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Effect of Sodium Chloride on Plasticity, Swelling and Compressibility Characteristics of Organo-Nanoclay Amended Bentonite

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Abstract. Compacted layers of soil and bentonites have been employed as hydraulic barriers in waste containment applications. They are effective in preventing leachate from reaching the surrounding soil and groundwater. However, in the presence of inorganic salts, heavy metals, and organic contaminants in the leachates, the properties of the liner material change, limiting its effectiveness as a liner material. Researchers have demonstrated that organoclays can effectively control and adsorb organic pollutants from wastewater and leachates. Hence, bentonite amended with organoclay can be used effectively as a liner material. The effect of a common inorganic salt in leachates, NaCl, on the geotechnical properties of organo-nanoclay amended bentonite is examined in this work. A series of tests were conducted using NaCl solutions at concentrations of 0 (DI water), 0.1, and 1N, and its influence on organoclay amended bentonite was investigated using free swell test, Atterberg limit's test and consolidation test. The experiments' outcomes showed that adding organoclay reduces salts' effect on its liquid limit, plasticity index, free swelling, swelling potential and compressibility of bentonite.

Keywords: organoclay; swelling; inorganic contaminant; landfill liner

1 Introduction

Bentonite-based liners have been employed for various geotechnical applications such as landfill barriers and covers, vertical cutoff walls and permeable reactive barriers for several waste types. These applications are mainly due to the peculiar characteristics of the montmorillonite clay mineral present in bentonite. Due to the presence of this mineral, it possesses high specific surface area, high cation exchange capacity, high retention characteristics, high swelling and thereby low hydraulic conductivity (Mesri and Olson, 1971). Previous research showed that the geotechnical properties of these bentonite-based liners are highly affected by the type and concentration of contaminants in leachate (Mishra et al., 2015; Ray et al., 2020).

The municipal solid wastes, as well as hazardous wastes, contain different types of inorganic, organic pollutants as well as heavy metals. The efficiency of bentonite liners drastically reduces when it is in contact with these pollutants, especially organic ones. Previous studies displayed a variety of bentonite amendments such as flyash-bentonite, zeolite- bentonite, sand-bentonite and soil-bentonite are employed to improve the efficiency of these liners (Prashanth et al., 2001; Kaya and Durukan, 2004; Rout and Singh, 2020). Modified bentonites are one solution to contain and retard the organic pollutants and increase liner efficacy (Sreedharan, 2013; Javadi et al., 2017).

Organoclays are modified bentonites produced by the replacement of inorganic cations present in the interlayer of bentonite with organic quaternary ammonium cations, thereby converting it from hydrophilic to hydrophobic and organophilic. The presence of organic cations increases the interlayer spacing and helps to adsorb organic pollutants from the leachates. The idea of utilizing organoclays for barrier applications has been studied for the past few decades. From the results, it was proved that organoclays could potentially adsorb organic pollutants from leachate and thereby prevent the contaminants from polluting surrounding soil and groundwater. However, the organoclays being a relatively costly material, it was suggested to utilize as a bentonite liner amendment.

Many researchers have studied the utilization of organoclays for adsorbing and removing various organic solutions and fuels (Gitipour et al., 1997, 2015; Burns et al., 2006). Akbulut et al. (2013) studied the geotechnical characteristics of anionic and cationic surfactant based organoclays. They discovered that the addition of any surfactants decreased the specific gravity, unconfined compressive strength, and maximum dry density of organoclays, but raised the optimum moisture content and swelling pressure of anionic surfactant based organoclays. Lee et al. (2012) and Benson et al. (2015) investigated the geo-environmental properties of organoclay-sand mixtures for applying in barrier applications. Javadi et al. (2017) had done an experimental investigation on organoclay amended silty clay to understand its advective and retardation effect under gasoline and naphthalene solution. They recommended employing an organoclay-silty clay mixture in a proportion of 10:90 to reduce hydraulic conductivity to gasoline with- out compromising hydraulic conductivity to water. An optimum combination of sand, bentonite and organoclay was suggested by Heidarzadeh and Parhizi (2020) for clay liner applications by studying the hydraulic conductivity and adsorption properties under different concentrations of phenol solutions.

Most of the previous studies focused on the effect of organic contaminants on the geotechnical performance of organoclays. However, there is a high chance of liner being in contact with inorganic solutions such as NaCl in liner applications. Hence the effect of such inorganic solutions on the performance of organoclay-based liners should be thoroughly investigated. To the best of my knowledge, very few studies were conducted on organoclay amended bentonite for barrier applications. However, no studies have been reported on the geotechnical performance of organoclay-bentonite liners when it is permeated with inorganic salt solutions. This study envisages the utilization of organoclay amended bentonite for various barrier applications under the effect of sodium chloride solution. The variation in plasticity and swelling characteristics of organoclay amended bentonite in sodium chloride solution is studied in detail by performing suitable experimental procedures.

2 Materials and Methodology

2.1 Materials

The bentonite used for the current experimental program was obtained from Rajasthan, India. The soil was thoroughly mixed, sieved through 75micron and stored in a cylindrical drum. And the nanoclay used for the bentonite amendment was an organically modified one. The basic properties of the bentonite and organoclay-bentonite mix are displayed in Table 1. A commercially available organoclay was purchased from Ultra Nanotech Private Limited, Bangalore, India, and the cationic surfactant used was dimethyl di(hydrogenated tallow) alkylammonium salt. The organoclay was based on natural bentonite and was off-white. The characteristics of organoclay as provided by the company are shown in Table 2.

For the present study, a mixture of bentonite and organoclay was used in the proportion of 90:10 by dry weight basis. This proportion is chosen based on the previous research works in this area (Ghavami, 2017; Javadi et al., 2017) and for effectively utilising this liner in the presence of both organic and inorganic pollutants. Since the concentration of organic contaminants in municipal solid waste (MSW) and industrial leachates was observed to be lesser when compared to inorganic pollutants, a lesser percentage of organoclay might be sufficient for effectively removing both organic and inorganic contaminants.

Table 1 Properties of bentonite and organoclay-bentonite (10:90) mixture

Properties	**Bentonite**	**Organoclay-bentonite mixture (BNC)**
Specific gravity	2.68	2.56
XRD d_{001} spacing (nm)	1.05	1.32
Liquid limit (%)	275	180
Plastic limit (%)	38	46
Free Swell Index (mL/2g)	36	18
Maximum dry density, MDD (g/cc)	1.36	1.34
Optimum moisture content, OMC (%)	35	34

Table 2 Properties of organoclay (provided by the company)

Properties	**Organoclay**
Moisture content, %	< 3
XRD d_{001} spacing (nm)	3.40
Loss on ignition (%)	56
500µ pass rate (%)	> 95
Particle size, D50 (µm)	< 10
Specific gravity	1.7
Modifier	Dimethyl di(hydrogenated tallow) alkyl ammonium salt

Permeant Solution

Based on the literature, the presence of sodium chloride ions was confirmed in MSW and industrial leachates (Dutta and Mishra, 2016). The permeant used for the present work is sodium chloride, and it was purchased from Sigma-Aldrich chemicals, India. The experiments were conducted on 0, 0.1 and 1 N concentrations of sodium chloride solutions. The respective concentrations were obtained by dissolving appropriate amounts of salts in 1L deionized water.

2.2 Methodology

The maximum dry density (MDD) and optimum moisture content (OMC) of the bentonite and organoclay amended bentonite was found using the mini compaction test explained by Sridharan and Sivapullaiah (2005). The plasticity characteristics of bentonite and organoclay amended bentonite were studied using Casagrande's test and thread rolling method based on ASTM D4318(2017). The procedure described in ASTM D5890 (2009b) was used to determine the free swelling of soil samples. The oedometer swell, time-swelling plots and compressibility characteristics for soil samples were obtained by performing an oedometer test based on ASTM D2435 (2011).

Characterization of bentonite and organoclay

The characterization of both parent materials was conducted using X-ray diffraction test, XRD (SmartLab, Rigaku Technologies, Japan), and Fourier transform infrared spectroscopy, FTIR. From the XRD results (Fig. 1), it was observed that the basal spacing of organoclay was much higher than that of bentonite. And also, the presence of Montmorillonite mineral was confirmed in both organoclay and bentonite. From the FTIR studies (Fig. 2), the hydrophobic characteristics of organoclay were approved by the absence of peak at 3400cm^{-1} and by comparing the reduced peak intensity at 1640 cm^{-1}. The presence of additional peaks at 2921 cm^{-1} and 2951 cm^{-1} represents the intercalation of organic alkyl ammonium compounds in organoclay. The peaks at 789 cm^{-1} and 687 cm^{-1} for bentonite represent the presence of quartz content in bentonite.

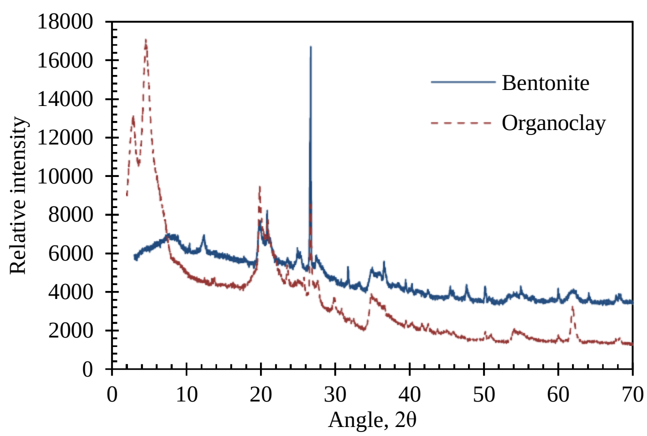

Fig. 1 XRD results of bentonite and organoclay

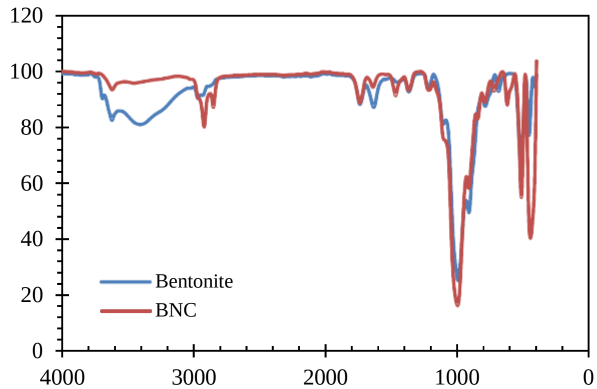

Fig. 2 FTIR results of bentonite and organoclay

3 Results and Discussions

3.1 Compaction characteristics

The MDD and OMC of bentonite and organoclay amended bentonite mixed with DI water were determined by performing mini compaction test. The MDD and OMC were observed for bentonite as 1.36 g/cc and 35%, respectively. At the same time, organoclay amended bentonite showed a value of 1.34 g/cc and 34%, respectively. The slight reduction in OMC for the organoclay-bentonite mixture could be attributed to the less water affinity of the organoclay fraction in the mix. The reduced value of specific gravity of organoclay-bentonite mixture might be due to the difference in soil fabric and increased basal spacings of organoclays. The alteration of soil fabric (formation of flocculated structure) and the increased basal spacings of organoclays might be the reason for reduction in specific gravity. This reduction may result in the decreased value of maximum dry density for BNC (Akbulut et al., 2013).

3.2 Plasticity characteristics

The liquid limit of bentonite and organoclay amended bentonite when permeated with different NaCl salt solutions was determined using Casagrande's method. It was observed from Fig. 3 that the liquid limit of both bentonite and organoclay amended bentonite decreases with an increase in salt concentrations. In bentonite, the diffused double layer reduction and flocculation of soil particles occur in saline environments, which can be described as the possible reason for the decrease in plasticity properties. In BNC mixtures, the organoclay fraction tries to reduce the interparticle repulsion and water holding capacity due to its hydrophobic nature. The presence of sodium chloride further minimises the repulsion between particles; therefore, the liquid limit of the BNC mix reduces. The plasticity index of both bentonite and BNC was also significantly reduced as there is only a slight increase in plastic limit for both soil samples in the presence of sodium chloride solution.

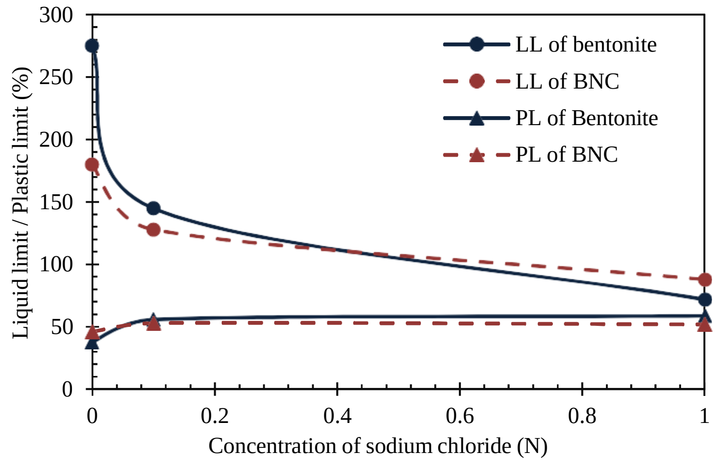

Fig. 3 Variation in plasticity properties of bentonite and organoclay amended bentonite in the presence of various concentrations of NaCl salt solutions

3.3 Swelling characteristics – Free Swell and oedometer swell

To understand the swelling properties of organoclay amended bentonite in saline conditions, free swell and oedometer tests were conducted at different concentrations of sodium chloride solutions. Both results showed that the presence of inorganic salts significantly reduces the free swell and oedometer swell of organoclay amended bentonite. However, the effect of inorganic salts on organoclay amended bentonite was comparatively less than that of bentonite. At higher concentrations of the solution, both samples displayed almost similar swell values.

Adding salt solutions stabilizes the surface charge of the bentonite and decreases the adsorbed water. This process tries to shrink the clay particles, reducing swelling considerably as the salt concentration increases (Rout and Singh 2020). Sodium bentonites are very sensitive to a saline environment, so a drastic reduction in swelling was ob- served when sodium chloride solutions replaced the permeant. Adding 10% organoclay to bentonite reduces the effect of salt solutions on bentonite. From Table 3, it was observed that the addition of 1N NaCl solution showed almost identical swelling as bentonite. When the permeant is replaced from DI water with 1N NaCl solution, a percentage reduction of 86.11% and 77.77% were observed for free swelling value. Similarly, oedometer swell also showed a significant decrease for bentonite, and comparatively lesser swell for organoclay amended bentonite samples.

Table 3 Free Swell Index and Oedometer swell of bentonite and organoclay-bentonite mix when inundated with different concentrations of sodium chloride

Concentration of NaCl (N)	**Free Swell Index (ml/2gm)**		**Oedometer Swell (%)**	
	B	**BNC**	**B**	**BNC**
0	36	18	36.8	29.4
0.1	14	12	20.9	9.5
1	5	4	10.9	6.7

Fig. 4 displays the time-swelling plot for bentonite and BNC when permeated with 0, 0.1 and 1N concentrations of NaCl solution. It was observed that the increase in salt concentrations tends to suppress the swelling of both bentonite and organoclay amended bentonite. At any concentrations, organoclay amended bentonite showed lesser swelling than bentonite. The organoclay fraction present in the mixture may suppress the swelling of bentonite due to its peculiar hydrophobic characteristics (Sreedharan 2013). This might be the reason for the reduced swelling value of organoclay-bentonite mixture. The results showed that the swelling characteristics of organoclay amended bentonite depends on the concentration of inorganic salt solutions. However, at very high concentrations, the swelling properties tend to converge to almost the same value for both the soil samples.

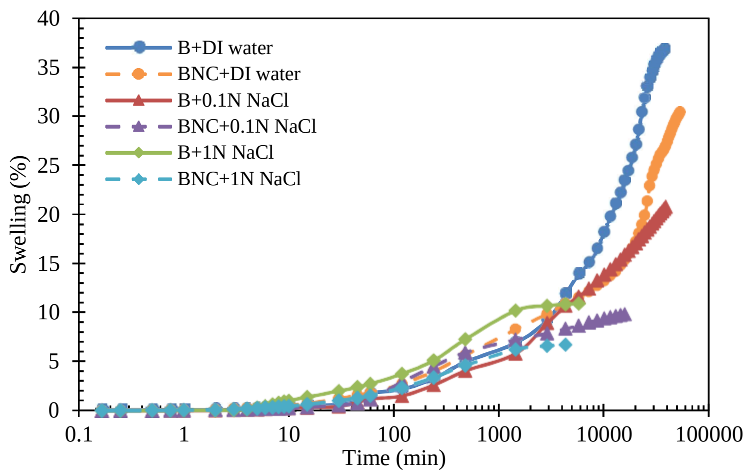

Fig. 4 Time-swelling plot for bentonite and BNC when permeated with sodium chloride salt solutions

3.4 Compressibility characteristics

Fig. 5 showed the variation in void ratio and pressure (e-log P) curve for both bentonite and BNC at different concentrations of NaCl solutions. A higher reduction in the void ratio was observed for bentonite samples inundated with DI water. As the swelling is maximum for that sample, higher compressibility was observed. For BNC samples, the presence of organoclay fraction reduces the water affinity, and the associated reduction in swelling may be the reason for the reduced compressibility of BNC samples. When the concentration of NaCl increases, there is a reduction in compressibility observed for both bentonite and BNC samples. However, the effect is comparatively lesser for BNC samples. When the NaCl concentration increases from 0 to 0.1N, more reduction in compressibility was observed. The difference in compressibility decreases when the salt concentration increases from 0.1 to 1 N.

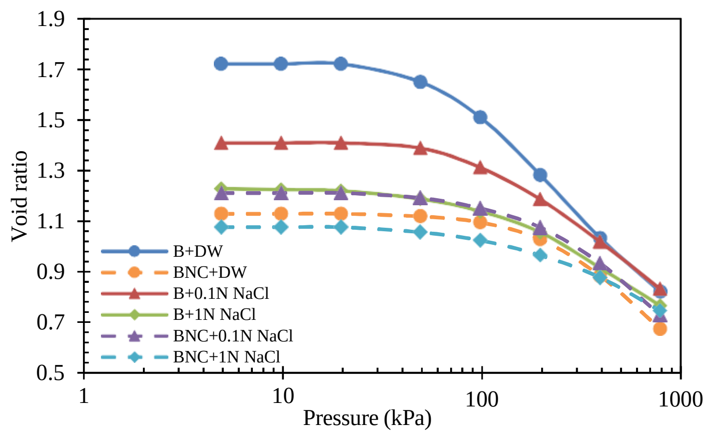

Fig. 5 e-log P curve for bentonite and BNC at different concentrations of NaCl solutions

3.5 Conclusions

Various geotechnical experiments were performed on organoclay amended bentonite to study its geotechnical properties such as plasticity, swelling and compressibility under saline conditions. The following conclusions were observed:

- The plasticity, swelling and compressibility characteristics of bentonite is greatly affected under saline environment. This is due to the reduction of diffused double layer thickness when the concentration of sodium chloride increases.
- The plasticity characteristics of organoclay amended bentonite decrease with an increase in sodium chloride concentrations. The organoclay fraction tends to reduce the interparticle repulsion, thereby reducing its water holding capacity.

- BNC samples showed a significant swelling and compressibility reduction when inundated with sodium chloride solutions. The decline is due to the hydrophobic nature of the organoclay fraction, which reduces the interparticle repulsion and allows the particles to flocculate.
- At higher concentrations, both bentonite and BNC showed almost similar values of plasticity and swelling.
- Even though the geotechnical characteristics of both bentonite and BNC change drastically under saline environment, the effect on BNC samples was comparatively lesser than that of bentonite.
- The organoclay can be used as an amendment for bentonite liner even under saline conditions.

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