2011 2nd International Conference on Environmental Science and Technology
IPCBEE vol.6 (2011) © (2011) IACSIT Press, Singapore

Behavior of nanoclay as an addetive in order to reduce Kahrizak landfill clay permeability

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Abstract—**Landfill leachate is one of the greatest environmental concerns. The major potential environmental impact of landfill leachate is that it can pollute groundwater, surface waters and soils. Among these contaminations, groundwater pollution is probably the most severe environmental impact from landfills. Geomembranes have usually been considered for the utilization in design and construction of landfill liners; however, due to improper construction and management which may lead to leachate leakage, low permeable liners such as clay barriers are being used with synthetic materials. The aim of the present study is to evaluate the effect of nanoclay on permeability and swelling of a compacted Kahrizak landfill clay liner. The results showed that 4% nanoclay significantly reduced permeability ($3*10^{-9}$ to $7.74*10^{-11}$ in neutral, $3.66*10^{-9}$ to $7.9*10^{-10}$ in acidic and $3.25*10^{-9}$ to $5.24*10^{-10}$ cm/s in alkaline condition). The results satisfied the construction of clay barriers with nanoclay in order to prevent leachate penetration, consequently reduces the operation cost.**

Keywords-leachate; permeability; nanoclay; landfill; Kahrizak clay

I. INTRODUCTION

It has been reported that in Tehran leachate leaked from unsanitary landfills is contaminating the surrounding soils and groundwater. This problem is increasing due to population growth and development of technologies; as a result, finding a way to reduce this infiltration is inevitable. Synthetic materials such as geomembrane made of polyethylene sheet are one of the options to prevent leachate migration, but their long decomposition period and sensitivity to sunlight have made their use less appropriate. Another option can be compacted clays. These compacted clays or mixtures of local soils with clay are frequently used to achieve very low hydraulic conductivity barriers and prevent subsurface contamination [1].

Compacted clay liners should meet the following criteria:

a) Low permeability
b) low swelling
c) Proper resistance to shearing
d) Low shrinking [2].

Typically the hydraulic conductivity of compacted clay should be less than 10^{-7} cm/s for soil liners and covers [3].The required liner thickness for domestic and light industrial waste types is to be 0.6 m for compacted clay liners [3, 7].

Hydraulic conductivity is one of the most important engineering properties of soil, its importance is further increasing because of its vital role in finding acceptable solutions to problems in environmental control and in dewatering and filtration applications [4].

The essential nanoclay raw material is montmorillonite, a two to one layered smectite clay mineral with a platy structure with van der Waals force between the neighboring layers [8]. The thickness of each layer is about 1 nm, diameter from 10 nm to several microns, and the interlayer space around 1 nm depending on the modification methods [5]. Due to its high aspect ratio and good physical and thermal properties, nanoclay has the potential for exceptional improvements in barrier, flammability resistance, thermal and mechanical properties for polymer composites at very low filler loading [9].

A study has been performed in order to reduce soil permeability by the use of silica fume [6] and some have used bentonite in sandy soil [4, 6, 10-12]. In the present research the application of nanoclay in reducing soil permeability is investigated.

II. MATERIALS

A. Soil prepration

The clay material originated from Kahrizak landfill in south of Tehran, Iran. The ASTM standard tests (D422 and 421, D698 and D4318) [7] were conducted in order to determine their physical properties such as particle size, maximum dry unit weight and Atterburg limits. The grain size distribution curves, consistency limits and index properties of clay are given in figure 1, table 1 and table 2 respectively.

The clay is classified as MH by the unified soil classification system.

The chemical composition of clay particles were analyzed by XRF using X΄Unique 2 (Philips, Netherlands) and are given in table 3. As it is investigated by USEPA, compacted clay liners should have at least 30% fine particles, the amount of gravel content shouldn't exceed 10% of the particles and the plastic index should be greater than

10% and less than (30-40%) in order to reach 10^{-7} cm/sec permeability.

B. Nanoclay

Montmorillonite is a type of soil frequently used in landfill liners, slurry walls and many other geoenvironmental applications, due to its expansive characteristics and low hydraulic conductivity [1]. Hydrophilic nanoclay used in this study is MMT/Na^+ was prepared by ATP Company and its specifications are presented in table 4.

C. Leachate

The leachate used in this study originated from Kahrizak landfill in south of Tehran, Iran and its properties such as contamination and amount of cations by induced couple plasma (ICP), are given in table 5 and 6 respectively. Chemical Oxygen Demand (COD) was determined according to standard method [8]; the contamination level of COD was 140000 mg/l.

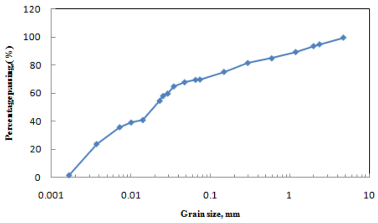

Figure 1. The grain size distribution curve of Kahrizak clay

TABLE I. CONSISTENCY LIMITS OF KAHRIZAK CLAY

Kahriz -ak clay	Consistency limits of Kahrizak clay		
	Liquid limit (%)	*Plastic limit (%)*	*Plasticity index (%)*
amount	50.39	32.14	18.25

TABLE II. INDEX PROPERTIES OF KAHRIZAK CLAY

Kahriz -ak clay	Index properties of Kahrizak clay	
	Density γ_s (KN/m^3)	*Clay content (%)*
amount	20.26	8

TABLE III. CHEMICAL COMPOSITION OF KAHRIZAK CLAY

Kahriz -ak clay	Amount of chemical composition of Kahrizak clay	
	Chemical composition	*Amount (wt %)*
	Na_2O	0.65
	MgO	3.4
	Al_2O_3	14.2
	SiO_2	50.5
	SO_3	0.41
	K_2O	2.32
	CaO	7.2
	MnO	0.19
	Fe_2O_3	7.8

TABLE IV. NANOCLAY PROPERTIES USED IN THIS WORK

Kahri-zak clay	Nanoclay properties		
	Distance between layers (nm)	*color*	*Density γ_s (KN/m^3)*
amount	1.2	Off white	19

TABLE V. AMOUNT OF CATIONS IN KAHRIZAK LEACHATE, PPM

Kahri-zak clay	Amount of cations in Kahrizak leachate	
	Cations	*Amount (ppm)*
	Al	12
	B	22
	Ca	8700
	Fe	320
	K	6500
	Mg	1900
	Mn	60
	Na	11750
	Sr	45

TABLE VI. KAHRIZAK LEACHATE PROPERTIES

Kahri-zak clay	Kahrizak leachate properties		
	Conductivity,k (ms/cm)	*COD (mg/lit)*	*PH*
amount	67.6	140000	7

III. METHOD

A. Compaction test

Standard proctor test ASTMD 698[7] was performed in order to find optimum water content and also maximum dry unit weight of Kahrizak clay (KC) and its compositions. Figure 2 shows the compaction curve of Kahrizak clay . As it is shown optimum water content was 27.16%.

B. Kahrizak clay – nanoclay prepration

At first Kahrizak clay was dried in a heating oven at approximately 105 °C before using in the mixtures for 24 hours. To prepare the mixture, the required amount of Kahrizak clay and nanoclay were measured by weight and mix together then the required amount of water was added to the mixture.

C. *Permeability test*

According to the ASTMD 5084 [7], falling head permeability test were performed. In this laboratory work , five moulds (L: 6cm, D: 10cm and 2mm thick) were prepared and two porous stone were subjected above and beneath the specimens. The material of moulds was stainless steel in order to prevent corrosion. During the test no swelling was allowed to occur.

In this test the heads h_1 at time t_1 and h_2 at time t_2 were measured in a standpipe of area a (6mm wide, 100 cm high) and the leachate was allowed to flow through the soil of area A and length L. The coefficient of permeability or hydraulic conductivity (k) is determined by following formula:

$$K=2.303\,\frac{aL}{At}\,log\,\frac{h_1}{h_2} \qquad (1)$$

Where t is the time difference between two records. It should be considered that the value of k is dependents on the properties of fluid (Kahrizak leachate) and the porous medium (Kahrizak clay).

Samples with 1%, 2%, 3%, 4% and 5% of nanoclay were saturated in water for two weeks and then subjected in permeability test to ensure the result. Before testing, the leachate was filtered with a qualitative P5 filter paper to remove solid particles with diameters N5–10 µm [2]. Each test was done in triplicate and at different leachate pH of 4.8, 7 and 9 which was adjusted with pH meter (340i, WTW, Germany) . It should be noted that pH of Kahrizak landfill leachate in acidic conditions never decreases 4.8.

D. *Swelling test*

In order to calculate the amount of swelling of the specimens, the prepared moulds were subjected to the water at different pH's of 4.8, 7 and 9 for about two weeks. Finally the measured clay height was divided by the initial height to calculate the swelling percent of the compositions.

E. *Cation exchange capacity test*

As the cation exchange capacity (CEC) is one of the important properties of clay minerals, several tests were done in order to find CEC of the composition mixtures. Furthermore as common CEC methods like ammonium acetate [10] or barium chloride [11] are very time consuming and for natural materials results are often poor [12], the silver thiourea method was examined for the determination of CEC [12]. Table 7 shows exchangeable cations and CEC data ($\frac{\text{meq}}{100\text{ g soil}}$) for Kahrizak clay (KC), leachate penetrate Kahrizak clay (LPKC) and leachate penetrate Kahrizak clay – 4% nanoclay (LPKC-4%nanoclay).

IV. Results and Discussions

A. *Effect of nanoclay on consistency limit*

The effect of nanoclay content on liquid limit, plastic limit and plasticity index are given in figure 3. The liquid limit and plasticity index increased slightly with increase in nanoclay content. It may be due to increasing composition aspect ratio which caused to absorb more water in order to flow upon application of a very small shearing force. However, the plastic limit decreased slightly as the nanoclay content increased. The correlation coefficient in this case is more than 0.9.

B. *Effect of nanoclay on permeability*

Figure 4 represents the effect of nanoclay content on the permeability of Kahrizak clay at different pH. At neutral pH, permeability rapidly decreased from $3*10^{-9}$ to $9.4*10^{-11}$ cm/s by adding 3% nanoclay, after that these values seemed to be less affected by nanoclay content ($7.74*10^{-11}$ for 4% nanoclay and $6.9*10^{-11}$cm/s for 5% nanoclay). As can be seen in figure 4 decrease in permeability value was more in acidic condition than alkaline situation. It should be mentioned that each data point represents an average of several tests. Figure 4 shows that however at neutral condition adding 3, 4 or 5% nanoclay seemed to have minor impact on permeability, in both acidic and alkaline situations permeability differs significantly. According to the results 4% nanoclay as an additive to reduce Kahrizak clay permeability was chosen.

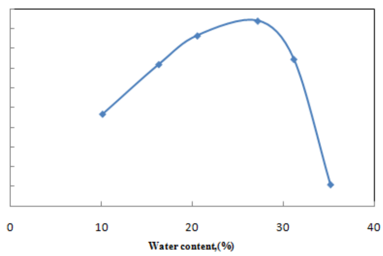

Figure 2. Compaction curve of Kahrizak clay

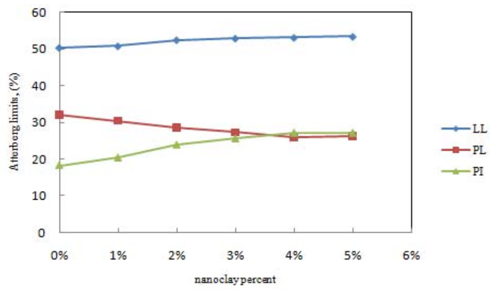

Figure 3. Influence of nanoclay on the consistency limit of Kahrizak clay

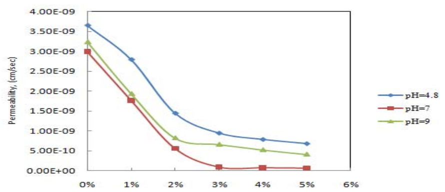

Figure 4. Effect of nanoclay content on Kahrizak leachate permeability at different pH

C. Effect of nanoclay on swelling

Figure 6 represents the nanoclay content against the amount of swelling for Kahrizak clay at three different pH (4.8, 7, 9). Some clay minerals such as montmorillonite are capable of adsorbing appreciable amounts of water into the interlayer's, between the individual silicate layers of the structural lattice (the tetrahedral and octahedral layers), which results in a high swelling potential [13]. It can be seen that the percentage of swelling increased with increasing nanoclay content from 16.67 to 41.82, 23.33 to 45.45 and 15 to 38.18 at pH 7, 4.8 and 9 respectively. It was observed that the maximum swelling was occurred in acidic condition and it reached to its minimum value at alkaline range. The R-squared(R^2) is quite high (0.94).When rigid mould surrounded the specimens , sufficient overburden placed on it and swelling happened, a kind of internal swelling occurred, which can filled the pores and reduced permeability [14]. Despite having maximum swelling at acidic condition, it was observed that maximum permeability occurred at this range (figure 5). Esmaeli et al. [14] explained this situation by soil flocculation which increased permeability in comparison with natural and alkaline condition. Furthermore, in alkaline condition because of flocculation and lower swelling, higher permeability was obtained than neutral condition [14].

As it was mentioned by Brandle [2] the landfill liners should have low swelling. Since this composition is about to use in landfill liners, by considering 3 meter waste with 700-800 $\frac{Kg}{m^3}$ density, a 0.25$\frac{Kg}{cm^2}$ overburden was placed on the specimens and no swelling occurred for any compositions so this procedure is appropriate for landfill operation.

D. Effect of nanoclay on cation exchange

Electrostatic attraction between the ions in a solution (leachate) and the soil colloidal surface is counteracted by diffusion, which creates a diffuse double layer (DDL) [15]. The thickness of this layer depends upon the type and concentration of the ions in the solution [13]. Ions with lower valency yield thick cushioning effect, means that the repulsion forces are greater than the weak dipolar attraction forces thus the clay remains dispersed [13]. Whereas ions with higher valency reduce the thickness of the (DDL) as well as the cushioning effect, so dipolar forces overcome the repulsion forces and form flocs. Dispersed clays have a lower hydraulic conductivity due to the particles that blockage the pores in the soil matrix and therefore, have lower potential infiltration velocity [13]. In order to determine the effect of cation exchange capacity (CEC) on soil permeability CEC tests were conducted.

Table 7 shows CEC value of three composition mixtures. As can be seen, the sum of mono-valent ions and CEC value in the composition with 4% nanoclay, are less than leachate penetrate Kahrizak clay (LPKC), which means that nanoclay helped the composition to maintain its mono-valent ions between layers so the composition remained more dispersed than LPKC, hence lowered hydraulic conductivity.

E. SEM of samples

Small samples of composition mixtures were taken for scanning electron microscope to determine the effect of leachate and nanoclay on the structure of the compositions. SEM photograph of KC, LPKC and LPKC-4% nanoclay are shown in figure 6 respectively. A comparison of figure (a) and (b) shows that the leachate made Kahrizak clay to swell. As can be seen in figure (c), nanoclay clusters were formed in the composition and the distance between clusters were small that the composition remained dispersed. This event can improve permeability and compressive strength of the compositions with nanoclay.

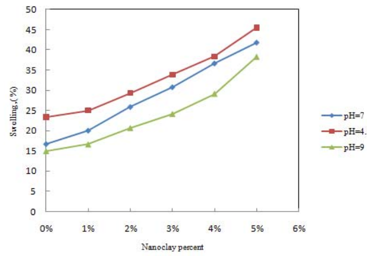

Figure 5. Influence of the nanoclay content on the percentage of swelling

TABLE VII. CEC VALUES OF THREE COMPOSITION MIXTURES

Table Head	**composition mixtures**														
	LPKC-4%					***LPKC***					***KC***				
amount (meq/ (100 g soil))	Na	K	Ca	Mg	CEC	Na	K	Ca	Mg	CEC	Na	K	Ca	Mg	CEC
	25.4	0.45	88.1	7.5	121.51	46.63	10.1	100.3	0.875	157.8	25.4	0.45	88.1	7.5	121.51

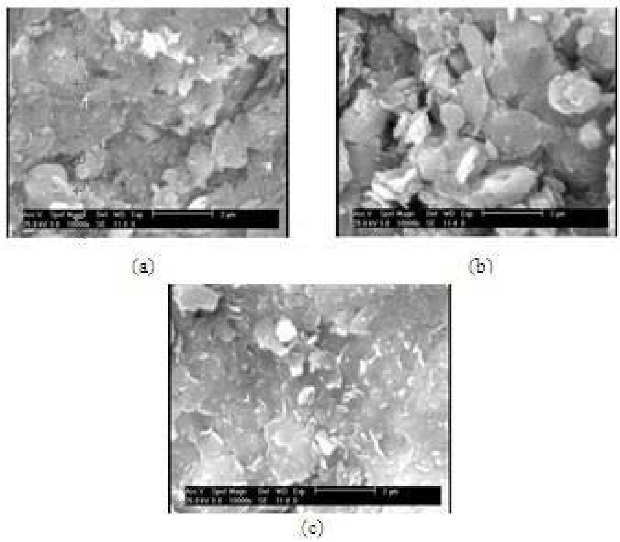

Figure 6. SEM of samples: (a) KC (b) LPKC (c) LPKC-4% nonoclay.

V. CONCLUSION

The effects of adding nanoclay to kahrizak landfill clay was investigated and the following results were obtained:

1) While the plastic limit slightly decreased, the liquid limit and plasticity index increased slightly as the nanoclay content increased. At 4% nanoclay, the type of soil in composite samples changed from high plastic silts (MH) to high plastic clays (CH).

2) Permeability rapidly decreased by adding 3% nanoclay after that it seemed to be less affected by nanoclay content, however at neutral condition adding 3, 4 or 5% nanoclay seemed to have minor impact on permeability, in both acidic and alkaline situations permeability differed significantly. As a result of that 4% nanoclay was chosen as an additive to reduce Kahrizak clay permeability.

3) The experimental results showed that the percentage of swelling increased as the nanoclay content increased. Greater swelling was observed in acidic condition than in neutral condition. Yet swelling in neutral condition was more considerable than in alkaline range.

4) The sum of mono-valent ions and CEC value in the composition of Kahrizak clay with 4% nanoclay was less than of that for leachate penetrated Kahrizak clay meaning that nanoclay helped the composition to remain dispersed.

5) Scanning microscope electron showed that leachate caused Kahrizak clay to swell. In the composition with 4% nanoclay, nanoclay clusters were formed so close to one another and kept the whole composition dispersed. As a result of that improvement in permeability and compressive strength of the compositions with nanoclay had occurred.

6) The experimental results showed that nanoclay have positive effects on permeability. As 4% nanoclay significantly reduced permeability to 7.74*10-11 so the required liner thickness can be performed less than 0.6m therefore the cost of the operation will reduce.

ACKNOWLEDGMENT

The authors are grateful to the Amirkabir University of Technology research fund for the financial support. In addition, the authors wish to thank Ms. Lida Ezzedinloo, Mr Taghi Bahrami and Mr Reza Javadi for their assistance during experiments.

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