing nanoparticles.
- Determination of mechanical response of the compound matrix with addition of nanoparticles.

1.5 Scope of study

The study of the hazardous waste placement into the underground repository is a controversial topic. Whether to use the nuclear fission reaction to generate power with anticipated risk, has been a topic of debate. However, day by day, the scarcity of energy is emerging and blessings of technology are embraced to solve the present scarcity. Along with

the use, the generated radioactive waste has to be dumped safely. Therefore, the study is important to reduce the risk. This study intends to propose a new matrix, which is the compound of bentonite nanoparticles with the conventional bentonite sand buffer. It is realized that the nanoparticles will improve the hydraulic and mechanical behaviour. The introductory test results are presented in this area of research encircling the saturated behaviour of bentonite clay using distilled water. The concept of this study can be implemented in other engineering problems. The concept can be beneficial for improved landfill linear design with reduced permeability. It can be also useful as sealing materials around the mining wells.

Chapter 2: Literature Review

2.1 Background

The effect of nanoparticles mixed with a bentonite sand buffer has not been discussed in any previous literature. However, earlier studies focused on the bentonite sand buffer used in the repository condition. Improving the quality of the barrier material, by increasing the material strength and reducing the hydraulic conductivity, could be a study of great importance. The earlier studies over the deep geological repositories with the relevant barrier material are discussed in this chapter. This chapter also discusses about the material and conventional sample preparation methods. The literatures consisting laboratory tests results are also conferred to predict the hydraulic and mechanical behaviour of the barrier material. This chapter also includes the literature discussing about the nanoparticles assimilated improved behaviour that encouraged conducting this research.

2.2 Deep Geological repository (DGR)

An overview of a deep geological repository is discussed in Schäfer et al. (2012). The nuclear waste is buried in to vaults 200-1000 m (Guo et al., 2010) below the ground surface. A remote underground facility that encapsulates the hazardous waste is known as deep geological repository (DGR). The hazardous material is placed in the hard rock strata (Lee and Tank, 1985), generally within the plutonic rock (Lopez et al., 1984). Gens et al. (2002) studied the properties of host rock suitable for the repositories. Keeping the radioactive waste in a controlled facility for cooling down, takes a long time and is costly. Previously, various methods have been adopted to dispose radioactive waste. The common and the best-accepted solution are isolating the waste into a deep geological repository (Bodansky, 2004; Roffey, 1990; Pusch, 1982). Different countries use a different concept for dumping the hazardous

waste depending on their geological condition. Studies with the barrier materials have been conducted and funded by various agencies, namely: NAGRA (National Cooperative for the Dsposal of Radioactive Waste) in Switzerland; SKB (Svensk Kärnbränslehantering AB) in Sweden; JAEA (Japan Atomic Energy Agency) in Japan; ENRESA (Empresa Nacional de Residuos Radioactivos SA) in Spain, BGR (Bundesanstalt für Geowissenschaften und Rohstoffe) in Germany and BRIUG (Beijing Research Institute for Uranium Geology) in China. The underground research laboratories (URL) were built for conducting research, for instance: Mont Terri Rock Laboratory in Switzerland. The Canadian system of hazardous waste disposal is done by NWMO (Nuclear Waste Management Organization) and the disposal methods are described in Priyanto et al. (2008) which is similar to the Swedish concept. Various methods are followed for emplacing the nuclear waste canisters the repositories such as in-floor emplacement system and in-room emplacement system (Hobbs et al., 2005). The in-room system is mostly adopted in Canada (Dixon, 1994; Dixon et al., 2002).

2.3 Engineering Barrier system (EBS)

The engineering barrier system (EBS) within the deep geological repository is installed to minimize the intrusion of the underground water in to the underground hazardous waste containment system. It is also desired to achieve safety and long-term improved performance of the EBS. An overview of EBS is presented in Rowe (1995). The EBS consists of several components, like the canister, the buffer material and the backfill materials (Kim et al., 2011). The canister outer shell is composed of copper and a nonabrasive material. Zirconium alloy is used in the inner container with a titanium-sealing cap. The purpose of backfill is to stabilize the vault by keeping the buffer in place and preventing the water intake (Dixon, 1994). The buffer material encircles the canisters with several impermeable layers around them. The buffer material mainly includes clay type (eg. bentonite) material and sometimes a mixture of clay and sand.

Recently, multiple layer barrier system has become familiar (NUKEM, 2003). The concept of repository design in multiple barriers includes, use of bentonite sand buffer (BSB) and clay layers of varying density such as highly compacted bentonite (HCB), light backfill (LBF) and dense backfill (DBF) (Russell and Simmons, 2003; Maak and Simmons, 2005; Siddiqua et al., 2014). To fulfill the role of filtration and imitating underground loading conditions, Schäfer et al. (2012) recommended that the dry density of the barrier material should be greater than 1.65 Mg/m³ and enlisted desired buffer characteristics. To establish a reliable numerical model (Thomas et al., 1996; Guo et al., 2010; Thomas et al., 2009) of the clay barrier system, extensive study was carried out in the underground research laboratories (URL). Some of the research also includes determining radionuclide mobility (Mori et al., 2003; Geckeis et al., 2004; Guo et al. 2010) through the barrier material.

2.4 Materials

Concrete could be a choice for sealing the hazardous waste. It has some disadvantage to use in the DGR, such as shrinkage, seepage and crack formation in long run. Martino et al. (2006) studied the durability of concrete in the repository environment. Martino et al. (2006) reported the investigation result on the cement material surrounding the hazardous waste. He found concrete to be poor a buffer material. The main reasons behind the poor behaviour were due to the varied pH, widespread thermal gradient and salinity condition. Moreover, the precast concrete reduced the heat of hydration but the carbon footprint remained prominent, which is another environmental issue. Yet, bentonite clay buffer has been proved durable in long-term use, environment friendly and efficient. Hence, it is conventional practice to use the bentonite materials as the engineering barrier material.

2.4.1 Bentonite and bentonite sand buffer

Bentonite has been proposed in deep geological repositories as a barrier material (Gates et al., 2009; Thomas and Cleall, 1997; Cleall et al., 2011). Lopez and Dixon et al. (1984) mentions in their article that dried bentonite shrinks less than the other type of clays and its engineering properties remain same. This is an advantage for using bentonite instead of other clays. Sodium bentonite is superior to the Calcium bentonite in DGR environment because of its high swelling capacity (Castellanos et al., 2008). Komine (2004) used the sodium bentonite with a 48% montmorillonite content and 64.5 clay content and found the liquid limit 473.9%, plasticity index 447.3% and cation exchange capacity 0.732 meq/g. Swelling property of bentonite seals the containment system, which is the primary objective of the safe containment system. Therefore, sodium bentonite (Low, 1979; Singh, 2007; Rao et al., 2008) is mostly used in this field. Bentonite can be used in the repositories either in pure form or in mixed form (Hummel, 2008). Pure bentonite was used in the SKB project (Johannesson, 1999) in Sweden. JNC members (1999) studied 30% silica sand with 70% bentonite in Japan.

In the Canadian concept, bentonite is proposed in multi-barrier system. The hydraulic and mechanical behaviour of DBF and LBF material is discussed in Priyanto et al. (2008). Siddiqua et al. (2011 and 2014) revealed DBF and LBF behaviour, which was subjected to varied salinity condition. Cowl and Leung (1991) studied effect of salinity on the bentonite used in the landfill linear. Bentonite sand buffer is essential for the clay barrier system and it is successfully used in the repositories (Dixon, 1994). Bentonite sand buffer by the dry weight proportion is the same amount of sand and bentonite mixture (Wardrop et al., 1985; Boonsinsuk et al., 1991). Lopez and Dixon et al. (1984) stated the following advantage of using bentonite sand buffer in the repository: pure bentonite has a density of 1.24 Mg/m³ and sand increases the density of BSB after mixing with bentonite. Moreover, additional sand improves the strength, creep behaviour along with thermal and hydraulic conductivity (Mitchell et al., 1968). Previous research on BSB indicates towards the widespread effort to study the engineering properties of BSB (Siemens and Blatz, 2009; Tien et al., 2004). Komine (2004) also mentioned the maximum dry density attained for the BSB material was 1.66 g/cc corresponding to the optimum water content of 17.5%. Tanaka et al. (1997) studied BSB material to examine the uniqueness of the swelling equilibrium line (SEL) for the primary and secondary consolidation behaviour. For this study, it is essential to know the behaviour of clay material. Clay structure and its typical behaviour are discussed in the following two sections.

2.4.1.1 Clay Mineralogy

Literature indicates that clays have been used in landfill liners (Chalermyanont and Chalyrmont and Arrykul, 2005; Kayabali, 1997; Kenny et al., 1992) and as a barrier for diesel fuel as a mixture of sand and bentonite (Leppin et al., 1996). Clay mineralogy and crystallography controls the texture and chemical properties of the cohesive soil. Clay dominates in an equal proportionate mixture of clay and sand. The three important clay minerals are kaolinite, illite and montmorillonite. Bentonite is a type of clay rich in montmorillonite minerals (fig. 2.1). Wersin et al. (2007) studied the alteration of the physical feature of bentonite, to illite. In general, the fine clay has specific gravity of 2.655, plasticity

index of 394.6%, and cation exchange capacity of 90 meq/100 g, as reported by Taha M and O (2012).



Figure 2.1 Montmorillonite mineral crystals (modified from SIPAG BISALTA)

Montmorillonite has lateral dimension varying from 1000 Å to 5000 Å (Das, 2012) and thickness of 10 Å to 50 Å. The specific surface is about 800 m²/g. Mineralogy of montmorillonite is combination of silica tetrahedrons sheet and aluminum octahedron sheet about 1 nm apart (fig. 2.2). Both of these sheets are attached to one another with water molecules and exchangeable cations.



Figure 2.2: Montmorillonite inter-planer spacing

A net negative charge prevails on clay surface because of isomorphs substitution of ions. The charge of the particle and swelling phenomena can be described using the diffuse double layer theory. Various physical and chemical properties such as volume change in clays and swelling capacity are influenced by the existence of diffuse double layer in the clays.

2.4.1.2 Diffuse Double Layer

Clay mineral carries overall negative charge but maintains a net neutral charge. The negative charge is balanced with the exchangeable cations (fig. 2.3) on the clay surface held by electrostatic attraction. Therefore, when the water is added to the clay, the dispersed cations surround the clay and form a shield of cation and dipole water molecule known as the diffuse double layer (Das, 2012; Mahmood et al., 2000). The water molecules are retained tightly with the clay minerals known as double layer water or fixed water (Mitchell and Soga, 1976). The diffused layer surrounding the clay particles has a strong influence on the engineering properties of montmorillonite clays (Schanz and Tripathy, 2009), such as specific surface area, cation exchange capacity and swelling, which influence the clay properties (Zhang, 2007; Wilson, 1999, Pusch and Karnland, 1988). The repelling force between the clay molecules tends to keep the clay particles apart and the swelling occurs. The swelling property makes clay vulnerable to use as a construction material, but exhibits a greater advantage for the repositories.



Figure 2.3 Ion distribution in between clay particles (after Siddiqua et al., 2011)

2.4.2 Nanoparticles

Nanoparticles are the particles having small dimensions, generally less than 100 nm (Zhang, 2007; Paul and Robeson, 2008) that can improve the matrix property drastically (Zhang et al., 2004). Some irreversible changes (Jacquet et al., 1990; Zhang, 2007; Tsang, 2000) take place in the matrix for using the nanoparticles. The advection of water in the repositories, which is determined less than 1 mg/ml (Schäfer et al., 2012), mainly caused by erosion in the barrier material and formation of micro cracks with varied thermal gradient. The initial erosion of the clay barrier system also resulted from the material porosity (Kaoser et al., 2006) and other parameter, such as dry density and cation exchange capacity (Missana et at., 2008). The nanoparticles of the bentonite could be a solution to this problem because it fills the nanopores and it has very high delamination resistance (Alomari et al., 2013). The clay nanoparticles morphology, including specific surface area, nanoporosity and surface charges, were studied in Zhang (2007).

Preparing nanoparticles mostly depends on the minerals (Hochella et al., 2008). The nanoparticles occur either from natural phenomena or by finely pulverizing the particles. Some studies on the naturally found nanoparticles show varied mechanical behavior and particle instability (Madden and Hochella, 2005; Chernyshova et al., 2007; Liu et al., 2008). The artificially produced nanoparticles are available in various forms such as powder, suspension and colloidal form (Buzea et al., 2007). Nanoparticles morphology can be divided into three broad types' nanoplatelets, nanowires or nanotubes, and nanodots (Zhang, 2007). Most clay mineral such as bentonite are flaky shaped having just one direction, which is also known as nanoplatelets.

Very little has been reported in the geotechnical field on nanoparticles compared to other fields (Kumar et al., 2008; Poole et al., 2003; Rana et al., 2009; Mondal and Marks, 2007). Fewer experimental studies on nanoparticles diffusion (Molera and Eriksen, 2002) in clays have been reported. Alonso (2009) performed experiments on nanoparticles diffusion with gold (Au) nanoparticles and found diffusion is higher at low density. Nevertheless, Nakagawa and Ishiguro (1994) confirmed that the coefficient of permeability varies with pH. Various studies are also available on nanoparticle associated radionuclide transportation (Kersting at al., 1999; Utsunomiya et al., 2009) through the barrier material.

Applications of nano-composites were depicted in the study of Paul and Robeson (2008). In the field of concrete, the cost efficient (Jonckbloedt, 1997) nanosilica fume (Schuiling, 1986; Lieftink, 1997) was studied. Quercia and Brouwers, (2010) mentioned that nanosilica in concrete was highly cost effective, though it slightly decreases the strength. However, it improved microstructure, density and bonding and at the same time decreased the porosity and hydraulic conductivity. Widespread studies on strength and deformation of the nanoclay matrix was reported in (Di Maio, 2004; Zhang et al., 2003; Mu et al., 2003; Vaia et al., 1996; Morgan and Gilman, 2003; Ahmadi et al., 2004; Ray and Okamoto, 2003). It was also reported that fillers as if nanoparticles increase strength and improve hydraulic behaviour (Fornes et al., 2004). The Permeability, swelling capacity (Borchardt, 1989), compression strength and cation exchange character of nanoclay was studied by Kananizadeh et al. (2011) for the landfill barriers. Other studies mentioned improved liquid limit and increased load-bearing capacity for additional nanoparticles to the soil (Pamukcu, 1991). Moreover, some research also concluded that silica sol (colloidal nanoparticles solution) reduces hydraulic conductivity (Funehag and Gustafson, 2008). All of the stated literature
encouraged the author to conduct the laboratory-based research on the BSB material with additional nanoparticles.

2.5 Methods

After the nanoparticles preparation, they had to be mixed with the original matrix in exact proportion and then laboratory experiments were conducted. Several tests were required for the study of the behaviour. The study of the material behaviour can be broadly divided into three groups: general behaviour, mechanical behaviour and hydraulic behaviour.

2.5.1 Preparation of nanoparticles

Nanoparticles can be prepared either by synthesis or by pulverization process, which is known as mechanical attrition. Not many literatures have been reviewed on synthesis process for the bentonite material. Sobolev et al. (2009) used the sol-gel production method also known as organic method. In the study author added organometallics in the solvent to change the pH of the solution. Afterwards the prepared solution is preserved for substantial amount of time, then filtered and dried for preparing a concentrated dispersion. Another method is vaporization of silica discussed in Quercia and Brouwers (2010) where quartz (SiO₂) was converted into nanosilica at a temperature between 1500 to 2000 °C by using an electric arc. Taipodia et al. (2011) proposed the laboratory set up (fig. 2.4) to prepare nanoparticles. It breaks particle into nanosize under 80-100 Kg/cm² pressure and the dispersion is created while heating chamber at 3000 degree Celsius.



Figure 2.4 Nanoparticles preparation (modified from: Taipodia et al., 2011)

The biological method to produce spherical shaped nanosilica was proposed by Estevez et al. (2009) using the California red worms. Biological waste materials that contain SiO_2 , were fed to the worms between 50 to 100 °C and nanosilica was produced by precipitation method (Iller, 1954). On contrary, expert manufacturer, do not assure the crystallographic structure with the synthesis process.

Consequently, pulverization could be the most acceptable method for preparation of bentonite material. Nanosoil preparation with the ball mill pulverizer was mentioned in the study of Majeed and Taha et al. (2009). In the study author mentioned that, by using Fritsch Planetary mill Pulverisette 6 the final fineness of 40-80 nanometer was produced by pulverizing the slurry of clay prepared with water. Pulverization was done for 10-13 hours with 20 number of corundum balls. Instead of water, isopropyl alcohol (IPA) could be a better dispersant which was used in Seth et al., (2010). Being a volatile liquid, it allows drying the sample easily. It has higher boiling point among the other alcohols. Nevertheless, ultra-sonication can be useful to de-agglomerate the nanoparticles (Sanganwar et al., 2009) after pulverization.

2.5.2 Microstructure analysis

The preparation of nanoparticles is generally followed by the microstructure study to ensure the prepared nanoparticles have the desired quality. Therefore, the particle size was determined and then the chemical composition and the crystal structure were analyzed. Pieri et al. (2006) established the model for determining the particle size using Zetasizer and Mastersizer. These are laser based instruments that give the particle size distribution within very short period by passing dynamic scattering light (DSL) (Murdock et al., 2007). While passing the DSL, diffraction pattern can be found for the dilute solution of the nanomaterial, which are generally prepared with approved dispersant. These methods are reliable and faster than the conventional hydrometer test. The instrument requires some basic Mie parameters (Bhatt, 2013; Tounsi et al., 2006) for the solvent and the nanomaterial. The measurement is based on the Derjaguin and Landau, Verwey and Overbeek (DLVO) theory (Verwey et al., 1948).

The scanning electron microscopy (SEM) is essential for the micro structural study of materials. Importance of microstructure has been studied in (Leroueil and Vaughan 1990). There have been many studies over SEM analysis (Qing et al., 2007; Senff et al., 2009; 2010; Lin et al., 2008; Ji 2005; Li 2004; Delage et al., 2006) where images were taken at a magnified level to study the shape and size of the material. Moreover, an additional device with the SEM device can measure the elements in the sample. Energy dispersive X-ray spectroscopy (XEDS) is very useful to see the chemical intrusion in the matrix that may take place after pulverization of the bentonite material.

While studying the effect of nanoparticles the study of alteration of the physical feature of bentonite to illite is important, beyond 150° C (Wersin, 2007). X-ray diffraction

analysis (XRD) (Mitchell and Soga, 1976; Norrish, 1954; Ferrage et al., 2005) is generally preferred to analyze the crystallographic structure of the composite. Mollins et al. (1996) conceptualized the bentonite sand buffer into a two-phase gel system and characterized the crystals using the XRD analysis.

2.5.3 Mixing

Dixon et al. (1994) discussed about preparation of bentonite sand buffer to ensure consistent material mixing. After buffer preparation, placing the mixture in cold storage (0°C) was suggested by Tanka et al. (1997). The suggested process (To et al., 2011) for mixing nanoparticles with a matrix was done with water and then the mixture was put in to a beaker. The beaker was then placed in an ultrasonic bath with water for 2 hours. The second method consists preparing dry soil mixture with nanomaterials and then adding water into the mixture, which is done in into two stages (To et al., 2011). Initially premix or hand mix was adopted, the quantity of soil was divided into ten layers and each layer was mixed with the required amount of nanomaterial. Then, 3 hours of vigorous mixing of the nanoparticles with the matrix was specified in the same article.

2.6 General Behaviour

The general behaviour like particle size distribution, specific gravity, water content, bulk density, cation exchange capacity (CEC) and surface area are important to distinguish the clay behaviour. The Cation exchange capacity (CEC) can be determined by ammonium acetate method at pH 7 (Grim, 2011; Thomas and Cleall, 1982). The specific surface area of the bentonite can be determined using ethylene glycol mono ethyl ether (EGME) method (Heilman et al., 1965; Cerato et al., 2002). Although, the test process is discussed in the

materials and method chapter and results are presented in the result and discussion chapter and few general test results were reviewed from the early studies.

2.7 Mechanical behaviour

The index properties, compaction, compression behaviour are directly related to the mechanical stiffness of the material. On the other hand, the elastic modulus, compression index and swelling index can be derived from the consolidation test. This behaviour is also related to the mechanical behaviour and the methods are discussed latter in this section.

The plasticity index is correlated to the compression behaviour of clay. Therefore, liquid limit and plastic limit is essential, to study the mechanical behaviour. ASTM D4318 covers the determination of the liquid limit, plastic limit, and the plasticity index. A device consisting of a brass cup named Casagrande apparatus is used to determine the liquid limit of cohesive soil. Numbers of cranks were recorded with the specimens of varied water content to close the groove junction to 13 cm length. Budhu (2008) suggested that number of cranks should lie between 15-35 blows. To determine the water content ASTM D2216 could be useful. On the other hand, plastic limit was determined by pressing and rolling the sample into a 3.2-mm (1/8 in.) diameter thread. Three specimens were generally collected from the different length of the thread for the water content determination.

Generally, the compaction test was done following the ASTM 698 code, based on transferring the standard compaction energy. The standard compaction is done in a 10.15 cm diameter and 11.7 cm height steel mold with 2.5 kg weight falling from 30.5 cm height. Three layers of soil were used for compacting with 25 numbers of drops. On the other hand, the modified compaction test uses 4.54 kg weight falling from 45.7 cm in five layers. The dry density and moisture content were calculated to determine the optimum moisture content.

Sometimes, the effective montmorillonite dry density (EMDD) (Dixon, 2002; Kjartanson et al., 2003; Stroes-Gascoyne, 2006; Pusch, 2001) is determined for bentonite sample, which is a normalized value with respect to the montmorillonite fraction in the total clay matrix. However, another method has been utilized in the study of Sridharan and Sivapullaiah (2005) that requires only 1/10th of the soil sample to get the same results. Mini compaction mold is 3.81 cm in diameter and 10 cm in height. Additionally this test is also suitable for the fine-grained soils having particle size less than 2 µm. In a mini compaction test, 36 numbers of falls in three layers are required either for standard one 1 Kg or 2.5 kg weight for the modified one. Nevertheless, the static compaction test (Boonsinsuk et al., 1991; Reddy and Jagadish, 1993) was also advantageous in various ways for instance it employs static force, thus the soil grains gets less affected and the soil structure is retained. However, its main disadvantage was that, it required a hydraulic pressure to be applied also known as static compaction pressure (Wang et al., 1991) which can fluctuate beyond pre-consolidation pressure.

The unconfined compression test could be done according to ASTM D2166. ASTM recommends a strain rate range 0.5 to 2 % is acceptable for the unconfined compression test. A deformation rate of 1.27 mm/min was maintained in Kananizadeh et al. (2011) to determine compression behaviour. The research also found that the unconfined compression test results give improved behaviour for additional nanosoil with sample size of 35 mm diameter and 70 mm height.

The compression and the swelling index could be found from the consolidation test (Das, 2012). Jahromi and Khodaii (2009) found the stiffness of the bitumen matrix after introducing the nanoclay improved drastically. The improvement of liquefaction behaviour

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using nanoparticles concluded that 5-10% of nanosilica reduce liquefaction potential by increasing the compressive strength and at the same time decreasing the strain (Cai et al., 2012; Gratchev et al., 2007).

2.8 Hydraulic behaviour

Hydraulic conductivity is very important parameter for determination of water advection, through the material. Kananizadeh et al. (2011) used ASTM D 5084 to determine the permeability. On the other hand, the ASTM D 2435 is followed for the one-dimensional consolidation test of the fine soils. Oedometer (Castellanos et al., 2006) is used for the onedimensional consolidation test, shown in fig. 2.5. Siddiqua et al. (2011) successfully determined the hydraulic conductivity using the consolidation test result. Craig (2004) proposed the equation for determination of coefficient of volume compressibility relating the void ratio and the applied load. The coefficient of consolidation found from the onedimensional consolidation test is used to find the hydraulic conductivity. Prior to determining the coefficient of consolidation, the pre-consolidation pressure (Butterfield, 1979) is important to know. The pre-consolidation pressure can be found using the Casagrande method, Tyler method or the rectangular hyperbola method (Das, 2012).

The constant volume test is applicable to the high swelling clays and described in Sridharan et al. (1986). The vertical loading was applied within the temperature range of 22 ± 5 °C to conduct a constant volume consolidation test. For the high swelling pressure, the samples tend to move back to its original height even it is loaded. The higher load was applied when the swelling pressure exceeds the original sample height, keeping the volume constant. Rao et al. (2008) found the swelling increases with the density while studying with nanoparticles. Batenipour (2012) studied the primary and secondary consolidation behaviour

of the permafrost. A number of studies have been carried out on the compressibility behaviour of expansive clays, covering a wide range of applied pressure (Marcial et al., 2002). Compressibility also gets affected by temperature (Eriksson, 1989; Oswell, 1991; Gray, 1936; Finn, 1951; Campanell and Mitchell, 1968; Demars and Charles, 1982; Tidfors and Sallfors, 1989). Moreover, swelling behaviour (ASTM 5298; Alonso et al., 1999) can be determined using modified oedometer cell. Madsen and Müller-vonmoos (1985) used a modified oedometer to measure the swelling pressure of compacted bentonite. However, Powell (2010) concluded that the coefficient of consolidation and effective stress is affected by the disturbance and disturbance on samples.



Figure 2.5 Consolidation device (schematic)

2.9 Summary

Güven (1992) found nanoparticles have higher specific area and cation exchange capacity (CEC) value. He also found that the zetapotential of the nanoparticle are such that it tends to agglomerate together. While extraction of nanoparticles from several available natural soils (Li et al., 2012) found that, the zeta potential decreases with higher P^{H} .

Nakagawa and Ishiguro (1994) reported that the saturated hydraulic conductivity of an allophonic soil was highest at pH 6 and decreased by introducing nanoparticles. Kananizadeh et al. (2011) studied the effect of hydraulic conductivity of leachate, using nanoclay and found the permeability decreased sharply from $3x10^{-9}$ to $9.4x10^{-11}$ cm/s by adding 3% nanosoil to the linear. The XRD analysis in the same article showed that particle's inter-planer distance decreased from 12.54 to 10.32 Å, which validated the decreased permeability result. Alonso et al. (2011) determined the diffusion coefficient of compacted clays 10^{-18} - 10^{-19} m²/s with additional nanoparticles. Taipodia et al. (2011) found addition of salt nanoparticles, decreases permeability and compressibility.

Large increase in plasticity index (Zhang, 2007; Majeed and Taha, 2013) was encountered with increasing bearing capacity (Pamukcu, 1991). Kananizadeh et al. (2011) study also mentioned that, the liquid limit and plasticity index increased with increase in nanoclay content and the optimum water content decreased slightly for adding the nanosoil. On the other hand, the same study concluded that the maximum dry density showed little improvement and swelling increased as the nanoclay content increased. Majeed and Taha (2013) found higher compressive strength for adding nanosoil to the matrix. Liu et al. (2008); Gratchev et al. (2007) also found 5-10% nanosilica reduced liquefaction potential by increasing the compressive strength and at the same time decreased the strain. Quercia and Brouwers (2010) mentioned that nanosilica in concrete is highly cost effective and it improved microstructure and bonding and decreased the porosity. From the SEM image Kananizadeh et al. (2011) found the pore size decreased and consequently lower permeability was attained.

Chapter 3: Materials and methods

3.1 Materials

Bentonite sand buffer (BSB) is one of the important components of the multiple barrier system. In this study, BSB is studied with varying amount of bentonite nanoparticles with the conventional bentonite sand buffer. Sand particles are larger than the clays and the pores of the sand are filled with the clays that help to prepare a dense composite. It can withstand the load coming from the rock strata and reduce the hydraulic intrusion. Additionally, the sand increases the thermal conductivity of the material. Thus, the high temperature of the nuclear waste can be dissipated sooner. The materials used for this study is silica sand and bentonite, both supplied by Atomic Energy of Canada Ltd (AECL). Nevertheless, for preparing the samples, the reverse osmosis (RO) water was used. While pulverizing the isopropyl alcohol was used. Getting consistent results from the sample depends on the general properties of the materials. Regenerating the same result may be impossible even at the most controlled situations. Therefore, some of the important material properties are discussed in the following sections.

3.1.1 Silica sand

Sand (fig. 3.1) is a granular type of soil mainly derived from the weathering process of the rocks. Soil particles having particle size less than 2 mm but greater than 0.0625 mm are specified as sand by American Society for Testing Materials (ASTM). It is a nontoxic material, abundantly found in nature and extensively used in the construction. Due to diverse range of particle size, it is sometimes subdivided into sub categories such as course sand, medium sand and fine sand. The shape, colour and particle size distribution of sand varies vastly from their origin. The shapes also vary from round to angular shape depending on weathering process. The silica sand is the most common types of sand. Quartz is the main forming mineral of silica sand, occurring from natural sandstone. The chemical compound of silica sand is silicon dioxide (SiO₂). Its refractive index is 1.54 and specific gravity 2.65 (Das, 2012). Having well-graded particle size distribution, it withstands higher mechanical stress. Due to the thermal expansion property, it is suitable in the repository condition at high temperature around canisters.



Figure 3.1 Sand sample

3.1.2 Bentonite Clay

Bentonite (fig. 3.2) is fine clay composed of high swelling minerals like montmorillonite. Usually, the sodium bentonite clay is used into the clay barrier system. The reason behind it is less hydraulic conductivity, self-sealing capacity and swelling characteristics. Different types of bentonite are available throughout the world. Sodium bentonite, Calcium bentonite and potassium bentonite are the most common. Sodium bentonite and Calcium bentonite is available abundantly in nature. The Sodium bentonite has great swelling properties and large absorption capacity. For the swelling behaviour, the Sodium bentonite can seal itself, which makes it very suitable for the repository condition. This kind of bentonite is also used as a sealing material in the landfill liners, around the piles and oil and gas extraction pipes. On the other hand, Calcium bentonite is reactive and not stable at higher temperature. Another type of bentonite is the Potassium bentonite or K-bentonite, which is rich in illite and not suitable for the repository condition at all.



Figure 3.2 Bentonite sample

As received in the laboratory, the Wyoming bentonite is in powder form. This kind of bentonite is available in the Wyoming, Montana and South Dakota in USA. The source of bentonite is chemical weathering of volcanic constituents. The Wyoming bentonite is rich in sodium content and used in the bentonite sand buffer. It is composed of at least 70% montmorillonite with the remaining being quartz and illite. The main mineral montmorillonite is a flaky shaped particle with monoclinic crystal. In addition, the particles are negatively charged. This type of clay has an average particle size 15-20 micrometer. Being small in dimension, the surface area is 750 m²/g. This type of clay can adsorb 7- 10 times of its own volume and swell 18 times of dry volume. The specific gravity of bentonite is 1.74 and the refractive index varies in between 1.48 to 1.53. The cation exchange capacity (CEC) of bentonite is 76 meq/ 100 g (Dixon et al. 1994). It has extremely high plasticity index, which is the result of large surface area.

3.1.3 Bentonite Nanoparticles

The bentonite nanoparticles are derived from the available bentonite; the preparation process is described in chapter 4. Being the same chemical composition, it shows similar kind of behaviour as bentonite. However, the surface area, cation exchange capacity and particle can largely change. The bentonite nanoparticles are prepared and kept in plastic bottles (fig. 3.3) after the ball milling process in the laboratory.



Figure 3.3 Nanoparticles samples in bottle

3.1.4 Isopropyl alcohol

The isopropyl alcohol (IPA), rubbing alcohol or the 2-Propanol is known as an antiseptic solution (fig. 3.4). It was used for preparing the nanoparticles of bentonite. Isopropanol is highly flammable and cause dizziness when inhaled or ingested. Caution had been taken to work with isopropyl alcohol carefully. The bentonite material swells a lot when added to water. Water has dipolar ion that takes place between the clay layers and impels it to swell, which is the result of DDL. While using water, the volume of pulverized bentonite particle fills the whole volume of the bowl after expansion. The main problem with expansion is that the bentonite is not crushed properly with the zirconium balls, used in the ball mill pulverizer. Moreover, less amount of bentonite could be extracted when water was used. Nevertheless, the pressure of the bowl tends to increase, which is a susceptible to hazard. Therefore, 99% isopropyl alcohol was used which contains least amount of water in

it. The boiling point of IPA is 82.6 degree Celsius; refractive index is 1.3776 and viscosity 1.96 cP at 25 degree Celsius (Wikipedia, 2014).



Figure 3.4 IPA containing bottle

3.1.5 Reverse osmosis (RO) water

The water used for the laboratory test is collected from the distilled water module (fig. 3.5). The vapor is collected from the boiled water and condensed in liquid phase, inside the module. For further removal of the ions in the water, the device runs the condensed water through membrane in high pressure. While applying pressure the reverse osmosis technique is used to collect the reverse osmosis water. This water is preserved in clean plastic container. This water is used in the experiment because the ions available in the water may alter the property of the material. Therefore, the water provides the best purpose for the experiments. The effect of different salt concentration can be further studied after developing the preliminary dataset from this research with deionized water. The density of water is 1 g/cc at 4 degree Celsius, refractive index 1.33, viscosity 0.899 cP at 25 degree Celsius (Wikipedia, 2014).



Figure 3.5 RO water collection device

3.2 Methods

The study of barrier material requires extensive test and variety of simulation to be run before implementing the material into the repository condition. This thesis presents the earliest experimental data for the compound material behaviour with the introduced bentonite nanoparticles. With the supplied material series of laboratory tests were done. For conducting the laboratory tests, the samples were prepared in the Geomaterial Testing Laboratory of University of British Columbia Okanagan. The tests were conducted over different proportions of compound matrix to investigate the properties of the compound material. To find the best experimental results, the humidity and the temperature of the laboratory was controlled throughout the experimental process. Utmost care has been provided, to prepare almost similar type of sample. Then the mechanical behaviour has been found using the compaction, unconfined compression and consolidation tests behaviour. On the other hand, hydraulic conductivity was found from one dimensional consolidation test in oedometer. The general properties are first presented to conduct laboratory tests such as specific gravity, water content and particle size distribution, even some of the materials properties are reviewed from the earlier studies.

3.2.1 Preparation of samples

The bentonite sand buffer (BSB) was investigated in this study. The exception of using the BSB occurred in those cases where code restricted the use of sand in the experiments such as index property test. It is very important to mention that the nanoparticles were proportionately mixed with the dry weight of the bentonite content, not to the total weight of the BSB. After the experiments, the behaviour was compared with the control material, without any additional nanoparticles. Large amount of mixing was avoided to get non-segregated, homogeneous mixture. Various types of sample mixture were prepared for the experimental investigation: the BSB, bentonite and nanoparticles compound and the BSB and nanoparticles compound. The two distinct compound preparations are described in the following sections.

- Bentonite and bentonite nanoparticles compound.
- Bentonite sand buffer and bentonite nanoparticles compound.

Before preparing specimens, the sample of silica sand and bentonite were placed in two separate bowls and stored overnight in an oven at 105 and 110 degree Celsius respectively. The oven-dried samples were removed from the oven after 24 hours and then kept into airtight bags that no moisture can intrude. It also ensured that the materials were in thermal equilibrium. The prepared nanoparticles of bentonite were kept in air resistant bottle after preparation and particles do not get in to the contact with moisture.

3.2.1.1 Bentonite and bentonite nanoparticles mixture

Rotor mixer was used to prepare the bentonite and bentonite nanoparticles compound. The bentonite and bentonite nanoparticles compound was prepared in few steps. Firstly, the bentonite was taken into a clean stainless Cuisinart rotor mixture (fig. 3.6). The Cuisinart rotor mixture was used to make a homogeneous dry mixture of the materials. The requisite amount of the nanoparticles were determined and divided into three to five fractions. The nanoparticles fractions were poured into the rotor mixture at 5 minutes interval, to ensure a homogeneous compound. The rotor was rotated at a slow rate (speed level 2) to ensure that the dust was not formed. Nanoparticles had lesser weight, which enabled them to hover into the atmosphere for applying small agitation. Wearing the gloves and gas mask is essential because the nanoparticles can harm the respiratory system while inhaled.



Figure 3.6 Cuisinart rotor mixing device

One portion of this dry mixture was separated for conducting the index parameter, unconfined compression and compaction tests. The reason behind conducting the compaction test and compression test without sand was that, the nanoparticles were always proportionally mixed with respect to the bentonite content. Therefore, the effect of nanoparticles on bentonite could be distinguished when used without the sand fraction. The dry mixture was preserved at room temperature (22 degree Celsius) in airtight container. The samples were prepared by adding requisite amount of distilled water to the dry samples in 5-10 layers. The distilled water mixing was done at low temperature. Low to high temping was adopted in few stages, while preparing the samples. The rest of the dry mixture was kept at room

temperature for preparing the BSB and nanoparticles compound which is discussed in the next section. Each time different nanoparticles proportion was used to prepare the desired compound.

3.2.1.2 Preparation of bentonite sand buffer and bentonite nanoparticles mixture

The bentonite sand buffer (BSB) samples were prepared based on Dixon et al. (1994). Some modifications were adopted in Dixon et al. (1994) to accommodate the nanoparticles of bentonite into the matrix. The difference from the elaborated methodology was that, instead of using bentonite, the bentonite and bentonite nanoparticles dry mixture were used. The bentonite and bentonite nanoparticles dry compound was previously prepared and preserved, as discussed in the previous section. The masses of bentonite and sand were double-checked and measured. Prior to mixing the requisite amount of sand and distilled water were placed in a stainless steel mixing bowl and sealed with plastic wrap. The mixing was done in three main steps: mixing, temping and grinding. Initially the light mixing was adopted using scoops. The water-sand mixture and the previously prepared bentonite and bentonite nanoparticles dry mixture were sprayed in 5-10 layers and mixed lightly. While mixing, the adhered material over the mixing apparatus was continuously cleared using the scrapper. Varied proportion of bentonite and bentonite nanoparticles mixture were used to prepare various proportions of the bentonite sand buffer and bentonite nanoparticles compound. The mixing was done at lower room temperature (4 degree Celsius) to restrict the swelling. Having high surface charge and higher surface area the water droplets were inbounded by the bentonite material. Therefore, vigorous temping was essential. After getting a reasonably good mixture, intense temping was done to ensure the bentonite, water and the sand were perfectly mixed. The intense mixing was followed by a grinding step where the mixed

material was grounded against the wall of the bowl with the mixing tools. Then the samples were preserved into cold storage with in labeled plastic bags. Water content of the sample could be checked to confirm the attained water content.

3.2.2 Water content

The water content was calculated using the ASTM D2216. Water content is defined as the amount of water available to the dry weight of the sample. It is always presented in percentage. The ASTM multipoint liquid limit determination method, Method A, required at least three trials to be performed. Firstly, the weights of the empty cans (fig. 3.7) were determined and then the moist samples were put into the cans. The total weights of the cans with the moist soil were measured. The cans with the moist sample were left for 24 hours within oven at 105 degree Celsius. Afterwards, the dry weights of the samples were measured with the can. The water content is the ratio of the weight of the soil to the weight of the dry soil. Therefore, determination of water content was determined using eq. 01.

 $w = ((M_1 - M_2)/M_2) * 100 \%(01)$

where,

- w = Water content of the soil, in %.
- M_1 = Mass of wet soil, in g.

 M_2 = Mass of dry soil, in g.



Figure 3.7 Water content measurement container

3.2.3 Index properties

The index property test is recommended for the clays having particle size less than 425 μ m (No. 40 sieve). The average particle size of bentonite was in between 15-20 μ m and the nanoparticles of bentonite had a particle size range between 2-300 nm. Therefore, index property test was done for the bentonite and nanoparticles mixture without the sand. ASTM D4318 test method covers the determination of the liquid limit, plastic limit, and the plasticity index. 1% to 7.5% of nanoparticles were used to the dry weight of bentonite. To compare the improved behaviour of additional nanoparticles, the original bentonite (0% nanoparticles of bentonite) sample was also investigated. A mechanical device consisting of a brass cup named Casagrande apparatus (fig. 3.8) was used to determine the liquid limit of the cohesive soil. Liquid limit is the critical water content at which soil starts to act like liquid. 30 g of dry sample was taken and mixed with the RO water at lower temperature in three stages of mixing. Two third of the bowl was filled with the prepared sample such that the sample remain flat. Then a groove was cut using the grooving tool, at the middle of the specimen. The crank was rotated and the bowl dropped from a calibrated 10 mm height. This impact of falling closed the gap of the groove. The numbers of cranks were counted to close the groove junction about 13-cm. This procedure was followed for various nanoparticles compositions with varied water content. The multipoint liquid limit, Method A, required at least three trials to be performed at three different water contents. The amount of water was increased gradually and at the end of each step, water content was determined following the ASTM D 2216 method. Varied water content (log) verses count graphs were plotted and the liquid limit of the sample was found corresponding to the 25th no of crank.



Figure 3.8 Casagrande apparatus

ASTM D4318 also consist the methodology for determining the plastic limit of the clay sample. Plastic limit is the water content at which the sample starts to behave like plastic material. The plastic limit was determined by adding small amount of water to the sample. By pressing and temping, the sample could be rolled into a 3.2 mm (1/8 in) diameter and 12-inch long thread (fig. 3.9). For making the thread, first oval shape balls were prepared which were rolled over the glass plate. Wearing gloves is recommended because the moisture was absorbed by the skin and evaporated for the convection of heat. If the sample cracks down before the thread can be formed, small amount of water was added. Moreover, if excess amount of water was added the thread cannot be formed and the sample was dried by rolling over a dry glass surface. Three water content reading were taken for a single sample to verify the consistency of the plastic limit result according ASTM D2216. Finally, the plasticity index could be found from the difference of liquid limit and the plastic limit.



Figure 3.9 Plastic limit determination specimen and apparatus

3.2.4 Compaction test

The mini compaction (Sridharan and Sivapullaiah, 2005) tests were performed which requires only 1/10th of the sample, than the conventional compaction test. Both kinds of samples: the BSB and bentonite samples were investigated to determine the optimum moisture content and maximum dry density under influence of nanoparticles.





The compaction mold was 3.81 cm in diameter and 10 cm in height (fig. 3.10). The amount of water was varied from 5% to 55% of the total dry weight, while the tests. For compacting, modified compaction test with 2.5 Kg weight was performed that falls from 19.5 cm. Samples were compacted in three layers with 36 numbers of blows at each layer. After compacting, the collar was removed and excess soils were scrapped off and then the weights were measured with a scale. The density of bulk material could be found by using eq. 02 and eq. 03.



Figure 3.11 Mini compaction apparatus

Samples were taken out from the cylinder using an extractor (fig. 3.11). Three specimens were taken from three different locations of the extracted sample, generally from top, middle and bottom, to determine the water content using ASTM D2216. Average water content was found from the three water content results. The water content was increased and dry density and moisture content were determined. The graphs were plotted with water content against dry density. The peak point of the connecting curve gives the optimum water content and the corresponding maximum dry density.

$\gamma = M/V$	(02)
$\gamma_d = \gamma / (1+w)$	

where,

M= Mass of the moist sample, in g

V= Volume of the mold, in cc

 γ = Bulk density, in g/cc

 γ_d = Dry density, in g/cc

w= Water content, in %

3.2.5 Unconfined compressive strength test

ASTM D2166 is the complete manual for unconfined compressive strength test. The objective of the test was determining the unconfined compressive strength (q_u) of the specimen. The unconfined compressive test did not apply any lateral force to the sample. The strain-controlled test was recommended in the ASTM manual. The unconfined compressive strength (q_u) could be easily calculated (eq. 04) in this method. The assumptions were the angle of internal friction (ϕ) of the material equal to zero. However, it did not give the best result as compared to the triaxial test although it could depict the improved behaviour very quickly and easily. The sample before and after the unconfined compression test are shown in fig. 3.12 and fig. 3.13.



Figure 3.12 Unconfined compression specimen (compacted specimen)



Figure 3.13 Unconfined compression specimen (after failure)

The sample cylinders were prepared with bentonite, varied percent of nanoparticles and distilled water. To prepare the samples optimum amount of distilled water was used that could be found from the compaction test results. Again, the dry densities of the samples were maintained, following the compaction test results (fig. G.1). The height and diameter ratio of the cylinder, recommended by ASTM was from 2 to 2.5. In this case, the sample diameter of 38 mm and 76 mm height were used. The sample was taken out from the mold using the extractor (fig. 3.14) and the extractor mold was modified to fit with the mini compaction mold.



Figure 3.14 Extractor apparatus

The diameters and the lengths of the samples were measured after extraction. The extra heights of the samples were cut with sharp knife. The final weights and lengths were recorded. The compression force was applied using a controlled strain. The recommended strain rate by ASTM is 0.5 to 2%. The lowest strain rate (0.5%) was maintained to observe the loading behaviour. The 'Instron' universal testing machine (fig. 3.15) was used with modified jaw, for the unconfined compression test. The samples were carefully placed in between the jaws and load was applied and controlled by the software. The load and displacement was recorded automatically. After reaching to the peak load, the sample fails and the ultimate load values were used to determine the unconfined compressive strength (eq. 04). The strain was also determined by eq. 05.



Figure 3.15 Instron universal testing device

$q_u = P/A$		(04)
$\varepsilon = \Delta L / L_0 *$)*100	(05)

where,

q_u= Unconfined compressive strength, in kPa

 ΔL = Increment of length, in mm

L₀=Initial Length, in mm

 ε = Strain, in %

3.2.6 One-Dimensional Consolidation test

ASTM D2435 described the one-dimensional consolidation test method of the fine soils. Oedometer was used for the one dimensional consolidation test. With the consolidation test, the prepared BSB samples were examined, to find the effect of bentonite nanoparticles. The maximum dry density of BSB material was found 1.91 g/cc and corresponding optimum water content of 20%. To maintain expected density, required mass was calculated using the following equations (eq. 06 and eq. 07). When the calculated mass was compacted in the oedometer ring, the required density could be attained.

 γ = Bulk density of the mixture, in g/cc

 γ_d = Dry density of mixture, in g/cc

 ω = Water content, in %

V= Volume of the sample, in cc

M= Mass of bulk sample, in g

The soil specimen was restrained laterally and loaded in one axial direction, using the one dimensional consolidation device manufactured by GDS Instruments (fig. 3.16). The advantage of this device was that it acquires the load and displacement history by itself. To begin with, the lower hydraulic ram of the oedometer was set at 6 mm height because the instrument was capable do the swelling test and the instrument self terminates itself at 0 mm position. Nevertheless, the hydraulic ram had a travel distance of 15 mm. The LVDT, displacement-measuring gauge, was attached with the upper ram to take the displacement

reading from top end. The lower ram also determined the displacement of the sample from the bottom. After the compacted sample was filled inside the ring and then the ring was aligned in the oedometer cell. Afterwards, the upper ram was placed over the loadtransferring ring such that it just sits over it. In the meantime, the upper ram was leveled with a sprit level. Generally, 0.01 kN docking load was applied. An offset was applied using the control board to nullify all the readings.



Figure 3.16 GDS one dimensional consolidation device

A given load cycle was considered for applying the load on the specimen. The load cycles were set into the GDS software. Each increment was maintained until excess pore water pressures dissipated, while deformation under applied loading. Afterwards another load was applied with a load increment ratio (LIR) of two. The load cycle for the test were 3, 6, 12, 25, 50, 100, 200, 400, 800, 1600, 3150, 1600, 800, 400 and 200 kPa. Generally, the load was increased at an interval of 24 hr. However, at the initial stage with lower stress, the swelling occurred and the test was done with constant volume condition. In constant volume test, the sample was compressed with the load but the swelling occurred and the sample pushes back the piston towards the original position. Then the load was changed to the next

stage. This process was maintained up to the point of maximum swelling pressure. Afterwards the load was increased and a constant stress was maintained in the oedometer cell. Stress and deformation readings were taken with the time. The following equations (eq. 08 to eq. 12) are useful for determination of void ratio and other parameters calculation.

$H_{s}=M_{s}/(AG_{s}\rho_{w})$	(08)
$H_v = H - H_s$	(09)
$e_0 = H_v/H_s$	(10)
$\Delta e = \Delta H/H_s$	(11)
$e_1 = e_0 - \Delta e_{$	(12)
where,	
A= Area of the sample	
G _s =Specific Gravity of the sample	
M _s = Mass of soil, in g	
H_s = Height of solid in the soil specimen, m	

H_v=Height corresponding to the void, m

 ΔH = Change in height, m

e_o= Initial void ratio

e₁=void ratio after first loading.

 Δe = change in void ratio

A graph could be plotted with the applied pressure in one logarithmic axis and void ratios in another. The acquisition of the several important parameters like compression index (C_c), recompression index (C_r), swelling index (C_s), and coefficient of volume compressibility (m_v) and compressibility (a) could be acquired from the graph (eq. 13 to eq.

17). The pre-consolidation pressure and coefficient of consolidation (C_v) could be found precisely, using the Tylor's method or rectangular hyperbola method (Das, 2012). Thus, using the coefficient of consolidation (C_v) and volume compressibility (m_v) the hydraulic conductivity (k) could be calculated. Stiffness scent modulus (E) was also determined from the consolidation test.

$E = (\sigma_{v_1} - \sigma_{v_2}) / ((e_1 - e_2) / (1 + e_1)).$	(13)
$m_v = \Delta e / (1 + \tilde{e}) / \Delta P$	(14)
$a = m_v / (1 + e_0)$	(15)
$C_s = C_c = \Delta e / \log \Delta p$	(16)
$K = C_v \gamma_w m_v \dots$	(17)

where,

 σ_{v1} = Stress corresponding to void ratio e_1

 σ_{v2} = Stress corresponding to void ratio e_2

 m_v = coefficient of volume compressibility

a = coefficient of compressibility

è= the void ratio at earlier loading stage

E= One dimensional modulus

K= Hydraulic conductivity

3.2.7 Particle size distribution

Particle size determination for nanoparticles was one of the main objectives of this study. The particle sizes of sand were determined using the sieve analysis. On the other hand, the particle size of the bentonite could be found using the Mastersizer. The particle size distribution for the nanoparticles of bentonite was a challenge. For preliminary investigation of the size, the Zetasizer was used to determine the particle size distribution. For the final verification of the size, the SEM image analysis was used to render the particle size distribution.

3.2.7.1 Sieve analysis

Sieve analysis is the common method for determination of particle size distribution of sand, described in ASTM C136. The weights of the previously dried samples were measured. The sieves were stacked one over another; in this case, the sequence was 630 μ m, 425 μ m, 315 μ m, 160 μ m, 80 μ m to the pan (fig. 3.17).



Figure 3.17 Stacking of sieve

The weighed samples were spared, over the 630 μ m sieve and the cover was closed. The materials were agitated into the standard sieve shaker (fig. 3.18) for 8 minutes. After the shaking, the sieves were separated and the weight of the sample retained on each individual sieve was measured. The percent finer could be calculated along with the cumulative percentage (eq. 18 and eq. 21). Then, the particle size distribution curve could be drawn with the percent finer against the particle diameter. The total weight was checked and the loss was rechecked less than 1%. From the curve, some important information could be found about

the uniformity of the particle size. The D_{10} indicates the 10% of material's particle size less than the specific size. Similarly, the D_{30} and D_{60} could be found for the silica sands along with the coefficients (eq. 18 and eq. 21).



Figure 3.18 Sieve shaker

Percent retained = (retained weight/ total weight of the sample)* 100 %	(18)
Percent passing= (100-percent retained) %	(19)
Uniformity coefficient, $C_u = D_{60}/D_{10}$	(20)
Coefficient of curvature, $Cc = D_{30}^2 / (D_{60} * D_{10})$	(21)

3.2.7.2 Mastersizer

The Mastersizer (fig. 3.19) works based upon the laser diffraction methodology and advantageous for particle size ranges between micro scales. The monochromatic laser was passed through the suspension. The diffraction patterns were correlated to the particle size and final particle distributions were generated.



Figure 3.19 Mastersizer with Hydro LV

The Mastersizer 3000 apparatus has two kind of module. One is dry module and the other is the wet module. In the dry module, the dry sample was used to determine the particle size distribution. On the other hand, the bentonite nanoparticles had higher surface area and tend to agglomerate. Therefore, the wet module, Hydro LV was preferred because the pulverized suspension could be immediately fed into wet module. Before starting the test, the Hydro LV module was flashed with water two to three times. The water or the isopropanol was up to marked into the module flask. The ultrasonic level was set to 80%. Then the bentonite sample was fed into the device. The mixer was rotated at 3500 rpm. The bentonite was mixed with the solvent and the obscuration was generally tried to set within the desirable range of 10-14%. The software required the mie parameters of the materials for the particle size determination.

3.2.7.3 Zetasizer

The Zetasizer Nano S (fig. 3.20) is renowned for determining the nanoparticles size distribution. The advantage of Zetasizer was that it can produce the particle size distribution with little amount of nanosized sample.



Figure 3.20 Zetasizer nano S

Light scattering is the light interaction with electric field. In Zetasizer, the dynamic light scattering (DLS) was used for determining speed of suspended particle having Brownian motion. It used a laser frequency of 633 nm. At the same time, the absorbed quantity of scattering light was detected, which was generated from a photon incident over a dipole diffuse layer. This phenomenon oscillates the dipole layer and radiated energy.

Zetasizer measured the scattered energy and compared with the incident light intensity to find the particle size (eq. 22). Then the particle size was calculated from Stokes-Einstein equation, using assumptions: particles were spherical, homogeneous and the optical properties were known. For the tests, the cuvettes (the sample container) were up to marked with the sample and placed inside the device. Afterwards, only using the software the particle sizes were directly generated.

 $d_{\rm H} = kT/(3^*\pi^*\eta^*D)$ (22) where,

d_H= Hydrodynamic diameter

k= Boltzmann Constant

T= Temperature

 η = Viscosity

D= Diffusion Coefficient

3.2.7.4 SEM analysis

The scanning electron microscopy (SEM) test is described broadly in the preparation of nanoparticles chapter, which required a small amount of sample. The images extracted from the scanning electron microscope could be used to justify the particle size distribution results from the Zetasizer because of the agglomeration. However, to check whether the Zetasizer instrument gave good result or not, the SEM images were extracted. With help of Omnimet image analysis software the particle size were manually checked. At first, the image scale was calibrated after importing it to the software. Afterwards the particles were identified and shown with scale dimensions. Then the particle size database was exported to Microsoft excel and particle size histogram could be produced. The problem of this method was that it gives particle sizes at specific location rather than the global distribution.

3.3 Summary

In this chapter the materials, their general behaviour and the laboratory methods for determining the hydraulic and mechanical behaviour were discussed. The Wyoming bentonite and silica sand were used for the laboratory investigation. Preparing various types of compound mixtures with the material, using RO water was also discussed. Several laboratory experiments were planned for assessing the material performance. For determining the hydraulic behaviour, the hydraulic conductivity determination method from the one-dimensional consolidation test was elaborately discussed. The mechanical behaviour assessment was planned with the index property, unconfined compression test, compaction test. Some of the one-dimensional consolidation test parameters were also discussed to describe the mechanical behaviour.

Chapter 4: Preparation of nanoparticles

4.1 Background

In general, nanoparticles are defined as the particles having diameter less than 100 nm. Incorporating nanoparticles with the existing material can improve the property drastically. Nonopores exist in between the nanoparticles and thus nanoparticles resemble increased sorption characteristic. Introducing nanoparticles can improve the erosion of the barrier material and reduce the pore spaces between the matrixes. In this study, Sodium bentonite and nanoparticles derived from bentonite was used. The cause of choosing bentonite nanoparticles was that it would not introduce any chemical reaction with the conventional bentonite sand buffer.

4.2 Mechanism of ball milling

The milling in the ball mill apparatus is based on the relative hardness of the material and the hardness of the balls used for the milling. In theory, ball material having higher hardness than the bentonite material should be able to break the material into small sizes. The higher the ball diameter, the higher mechanical force is exerted. However, the interaction with the ball and material is another concern. Smaller balls sometimes interact better than the bigger balls and tear apart the material through the cleavage of the material. The bentonite has a soapy feel when added to water. It is white in colour with a monoclinic crystal. Its cleavage is perfect in one direction or basal. This earthy mineral has an uneven fracture. The bentonite particle size ranges between 2 to 100 micrometer and average particle size is in between 15-20 μ m. The information helped to determine the method for the pulverization. Dry or wet process both were applicable for pulverizing with a planetary ball mill. The mechanism of ball milling can be divided into few steps:
- 1. Mechanical force
- 2. Impact force



3. Abrasion with harder material

Figure 4.1 Planetery ball mill

The rotor of the planetary ball mill rotated (fig. 4.1) in a solar system manner. The bowl moved on its own axis and about its center of the pulverizer. Mechanical force was exerted on the material by the weight of the balls. The impact force acted when the materials falls in between two balls colliding together. The balls were able to exert the impact force to the material and breaks down the material along their cleavage. The impact force became ineffective, when the particles were small. In this case, small balls became effective to pulverize the material into nanosize. The abrasion takes place mainly between the bowl wall and the balls. All of these forces act together and crushes the material.

4.3 Preparation of nanoparticles

The Fretisch Pulverizer 7 premium line (fig. 4.2) had two bowls each had a capacity of 80 ml. For balancing the weight, same amount of sample and balls were placed in both of the bowls, which obstructed vigorous shaking of the machine. The pulverization were done with the wet samples because the dry samples agglomerated on the bowl wall and temperature rose very high. At high temperature, illite conversions were faster especially with the presence of Potassium (K). Moreover, higher speed could be attained in the wet pulverization process, which was advantageous from pulverization point of view.



Figure 4.2 Fretisch Pulverizer 7 premium line

The bowls (fig. 4.3) were tested for taking 21 bar of pressure but allowable up to 40 bars. When water was used with silica substances, it was monitored that the temperature rose up to 183 degree Celsius and the corresponding pressure was 21 bars. While for IPA, the temperature and corresponding pressure were relatively 129 degree Celsius and 20 bars. For safety, the temperature was always intended to keep as low as possible.



Figure 4.3 80 ml bowl of Fretisch Pulverizer 7

Generally, the balls were placed first and then the materials were placed into the bowl. Afterwards, the solvent like water or IPA were added to carry out pulverization in wet process. Then the program was set with the duration of milling, reverse cycle and the speed. The method presented in this chapter describes the bentonite nanoparticles preparation process. Setting certain parameter such as material of the ball, ball diameter, ball numbers, speed of the rotor and duration of pulverization were required before milling the material. Several trials were conducted with the Fretisch Pulverizer 7 premium line. For setting the ball size, rotational speed and duration, several trials were made with 10 g of bentonite sample and the results are presented in the chapter 5. Taha (2012) pulverized clay slurry in deionized water for 10-13 hours with 20 numbers of corundum balls using Fritsch Planetary mill Pulverisette 6 and the final fineness was obtained 40-80 nm.

4.3.1 Material, size and number of the ball

Harder ball material easily breaks the material and turns it into nanoparticles. Hardness of a material is the measure of resistance to the deformation characteristics while application of load. The hardness is calculated in different scale like Moh'r hardness, Brinell hardness, Vickers hardness, Rockwell hardness and Leeb hardness. These methods are generally used to quantify the hardness of a material and compare with another. Mohr's hardness is the most renowned scale of hardness. The Zirconia is harder than the steel material. Mohs' Hardness is 7 to 8.0 for zirconia oxide and 6.5 for steel. The grinding was done using zirconia and steel balls separately to find the effectiveness of the ball material. On the other hand, the hardness of bentonite is 1.5-2.0 in Moh'r scale. The experiment result inspired to use nonabrasive zirconia balls, to prevent the chemical intrusion from the balls. Zirconia balls were better for fibrous or flaky shaped material like bentonite. Two types of ball size were used in this study: 2 mm and 0.1 mm and shown in fig. 4.4 and fig. 4.5 respectively.



Figure 4.4 2 mm Zirconia ball



Figure 4.5 0.1 mm zirconia ball in container

Though smaller size balls less than 3 mm were recommended for preparing pulverized particle size less than 0.1 mm but varied ball size are tried to reinforce the experiment findings. At first, the 10 numbers of 10 mm zirconia balls were used in each of the bowl with varied milling time. Afterwards it was found that 5 mm steel ball using the Fretisch Pulverizer 6 provided improved particle size. Therefore, instead of using steel balls smaller diameter zirconia balls were used, because the hardness of zirconia was higher than steel. 200 steel balls were used, while using the 5 mm diameter steel balls in the 250 ml bowl of Planetary mill Pulverisette 6. Finally, 100 g of the 2 mm and 100 g of the 0.1 mm Zirconia ball were chosen for the pulverization.

4.3.2 Speed of the rotor

The Fretisch Pulverizer 7 premium line had a maximum speed of 1100 rpm. It operated at 100-240 volt, 5-10 A and 50 /60 Hz frequency and required a power of 1100 Watt. The speed determined how fast the rotor would rotate. The speed was controlled digitally (fig. 4.6) with a tolerance of ± 2 rpm. The faster the speed, faster the grinding will be and the higher mechanical force will be exerted on the material. The energy required to pulverize material could be calculated using the equation proposed by Von Rittinger, which was effective for particle sizes less than 0.05 mm diameter. The equation suggested the power required for the particle size reduction from 2-100 micrometer range to 1-100 nm range. However, the empirical equation could not be relied because pulverization also varied with type of material. At lower speed, the material had to be pulverized for long period. Several trials were led to grind the bentonite particle. The trial speeds of the rotor were 200, 400, 800, 900, 1000 rpm.



Figure 4.6 Fretisch Pulverizer 7control pannel display

4.3.3 Duration

Duration is a function of running time and the pause time. The Fretisch Pulverizer 7 premium line was capable to set maximum 999 min pulverization and 99 min repetition cycles. For the research, the suitable duration was selected to prepare the nanoparticles

within a reasonable period. Enough time were provided to the sample to cool down, after the pulverization. At the early stage of the test in lower speed from 200 to 400 rpm the sample were pulverized for 20 min and cooled for 10 minutes. After increasing the speed to 800 rpm, the grinding time was lowered to 10 minutes and pause time of 10 minutes. Afterwards at higher speed like 1000 rpm, the grinding time was 2 min and the pause time was 5 minutes. The pause time for the pulverizer played an important role to lower the temperature and pressure of the bowl. Minor improvement was encountered in the particle size, after 90 minute grinding than the 60-minute grinding period with 0.1 mm zirconia ball at 1000 rpm. Finally, the nanoparticles were prepared using 100 g of 2 mm zirconia ball on each bowl for 30 minutes, which means 15 cycles of 2 minutes grinding period. After using the 2 mm balls same sample were used to pulverize with the 0.1 mm balls. 100 g of 0.1 mm zirconia balls were taken in each of the bowls and pulverized for 60 minutes. The result in the chapter 5 includes the finding from various trials and the effective pulverization duration finding process.

4.3.4 Solvent

The wet process was preferred over the dry process because in the dry process, agglomeration of the particles on the inner surface of the bowl occurs. Extensive heat was generated while the milling process. Therefore, to cool the process, the wet process was very effective and it ensured that the particle did not hover around the laboratory environment. While in wet process, the particles slide down from the wall due to lesser friction against the wall. The advantage of using IPA was that, it is volatile and helped to keep the environment cool. Being volatile solvent the IPA dries fast. Therefore, it became easier to dry the sample after milling. Another advantage was IPA has a high boiling point and low vapor pressure

compared to other alcohols. The main advantage of IPA was found after the particle size analyses of nanoparticles. It was found that the IPA gave slightly better particle size distribution than the water. For the milling, 50 ml isopropyl alcohol (IPA) was used in the 80 ml Zirconium Oxide bowl with 10 g of bentonite sample and 100 g of the Zirconia balls. The recommended amount of material to take in the bowl is 10-30 g. It was intended to keep enough space for the grinding operation, which was the main reason behind taking 10 g sample.

4.4 Extraction

The extraction process of the pulverized material was one of the laborious tasks. The samples were shifted to the workable containers from the pulverizer bowl. While shifting the material, it had to be separated from the zirconia balls. The 2 mm and 0.1 mm ball were used for the pulverizing. Separating those balls from the slurry was difficult. The whole work of extraction was conducted into a glove box (fig. 4.7). The main concern for using the incubator was to keep the area uncontaminated. It was mentioned that the nanoparticles could harm the respiratory system when inhaled. Owing to small size, it could pass through the skin and create dermal problems. Though the bentonite was not hazardous, the nanomaterial could be harmful.



Figure 4.7 Glove box

The sieves were used to separate the balls from the sample slurry. The mesh sizes for the separating sieves were 0.8 mm and 0.08 mm. The 0.8 mm mesh sieve was used for the 2 mm zirconia ball separation and the 0.08 mm mesh sieve was used for 0.1 mm diameter balls. The small diameter balls had chance to be mixed with the extracted sample if the sealing rubber band was not placed properly. The extracting apparatus (fig. 4.8) was equipped with a funnel, space for placing the sieve and a syringe. To use the syringe the air is first pushed in the sealed bowl and the increased air pressure pushes down the sample when kept upside down. The main problem while using this method was that the bentonite material was so sticky that the syringe was clogged when IPA evaporated. After using once the syringe needed to be thoroughly washed with the help of water.



Figure 4.8 Extraction device

4.5 Diluting, mixing and applying ultrasonic

The vortex mixture (fig. 4.9) was used to make homogeneous mixture of the pulverized bentonite with twice amount of the IPA volume. The main reason for using for using vortex mixture was that the material was mixed brusquely. For mixing, small amount of stiff slurry from the grinding bowl were collected and mixed with IPA. The maximum

speed of level 10 was used which was equivalent to 3500 rpm. After mixing, the homogeneous slurry was attained which was kept overnight in a beaker that the heavier particles settles at the bottom and the suspended dilute solution was collected. This process helps to separate the bigger particles and it ensures the uniform particle size of the prepared nanomaterial.



Figure 4.9 Vortex mixer

The derived bentonite nanoparticles solution was kept into 250 ml glass beaker and then placed into an ultrasonic bath. Ultrasonic wave helped to breakdown the agglomerated particles from each other. Sanganwar (2009) mentioned ultrasonication could be done to separate the agglomerated particles. While applying the ultrasonic wave with ultrasonic bath (fig. 4.10) the temperature was kept above 40 degree Celsius. It helped to evaporate most of the isopropanol and assign higher kinetic energy to the particles. After the ultrasonication the sample particle size were measured using the Zetrasizer nano S that was discussed in the material and method chapter. Moreover, the agglomeration capacity of the particles could be assessed with the zetapotential results.



Figure 4.10 Ultrasonic bath

4.5.1 Determination of zetapotential

The zetapotential is the charge available on the slipping layer (fig. 4.11) of a particle, the outer layer of the diffuse double layer. The significance of zetapotential is related to the particle colloidal stability. The increased particle charge increases the colloidal movement.



Figure 4.11 Zetapotential (Wikipedia, 2014)

The Zetasizer can also determine the zetapotential of colloidal suspension directly. After finding the zetapotential of the sample, the agglomeration capacity can be predicted. The vials known as cuvette (fig. 4.12) for particle size analysis are different from the zetapotential ones.



Figure 4.12 Zetasizer cuvette

Zetapotential is related to electrophoretic mobility, given by Henry's equation (eq. 27). The electrophoresis is the movement of charged particle under influence of electric field application. The zetapotential cuvette had two electrodes at both ends to apply the electric field. The electrophoretic mobility could be found by relating Doppler Effect on the particle due to application of voltage. Before doing the tests, the nanoparticles suspension with the isopropanol was taken at certain concentration and poured into the cuvette. The software requires the Mie parameters: viscosity, refractive index and absorption values for materials, to determine the zetapotential.

$$U_E = 2 \epsilon^* z^* F \text{ (ka)}/3\eta..... \text{ (eq. 27)}$$
 Where,

 U_E = Electrophoretic mobility

z= Zetapotential

ε=dielectric constant

η=Viscosity

a=particle radius

F (ka) = Henry's Function is 1.0 for nonpolar material and 1.5 for polar materials

K= electric double layer thickness presented as K^{-1} (Debye,s constant)

4.6 Drying

To conduct the laboratory test with the prepared nanoparticles, the nanoparticles needed to be dried. Without the dry material, the exact water content could not be maintained, for the geotechnical laboratory tests. The boiling temperature of the isopropyl alcohol was higher than the other alcohols, which helps to lower the bowl pressure while pulverizing. On the other hand, it resulted longer drying time, but compared to water it was favorable. The drying process was conducted with the isotemperature heater (fig. 4.13). While applying the temperature the sample was stirred simultaneously with the magnet needle at 200 rpm to obstruct the flock formation. After drying the particle size were again measured using the SEM analysis.



Figure 4.13 Isotemperature heater and magnetic mixture

4.7 SEM analysis

The dried samples were used for confirming the particle size, which was determined using the SEM images. Scanning electron microscopy (SEM) is a technique for acquiring high-resolution image of a material at micro scale. The SEM instrument focuses high-energy electrons over the sample that passes through several condenser lenses.

The accelarated electron was targetted towards the material and it relesed different signals depending on the absorbed energy from the electron. The energy difference was closely monitored by the sensor and the signals are processed to generate raster images. The Tescan Mira3 XMU Field Emission Scanning Electron Microscope was used. It provided high resolution (30 kV or 1nm) raster image of the material, placed in a vaccum condition with a chamber pressure of 150 Pa. The magnification range could varry from 2x to 1000000x. A sample size upto 145 mm can be mounted in the instrument. The greatest advantage of SEM was that it was a nondestructive test and the same sample could be used again and again for further analysis. For doing the test, the samples was placed over a metal seat with the background of a carbon surface. Knowing that the clay had negetive charge the particles were preprocessed with the Sputter coater that applies 5nm coating of Palladium to get rid of the ionization, which was responsible for the faulty image. Then the sample was placed into the machine and the images were aquired for several sites at varrying magnification. The processed image were analyzed using Omnimet sofware to determine the particle size in dry condition. The partcle size dimensions were exported to a database file and the particle size histograms were easily attained.

4.8 Chemical analysis

The chemicals present in the prepared nanobentonite needed to be examined because of the chemical intrusion resulting from the pulverizer balls. To ensure that the produced nanoparticles elements were indifferent from the original bentonite sample, the energy dispersive X-ray spectroscopy (XEDS) was done. An extra detector, Oxford X-Max silicon drift detector was connected to the SEM device. The mechanism was same except that the EDS device had an extra detector that can produce a spectrum pattern. Finally, the elements in the sample could be detected using Aztec software by comparing experimental spectrum with the existing spectrum of the elements. The interesting part of the XEDS was the composition of the material could be determined. However the results of Zirconia intrusion into the samples were too low to consider.

4.9 Crystallography Analysis

The X-ray diffraction is another nondestructive method for analyzing the crystallography of the minerals present in the sample. The EDS elemental composition could be compared with the X-Ray diffraction (XRD) analysis result to exactly determine the crystal formation of the composition. The crystal structure of the sample could be determined by studying the angle of deflected ray (fig. 4.14) and the intensity. The principal of XRD analysis was based on the scattered X-ray from the incident beam. The intensity and angle of incident was represented in a graph, which was detected by the detector.

Subsequently, the pattern was analyzed and the inter-planer distance could be measured using the Bragg's law. The lattice structure or the Miller indices were also found by using the X'Pert Highscore software from Pan Analytical. The software was able to determine the crystal composition of the sample by comparing the spectrums. The result found that the montmorillonite content was as high as 70% in the nanoparticles samples. The composition was nearly the same as original bentonite sample, with small deviation.



Figure 4.14 Deflected beam schematic diagram of XRD analysis

4.10 Summary

The mechanism and process of preparing nanoparticles using the ball mill pulverizer was discussed in this chapter. The effects of various controlling factors, that influence nanoparticles preparation, were described. The extraction process and the refining methodology of the nanoparticles were also discussed. The extraction was done inside the incubator with the extractor device. The refining of the nanoparticles was achieved by applying ultrasonic wave, abrupt mixing with the vortex mixture. Nevertheless, providing settling time and collecting the suspended solution improved the particle distribution. Finally, some advanced microscopic test methods were introduced for the confirmation of nanoparticles size, elements and crystals.

Chapter 5: Results and Discussions

5.1 Results

The results of the laboratory-based tests are summarized in this chapter. The chapter is chronologically arranged starting from the material properties, then preparation of nanoparticles to the mechanical and hydraulic behaviour of the compound material. While preparing the nanoparticles the particle size, chemical composition and crystal formations were conferred. The result showed that there was a substantial increase in the mechanical behaviour and decrease in the hydraulic conductivity, which was desired and considered as improvement.

5.1.1 Sand

The properties of the sand were discussed in the materials and methods chapter. The following SEM image (fig. 5.1) shows the microstructure of the sand particle.



Figure 5.1 SEM image of sand

The properties of sand generally vary with their particle size. Uniformly graded sand was used in this study, with a particle size range between 400-600 μ m. The particle size distributions of three sand samples are presented in the following particle size distribution curve (fig. 5.2 and fig. 5.3) along with the cumulative retained percentage. The sand particle size were uniform throughout the matrix, therefore all the curves lie over each other. The three samples had initial weight of 175.83 g, 180 g and 176.5 g, while sieve analysis and the amount of loss were 0.01 g, 0.11 g and 0.15 g respectively (table A.1).



Figure 5.2 Particle size distribution of sand



Figure 5.3 Cumulative percent against size of the particle

5.1.2 Bentonite

The bentonite used in this research was Wyoming bentonite, which was rich in Sodium bentonite. The following SEM image (fig. 5.4) shows the bentonite microstructure.



Figure 5.4 SEM image of bentonite

The particle size of bentonite was captured with the Mastersizer. Finally, the particles sizes were reassured using the SEM image, analyzed with the Omnimet image analysis software. The particle size of bentonite is shown in fig. 5.5. The Mastersizer particle size shows that 10 to 90% (Dx 10 and Dx 90) bentonite material had a particle size between 2 to 100 μ m. In fact, the average particle size (Dx 50) ranges between 14-16 μ m (table A.2).



Figure 5.5 Particle size range of bentonite from Mastersizer

On the other hand, the image analysis software reveals similar particle size distribution of the bentonite material at two different magnification level 1 KX and 0.1 KX

(fig. 5.6 and fig. 5.7). It illustrates that about 95% of the bentonite particle has a particle size less than 15 μ m.



Figure 5.6 Particle size histogram of bentonite after SEM image analysis



Figure 5.7 Cumulative percent against particle size from SEM image analysis

The bentonite sample had residual water in it. Therefore, the water content would participate while doing the geotechnical tests, using the bentonite samples. Therefore, it was essential to know the water content of bentonite and using the dry materials for preparing the mixture. Experiment results shows that the bentonite used in this study had a residual water content of 7.87% (table 5.1).

Weight of	Weight of can	Weight of can	Weight of	Wight of	Water
empty can (g)	with wet soil (g)	with dry soil (g)	soil (g)	water (g)	content
					(%)
21.57	22.53	22.46	0.89	0.07	7.87

Table 5.1 Water content of bentonite sample

5.1.3 Bentonite sand buffer (BSB)

Bentonite sand buffer had various influential properties. For this study, the optimum moisture content and dry density played important role in the one dimensional consolidation test. For running the consolidation test, the dry density of the sample was maintained along with the optimum water content. The compaction test result (fig. 5.8) shows that, BSB material had an optimum water content of 20% and a dry density of 1.91 g/cc.



Figure 5.8 Compaction test result of BSB

5.1.4 Nanoparticles

Preparation of nanoparticles has been one of the most important assignments before conducting the geotechnical laboratory test with the compound matrix. This section summarizes the systematic effort to acquire the nanoparticles from the bentonite. The pulverization was done with different ball diameters, two types of ball material and dispersant, varied speed and widespread duration. The effect of pulverization with different controlling conditions is discussed in the following sections. A clear understanding can be established from the results in the following sections, for selecting the dispersant, ball material, ball size, duration and speed.

5.1.4.1 Ball size

The ball diameter for the ball mill process had an important role while preparing the bentonite nanoparticles. At first, the tests were run using two types of ball materials: zirconium and steel. Two different diameters of balls were also used for both of the ball materials at 200 rpm for 30 min effective duration, with water. It was observed from fig. 5.9 that the particle size distribution shifted towards the left (decrease in particle size) while using the zirconium balls. It was found that the zirconium balls were efficient than the steel balls, for pulverizing which was also established by the hardness theory. On the other hand, greater improvement in the particle size was attained after using smaller balls rather than the 10 mm balls of the same material. From the first phase of experiment, it was found that smaller ball size of Zirconia would be much more effective than the larger balls due to better interaction with the particles. In fact, 2 mm and 0.1 mm Zirconia balls were finally used in this pulverization process.



Figure 5.9 Particle size determination (30 min pulverize @ 200 rpm in water)

5.1.4.2 Solution

It was found that the wet samples were suitable for determining the particle size using the mastersizer or the zetasizer, because in dry condition the particles agglomerates together and showed faulty result. The greater advantage of the wet process was discussed in the material and method chapter in detail. However, with the progress of the experiment, the results of the early section encouraged using smaller diameter Zirconia balls and found 2 mm balls were suitable for pulverizing. Therefore, the water and the IPA were used in the pulverization process at 200 rpm for effective duration of 30 minute using 2 mm Zirconia balls. While using the wet process to determine the particle size distribution using the zetasizer, improvement was observed with the IPA over the water because it acted as a dispersant agent. Moreover, the dipole water molecule took place between the DDL layers that swells the material. As a result, the pulverization process was interrupted when water was used. On the other hand, IPA was found suitable in all other circumstances. It should be mentioned that the dispersant do not improve the particle size but provided better condition to keep the particles apart from each other. Subsequently improves the contrast of the result, acquired from the Zetasizer. However, the fig. 5.10 shows little improvement in particle size distribution using IPA.





Increasing the speed of the rotor, applies higher load on the material for a fixed pulverization period. Several tests were maneuvered to find the effect of speed on the material for duration of 90 minutes. The speeds used were 200, 400 and 800 rpm. The acquired knowledge from the earlier results, suggested using Zirconia balls having diameter of 2 mm in IPA solution. It was also found that with 800 rpm the average particle size of 295 nm could be attained. The following fig. 5.11 is plotted for three different speeds and found that the increasing speed gives smaller size of particle. Therefore, higher speed up to 1100 rpm was targeted to achieve with safe conditions.





5.1.4.4 Duration

In earlier literatures, it was mentioned that after 13 hours of pulverization the nanoparticles of soil could be attained. A faster preparation can be done at higher speed using smaller balls and suitable solvent. The 2 mm balls were used in the early experiments to find out the effect of speed on pulverized particle size. At the final stage, based on previous results Zirconia balls of 0.1 mm were used. Finally, 30 min, 60 min and 90 min duration pulverization were done using 2 mm balls. Afterwards the materials pulverized with 2 mm ball were pulverized again with the 0.1 mm balls. The following fig. 5.12 shows that using 2 mm Zirconium balls for 30 minutes and 0.1 mm zirconium ball for 60 minutes can give the best result. Increasing the duration to 120 minutes did not improve the size at all. Thus, the grinding was done with both 2 mm and 0.1 mm balls for total 90 min (30 min with 2 mm ball and 60 min with 0.1 mm ball).



Figure 5.12 Effect of duration on particle size (pulverizing with Zirconia balls @1000 rpm in IPA)

5.1.5 Zetapotential

The zetapotential was determined using the Zetasizer at a temperature 25 (°C) and pH 7. Zetapotential determines the particle agglomeration capacity. After pulverization, the particle zetapotential was determined. Zetapotential value of -16.8 mV to -19.3 mV was found (fig. 5.13) in case of nanomaterial whereas the bentonite zetapotential was found between -18.5 mV to -21.9 mV. The decrease in zetapotential in nanoparticles was due to the reduction in particle size and uniform distribution of charge within the matrix. It is usual for the particles to agglomerate with each other if the zetapotential value is in between -30 mV to +30 mV. It also indicated that the particle size distribution found from the laser-based technology could not be fully relied if the particles are agglomerated with each other. The accuracy of result mostly depended on the preparation of suspension with the solvent. Therefore, and particle sizes were reexamined with the SEM analysis for further investigation.



Figure 5.13 Zetapotential at 25° C and pH 7

5.1.6 Particle size distribution determination with SEM analysis

The samples were further studied in SEM image to confirm the particle size. Fig. 5.14 to fig. 5.21 shows SEM image of the nanoparticles with comparison to the original bentonite sample. By viewing, the improvement in the particle size can be observed. SEM image of the bentonite nanoparticles were taken at various magnification ranges: 25000 X, 50000 X, 100000 X and 250000 X.



Figure 5.14 25 KX magnification image of bentonite



Figure 5.15 25 KX magnification image of nanoparticles



Figure 5.16 50 KX magnification image of bentonite



Figure 5.17 50 KX magnification image of nanoparticles



Figure 5.18 100 KX magnification image of bentonite



Figure 5.19 100 KX magnification image of nanoparticles



Figure 5.20 250 KX magnification image of bentonite



Figure 5.21 250 KX magnification image of nanoparticles

The Omnimet image analysis software was found useful to determine the dimension of the particles (fig. C.1 to fig. C.4). The problem of analyzing the particle size distribution with the SEM image was that, the images were particularly for specific locations rather than the bulk sample. However, sizes from the images were extracted for varied range of magnification to capture the whole sample. The particle size histogram (fig. 5.22) and the cumulative curve (fig. 5.23) confirmed the particle size between 2 to 300 nm ranges, which comply with the previously analyzed with the laser based technologies. The separate histogram at each magnification level is listed in fig. C.5 to fig C.8. Therefore, from fig. 5.23 it can be concluded that 93.12% of the sample was less than 200 nm and 75.73% of the particles were less than 100 nm. Smaller slits can be useful for further refinement of the particle size.



Figure 5.22 Particle size histogram of nanoparticles from SEM image (samle size, n= 581)



Figure 5.23 Cumulative percentage of nanoparticles against particle size

5.1.7 Energy dispersive spectroscopy (EDS)

EDS is a revolutionary technology for doing the elemental analysis. During the pulverization, the Zirconia balls and the steel balls were used. The ball mill process was an abrasive process to prepare the nanoparticles of bentonite. While pulverization with the balls the elements of the balls intrudes into the pulverized material due to abrasion phenomena. Therefore, from the EDS result suitable ball material could be determined from the elemental point of view. The results (fig. 5.24) showed that while using the steel balls, the iron content

(Fe) was much higher in the nanoparticles sample whereas the amount of Zirconia was found less while using the Zirconia balls. The results were generated using the spectrum, after the ESD analysis and using the AZtech software. Fig. D.5 to fig. D.8 contains the spectrum of the electron images showed in fig. D.1 to fig. D.4. Eventually, Zirconia intrusion was found low, which was due to the hardness of the materials of the ball.



Figure 5.24 Chemical composition of samples under influence of pulverizer ball material

5.1.8 X-ray diffraction

The X-ray diffraction is used mainly to determine the crystal structure of the material. It was one of the groundbreaking inventions of this age and samples were acquired before and after the pulverization. The bentonite sample and the nanoparticles sample were used for the XRD analysis and the acquired patterns were presented with the crystal analysis (fig. 5.25 and fig. 5.26). Moreover, the crystal analysis referred that the bentonite forming crystals were retained after the pulverization and most of the crystals were the same. However, the analysis also refers that the percentage of montmorillonite content was above 70% (fig. 5.27).

This means that, the sample had high swelling capacity. The XRD patterns are shown in fig. E.1 to fig. E.3 and the crystal structure analysis results are shown in fig. E.4. From the summary in fig. 5.27 it was found that the illite content has increased up to 10%, which could be a result of higher temperature while pulverizing. Some of the research mentioned that at temperature more than 100 degree Celsius is prone to convert the bentonite into illite, especially with the presence of Potassium (K). Other than that, the crystal structures were quite similar.



Figure 5.25 XRD pattern and crystals in bentonite







Figure 5.27 Crystal composition comparison between bentonite and nanoparticles

The XRD analyses also confirm the miller index of the montmorillonite (table 5.2) content and the interlayer d spacing (fig. E.4) at the atomic level. For montmorillonite, the interlayer d spacing was found with a range of 2 Å to 12 Å. The analysis was done using the X'Pert Highscore software from Pananalytical.

Crystal system:	Monoclinic	
a (Å):	5.18	
b (Å):	8.98	
c (Å):	10.05	
Alpha (°):	90	
Beta (°):	101.4	
Gamma (°):	90	

 Table 5.2 Miller indices of montmorillonite

5.2 Compound matrix behaviour

The behaviour of the bentonite sand buffer and the nanoparticles are discussed in to two major sections: mechanical behaviour and hydraulic behaviour.

5.2.1 Mechanical behaviour

The mechanical behaviour describes the load bearing capacity of the material. The more load the material can take, the better it suits into the deep underground condition. Therefore, higher stiffness was expected and the results are discussed in the following sub sections.

5.2.1.1 Index property

Liquid and plastic limit testing was done with the sodium bentonite and the nanoparticles according to ASTM D4318. Liquid limit and plastic limit of the sodium bentonite was respectively 485.5% and 71.3%, which results the plasticity index of 414.2%. The results showed (fig. 5.28) improvement in the liquid limit (fig. F.1) and decrease in the plastic limit (table F.1). The plasticity index at 4.5 % additional nanoparticles was 519% when liquid limit was 554.96% and plastic limit was 35.96%. The outcome of this resultant

effect was increase in plasticity index. The plasticity index is related to the compression behaviour of the material. Higher the plasticity indexes, higher the compression resistance. Therefore, the preliminary index property test encouraged to run detailed investigation on the mechanical behaviour. The result of the index property also indicated that there was an optimum range of nanoparticles up to which the plasticity index improved and decreased again and remained steady afterwards. The optimum plasticity index was found at 4.5% additional nanoparticles.



Figure 5.28 Index property of compound matrix

5.2.1.2 Compaction test

The compaction test was done with the bentonite sample to determine the effect of nanoparticles. It was desired that the increase in plasticity index would increase the stiffness of the matrix. The compaction test result (fig. 5.29) indicated that the maximum dry density improved with additional 1% nanoparticles from 1.32 g/cc to 1.49 g/cc. The dry density was improved significantly up to 1.51 g/cc with 2.5% additional nanoparticles. However adding higher amount of nanoparticles did not increase the strength and the dry density and it remained steady (fig. G.1). On the other hand, the optimum moisture content of the sample
decreased with the additional nanoparticles. The optimum moisture content decreased sharply from 46% to 32% for 2.5% nanoparticles addition. After 4.5% additional nanoparticles, the optimum water content started increasing again and the maximum dry density started falling.



Figure 5.29 Compaction test result

5.2.1.3 Unconfined compression

The unconfined compression test indicated the bearing capacity as well as the shear capacity of the material. In other words, unconfined compression test was related to the mechanical behaviour of the material. The unconfined compression test result (fig. 5.30) suggested that the percentage of nanoparticles up to 4.5% of the bentonite content improved the strength of the material but the strength started falling from the peak with higher amount of additional nanoparticles. Fig. H.3 and fig. H.4 contains the test history and fig. H.1 and fig. H.2 contains the stress strain behaviour of the unconfined compression test. The original sample showed steady increment from 585.84 kPa to 710.62 kPa in unconfined compression strength. However, the similar improvement pattern was observed with the remolded

samples. Higher strength was attained with the remolded samples, which took place due to the particle redistribution and their interlocking behaviour.



Figure 5.30 Unconfined compression test result

5.2.1.4 One dimensional elastic modulus

Apart from the hydraulic conductivity found from the one dimensional consolidation test, some of the parameters were related to the mechanical behaviour of the sample. The graph (fig. 5.31) depicts that the one-dimensional elastic modules of the BSB material improved with the additional nanoparticles at three loading stages: 800, 1600 and 3150 kPa. At lower loads, it increased sharply up to 4% and was steady with higher percentage of nanoparticles addition. For the highest load (3150 kPa), it showed sharp improvement at 1% and a fluctuated improved behaviour with addition of nanoparticles. The test histories are shown in fig. I.1 to fig. I.15.



Figure 5.31 Variation of elastic modulus with nanoparticles

5.2.1.5 Void ratio

The void ratio of the samples, with variation of nanoparticles also varied. From the result (fig. 5.32) it could be found that, the void ratio increased at 2% additional nanoparticles at a certain applied pressure. Using the results in fig. 5.33 this behaviour could be explained. At 2% the swelling index was the highest, which caused the increase in void ratio at 2% additional nanoparticles. For instance, it increased from 0.24 to 0.37 at 800 kPa load at 2% additional nanoparticles.



Figure 5.32 Variation of void ratio with nanoparticles

5.2.1.6 Compression and swelling index

The results depicts (fig. 5.33) that the compression index (Cc) gradually decrease steadily with increased nanoparticles percentage. On the other side, the swelling index (Cs) increases with additional nanoparticles and started falling again after 2% additional nanoparticles. It could occur for the particle's microstructure and redistribution. From the result of index property, it could be assessed that for additional nanoparticles, the compression index was going to drop and the load resistance was going to improve. The values of the compression index (Cc) and the swelling index (Cs) are shown in the fig. 5.33.



Figure 5.33 Consolidation coefficients

5.2.2 Hydraulic behaviour

The improvement in hydraulic behaviour implies to the decrement of the hydraulic conductivity. When the hydraulic conductivity deceases, the intrusion of water is also decreases. The hydraulic conductivity relates to the hydraulic behaviour of the material. The hydraulic conductivity was measured from the one dimensional test result. The lower the hydraulic conductivity, the lesser is the water intrusion. The results show that in each of the loading stage the hydraulic conductivity decreases.

minimize the water intrusion. As well, the additional nanoparticles also decreased the hydraulic conductivity, which was confirmed by both of the methods. Results were summarized for the Tyler's method and the rectangular hyperbola method in fig. 5.34. It was found that at 800 kPa the hydraulic conductivity improved from 10^{-18} m/s to 6.8×10^{-20} m/s in Tyler's method. At 3150 kPa load, the conductivity was also found decreasing from 3.2×10^{-21} m/s to 1.5×10^{-21} m/s in the rectangular hyperbola method, which was a substantial improvement in the hydraulic behaviour.



Figure 5.34 Change in hydraulic behaviour of compound due to nanoparticles

5.3 Summary and discussions

In this chapter, results were presented in three major sections: materials general behaviour, nanoparticles preparation and confirmation and finally the compound matrix behaviour. Using the methodology stated in chapter-3, the results of the particle size of the material with few other important properties were presented. The preparation of nanoparticles from the bentonite samples were conversed in details. The factors influencing the preparation of nanoparticles were presented chronologically with sufficient evidence. The

selection of various factors for preparing the nanoparticles could be understood from the presented results. Afterwards the results of the chemical elements and crystal analysis of nanoparticles were depicted. Nevertheless, the chapter included the summary of the laboratory test results. The compound material showed improved behaviour, which could be recognized from the presented results. The improved behaviour was presented in two major sections: mechanical behaviour and hydraulic behaviour, for clear understanding. The acquired results and the improved behaviour are discussed in the following chapter with recommended future research.

Chapter 6: Conclusions and discussions

6.1 Summary

The research findings are briefly summarized in this chapter, which also include comprehensive analysis of the results. To obtain the objectives, nanoparticles-assimilated bentonite sand buffer and its hydro-mechanical properties were investigated.

The silica sand and Wyoming bentonite received from AECL were used for the laboratory studies. The nanoparticles were prepared from bentonite materials, using ball mill pulverizer. The XEDS elemental analysis was performed with the pulverized nanoparticles. The results suggested that pulverizing with the zirconia balls were suitable, because less chemical intrusion occurred in to the bentonite nanoparticles. Bentonite was pulverized for an effective duration of 90 minutes with 2 mm and 0.1 mm zirconia balls at 1000 rpm using IPA solvent. The bentonite had an average particle size around 15 µm. After pulverizing, the particle size of the pulverized material was determined using Zetasizer at preliminary stage and then rechecked with the Omnimet image analysis software. The particle size distribution confirmed that 75.37% particles were less than 100 nm and 93.12% particles were less than 200 nm. The XRD analysis results proved that the crystal structure of the original bentonite sample was intact except small rise in illite content, which could be the outcome of temperature rise inside the pulverizer bowl with the presence of potassium. The hydraulic and mechanical behaviour summarized in the following paragraphs showed that 4.5 % additional nanoparticles had greater effect on the matrix with an optimum behaviour.

The tests results indicated that the mechanical behaviour was influenced by the additional nanoparticles. The plasticity index was increased with addition of nanoparticles and maximum improvement was anticipated at 4.5% additional nanoparticles. The plasticity

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index improved 14.1%, from the original bentonite. At the same time, the maximum dry density of the bentonite improved by 14.3% with 30.4% decrease in optimum water content. Likewise, the index property, the optimum water content was found minimum at 4.5 % additional nanoparticles. At the same time, the maximum dry density increased and remained steady within 2.5% to 4.5% additional nanoparticls. The remolded unconfined compression sample reflected less improvement than the newly prepared ones. A newly prepared sample, displayed a compressive strength of 585.85 kPa and it increased gradually up to 710.62 kPa at 4.5% addition of nanoparticles. The compression tests results were validated using the compression index results (fig. 5.33), which decreased steadily with increased amount of nanoparticles. From the consolidation tests with three stages of loading (800, 1600 and 3150 kPa) phase in a constant volume method the void ratio was found to be steady, but then again an abrupt increase was monitored at 2% additional nanoparticles (fig. 5.32). The increase was due to the microstructural changes when the nanoparticles revealed the highest swelling property. This is again supported by the swelling index result (fig. 5.33). The swelling index increased at 2% additional nanoparticles and thereafter it decreased.

The hydraulic conductivity was one of the critical parameter that was intended to improve. The hydraulic conductivity of the one dimensional oedometer sample was determined according to the equation proposed by Craig (2004). The coefficient of consolidation was one of the key parameter for determining hydraulic conductivity. Uncertainty in obtaining the coefficient of consolidation determination from one-dimensional oedometer tests were kept in mind. Thus, the coefficient of consolidation was calculated using two methods to compare the results. Both of the methods gave the similar kinds of results. Additionally, it should be mentioned that the coefficient of consolidation from the rectangular hyperbola method was much consistent than the Tyler's method. Moreover, the coefficients of consolidation from the rectangular hyperbola were found slightly lower than the other one. Later on, a small statistical study was carried out for a confidence level of 95% with a sample size, n=2. The standard deviation of the results from the both of the methods lies between 0-0.443. The confidence interval was found to be quite small in number, the lowest being 0.001 and the highest is 0.614. Thus with a confidence level in between 95±.0001% to 95±0.614% it can be summarized that the hydraulic conductivity of the compound matrix decreased in all loading stages.

6.2 Recommended future works

The Preparation of nanoparticles could be a costly process. However, the time involved in the preparation can be minimized by introducing high-pressure extraction process with simultaneous sonication. The future study can be carried out with the refined nanoparticles derived from small opening membranes. The optimum amount of nanoparticles that exhibits the best performance of the matrix can be determined, conducting the regression analysis on the acquired data and performing optimization, considering the hydraulic and mechanical parameters. This study was mainly focused towards the BSB behaviour with additional nanoparticles prepared with distilled water but similar studies can be performed with other types of clay barriers. Similar research can also be carried out to investigate the effect of salinity on the clay barriers systems. The underground repository environment having varied thermal gradient generally reveals unsaturated behaviour, which can be an interesting topic of research. Finally, the study offers great scope for future development of constitutive models and numerical simulations.

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Appendices

Appendix A: Material particle size

(mu) əz	Weight retained (g)		Percer	Percent retained (%)		Cumulative retained (%)		Percent passing (%)				
sieve sı	Test-1	Test-2	Test-3	Test-1	Test-2	Test-3	Test-1	Test-2	Test-3	Test-1	Test-2	Test-3
<i>6</i> 3 <i>0</i>	26.61	28.32	27.64	15.13	15.75	15.68	15.13	15.75	15.68	84.86	84.25	84.32
425	134.47	134.56	133.88	76.48	74.84	75.97	91.62	90.59	91.65	8.37	9.41	8.34
315	13.3	12.8	13.0	7.59	7.13	7.41	99.2	97.7	0.66	0.77	2.27	0.92
160	1.07	2.33	1.15	0.61	1.29	0.65	99.82	99.02	99.72	0.17	0.98	0.27
80	0.09	1.41	0.32	0.05	0.78	0.18	99.88	99.80	99.90	0.11	0.19	0.09
0	0.21	0.35	0.16	0.11	0.19	0.09	100.00	100.00	100.00	0.00	0.00	0.00

Table A.1 Sieve analysis data of sand

Table A.2 Bentonite sample particle size (using Mastersizer)

Number of run (nos)	D ₁₀ size (μm)	D ₅₀ size (μm)	D ₉₀ size (µm)
1	1.62	15.8	83.1
2	1.59	15.2	72.6
3	1.61	15.7	84.5
4	1.56	14.7	66.6
5	1.57	15	71.3
6	1.6	14.7	64
7	1.51	14.7	71.9
8	1.52	14.9	74.6
9	1.53	15.2	83.4
10	1.52	14.9	75.7
11	1.5	14.6	70.6

Appendix B: Compaction Test result of BSB

Weight of mold with soil (g)	Weight of soil(g)	Weight of can (g)	Weight of can + moist soil (g)	Weight of can + dry soil (g)	Weight of soil (g)	Weight of water(g)	Bulk density(g/cc)	Water content (%)	Average Water content (%)	Dry density (g/cc)
1742.30	197.3	20.71	21.84	21.71	1.00	0.13	1.73	0.13	0.14	1.52
		21.29	22.17	22.06	0.77	0.11		0.14		
1796.00	251.0	21.23	21.78	21.70	0.47	0.08	2.20	0.17	0.18	1.86
		20.64	21.63	21.47	0.83	0.16		0.19		
1806.00	261.0	20.61	21.78	21.57	0.96	0.21	2.29	0.22	0.20	1.90
		21.42	23.17	22.89	1.47	0.28		0.19		
1803.00	258.0	20.96	22.25	22.00	1.04	0.25	2.26	0.24	0.24	1.83
		21.47	22.88	22.61	1.14	0.27		0.24		
1796.20	251.2	20.95	23.67	23.10	2.15	0.57	2.20	0.27	0.26	1.74
		21.30	24.07	23.49	2.19	0.58		0.26		

Table B.1 Compaction test data of bentonite sand buffer

Appendix C: Particle size analysis with SEM image



Figure C.1 25 KX image (analyzed with Omnimet)



Figure C.2 50 KX image (analyzed with Omnimet)

10 10		1000	
D1 : 0.06 µm	D15:0.08 um	D44 : 0.06 µm	D4 : 0.03 µm
	0.08 μm	D3 : 0.06 µm	D7 : 0.05 µm
D6 : 0.07 µ	m	D14 : 0.06 µm	D16 : 0.04 µm
	42 : 0.03 µm	(hun /)	D11 : 0.04 µm
D13 : 0.09 µm	D8 : 0.07 μm	5 : 0.08 µm D43 : 0.05 µm	. 0
1 and a	D17 : 0.05 µ	m D21:0.08	D18 : 0.04 µm
D47 : 0.04 µm	D9 : 0.05	um 531	D20 : 0.05 µm
NA A	D26 : 0.07 µm	D19 : 0.03 µ	
D48 : 0.08 µ	27 : 0.04 μm	772	D23 : 0.05 µm
	D25 : 0.07 µm	D24 012 pm	D22 : 0.08 µm
D39 : 0.05 µm	D33	0.08.um	D28 : 0.10 µm
		D31 : 0.	04 µm
D40 : 0.0	8 μm 10.	57 : 0.04 µm	D29 : 0.11 µm
1 - Car	D34 : 0.09 µm	2	D36 0.04 µm
D38	0.03 μm D35 : 0.03 μm	n	D30 ; 0.04 µm
SEM HV: 20.0 kV	WD: 2.22 mm	huntun	MIRA3 TESCAN
SEM MAG: 100 kx	Det: InBeam + SE	500 nm	VIERO NA CARACTERISTICS
BI; 10.00	Date(m/d/y): 01/15/14		UBCO SEMLAB

Figure C.3 100 KX image (analyzed with Omnimet)

D25 . 0.04 µm D25 . 0.04 µm D23 D16 : 0.04	0.000 µm D19: 0.10 0.02 µm µm	(ym) D18-0.04 ym D18-0.04 ym D17-0.05 ym	03:000 pm 15:007.ym
1812-000	D5 : 0.10 00 µm D8 : 0.05 µm	1971 0 1077 0 1021 0	1020 - 0.03 µm 102 µm 103 µm
D24 0.05	1010 0.09 µm	1222-10.03 µm.	D8 0.08 µm
D15	.0.06 µm	014 : 0.02 pr 9:0:11 pm	n D11 : 0,15 µm
SEM HV: 20.0 KV	WD: 2.22 mm	STREET, STREET	MIRAJ TESCAN
SEM MAG: 250 kx	Det: InBeam + SE	200 mm	united and the second s
BI: 10.00	Date(m/d/y): 01/15/14		UBCO SEMLAB

Figure C.4 250 KX image (analyzed with Omnimet)



Figure C.5 Histogram from 25 KX SEM image analyses



Figure C.6 Histogram from 50 KX SEM image analyses



Figure C.7 Histogram from 100 KX SEM image analyses



Figure C.8 Histogram from 250 KX SEM image analyses

Appendix D: Chemical analysis with XEDS



Figure D.1 100 X image of sand



Figure D.2 500 X image of bentonite


Figure D.3 500 X image of nanoparticles (site 1)



Figure D.4 500 X image of nanoparticles (site 2)



Figure D.5 EDS spectra of sand sample



Figure D.6 EDS spectra of bentonite sample



Figure D.7 EDS spectra of nanoparticles sample (site 1)



Figure D.8 EDS spectra of nanoparticles sample (site 2)

Appendix E: Crystal analysis with XRD











Figure E.3 Comparison of XRD patterns



Figure E.4 XRD analysis sample using Pananalytical software

Average water content (%)	Water Content	Weight of water (g)	Weight of soil (g)	Weight of can + dry soil (g)	Weight of can + moist soil (g)	Weight of can (g)	Trial no.	Nanoparticles Percentage (%)
71.33	50.94	0.27	0.53	21.23	21.50	20.70	1	0
	125.81	0.78	0.62	21.52	22.30	20.90	2	
	37.25	0.19	0.51	21.41	21.60	20.90	3	
43.06	43.86	0.25	0.57	28.93	29.18	28.36	1	Ι
	43.33	0.13	0:30	28.61	28.74	28.31	2	
	42.00	0.21	0.50	28.94	29.15	28.44	3	
48.31	55.56	0.20	0.36	21.86	22.06	21.50	1	2.5
	48.57	0.17	0.35	21.65	21.82	21.30	2	
	40.82	0.20	0.49	21.09	21.29	20.60	3	
38.22	40.00	0.24	09.0	22.02	22.26	21.42	1	4
	39.58	0.19	0.48	21.98	22.17	21.50	2	
	35.06	0.27	0.77	21.49	21.76	20.72	3	
35.96	34.00	0.17	0.50	21.93	22.10	21.43	1	4.5
	35.59	0.21	0.59	22.07	22.28	21.48	2	
	38.30	0.18	0.47	21.77	21.95	21.30	3	
65.03	66.67	0.32	0.48	21.18	21.50	20.70	1	5
	79.49	0.31	0.39	21.99	22.30	21.60	2	
	48.94	0.23	0.47	20.87	21.10	20.40	3	
40.04	35.09	0.20	0.57	21.97	22.17	21.40	1	7.5
	42.86	0.18	0.42	21.92	22.10	21.50	2	
	42.19	0.27	0.64	21.37	21.64	20.73	3	

Appendix F: Index property of compound matrix

Table F.1 Plastic limit data



Figure F.1 Liquid limit test data plot



Appendix G: Compaction test of BSB compound





Appendix H: Unconfined compression test summary

Figure H.1 Stress-strain curve of UC test (original sample)



Figure H.2 Stress-strain curve of UC test (remolded sample)



Figure H.3 UC test history (original)



Figure H.4 UC test history (remolded)

Appendix I: Consolidation test summary



Figure I.1 Consolidation test history (bentonite sample)



Figure I.2 Consolidation test history (compound sample)



Figure I.3 √Time and change in displacement (at 0% nanoparticles)



Figure I.4 $\sqrt{\text{Time and change in displacement (at 1% nanoparticles)}}$



Figure I.5 VTime and change in displacement (at 2% nanoparticles)



Figure I.6 VTime and change in displacement (at 4% nanoparticles)



Figure I.7 VTime and change in displacement (at 5% nanoparticles)



Figure I.8 One dimensional elastic modulus summary



Figure I.9 Void ratio against stress (0% nanoparticles)



Figure I.10 Void ratio against stress (1% nanoparticles)







Figure I.12 Void ratio against stress (4% nanoparticles)



Figure I.13 Void ratio against stress (5% nanoparticles)



Figure I.14 Using coefficient of consolidation from Tyler's method



Figure I.15 Using coefficient of consolidation from rectangular hyperbola method