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Application of Modified Clays in Geosynthetic Clay Liners for Containment of Petroleum Contaminated Sites

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ABSTRACT: In this research, hydraulic and sorption behavior of geosynthetic clay liners (GCLs) with ordinary and modified clay exposed to crude oil were studied. Both modified and ordinary bentonites were investigated to evaluate crude oil adsorption efficiency on the liners. Because soil permeability exposed to crude oil is a major parameter in measuring the contaminants migration in soils, the permeability tests were conducted on the clays. X-ray diffraction (XRD) analyses were also carried out to evaluate the adsorption of crude oil by bentonites. Following the tests, results of XRD analysis for modified bentonite samples indicated an average 63.2% interlayer increase after their exposure to the crude oil while that of ordinary bentonite was relatively insignificant (0.5 %). In case of permeability tests, modified bentonites showed much lower permeability values (5.2×10^{-9} cm/s) compared to ordinary bentonites (1.2×10^{-6} cm/s) when exposed to crude oil, hence denoting the viability of modified clays, instead of ordinary clays as GCLs materials at petroleum contaminated sites.

Key words: Geosynthetic Clay Liners, Crude oil, Modified bentonites, Permeability, X-ray diffraction analysis

INTRODUCTION

Even though oil is among the main necessities of modern society, however this resource can have negative effects on marine life, economy, and environment when out of control and can be one of the most destructive pollutant substances for the environment. The main environmental concern associated with crude oil is that it may cause significant hazards to human health and the earth's ecology during all stages of production, processing and consumption, if not handled carefully (Urum *et al.*, 2005). The major causes of environmental damage have been noted to be due to accidental spillages and sometimes intentional discharge of oil or oily wastes to water or land (Fig. 1) , through blow-outs from pipes and pumps, pipeline corrosion and spillages during transportation (CONCAWE, 1984).Soil and groundwater contamination with petroleum constituents can occur from small leaks to large ruptures in underground storage tanks (USTs) which present widespread environmental and public health concerns (Lijang and Guo 2012). Crude oil contains a complex mixture of compounds, mainly hydrocarbons. The major constituents of crude oil are grouped into four major categories, the saturated compounds, the aromatics, the resins, and the asphaltenes (Jokuty *et al.*, 2000). Geosynthetic Clay Liners (GCLs) are commonly used to prevent the leakage of the contaminants to groundwater resources. GCLs represent a relatively applicable technology (developed in 1986) which is currently gaining acceptance as a barrier system in solid waste landfills.

Adsorption of crude oil onto organo-bentonites is another important issue in the design of petroleum waste containment systems. Hence, the permeability and adsorption characteristics of GCLs exposed to crude oil were investigated in this research.

The objectives of this research are: 1) to measure the permeability of ordinary and modified bentonites exposed to crude oil, and 2) to evaluate the interlayer basal spacing changes of the clay particles due to the adsorption of crude oil constituents. To achieve these goals, permeability tests, XRD analysis and free swell tests were carried out.

*Geosynthetic Clay Liners (*GCLs) technology offers some unique advantages over conventional bottom liners and covers (EPA, 2001). The main

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Fig. 1. Brownfield contaminated site (NYSDEC, 2011)

advantages of GCLs are the limited thickness, the good compliance with differential settlements of underlying soil or waste, easy installation and low cost (Bouazza, 2002). As shown in Fig. 2, GCLs are comprised of a thin layer of sodium or calcium bentonite bonded to a layer or layers of geosynthetic materials. The geosynthetics are either geotextiles or geomembranes.A geomembrane is a polymeric sheet material that is impervious to liquids as long as it maintains its integrity. A geotextile is a woven or nonwoven sheet material made of polymer fibers which is less impervious to liquids than a geomembrane, but more resistant to penetration damages. Geotextiles-based GCLs are bonded with an adhesive, needle punching, or stitch-bonding, with the bentonite contained by the geotextiles on both sides.

Laboratory tests demonstrate that the hydraulic conductivity of dry, unconfined bentonite is approximately 1×10^{-6} cm/s. When saturated, the hydraulic conductivity of bentonite typically drops to less than 1×10^{-9} cm/s. The hydraulic conductivity of most GCL products ranges from about 1×10^{-5} cm/s to less than 1×10^{-12} cm/s (EPA, 2001).

Numerous studies have examined the applicability and chemical compatibility of bentonites and GCLs, having shown that the type and concentration of chemicals within the permeating fluid affect the hydraulic conductivity of the GCL. It has been reported that the hydraulic conductivity value increases as the concentration of the electrolytic solution increases (Katsumi *et al.*, 2007, Kolstad *et al.*, 2004, Shan and Lai, 2002, Petrov and Rowe., 1997). Bentonite liners are usually employed to prevent the migration of pollutants due to advection and diffusion. Studies have shown that organobentonites are more efficient in adsorption of organic pollutants in comparison with ordinary bentonites. Organophilic clays are synthesized by the ion exchange of quaternary ammonium organic cations onto the mineral surfaces of ordinary bentonites. Because of their organophilic nature, such modified bentonites have been proposed for use in earthen liners at waste disposal facilities (Grube *et al.*, 1987, Smith *et al.*, 2003).

MATERIALS & METHODS

Examples of organoclays application (also called organophilic clays) can be found in the literature (Lake and Rowe, 2005, Headley *et al.*, 2001, Boldt-Leppin *et al.*, 1996, Jaynes and Vance., 1996). Organoclays can be produced by exchanging the hydrated exchangeable cations of natural clay (usually bentonite) with various types of quaternary ammonium cations (Xu *et al.*, 1997) or by other techniques (Lo., 1992, Srinivasan and Fogler., 1990). In this research an amount of tailoring agent (hexadecyl-trimethyl ammonium (HDTMA) as quaternary ammonium salt (QAS)) equal to the cation exchange capacity (CEC) of the clay was weighed and dissolved in distilled water at laboratory temperature. Next, the mixture was added slowly to natural clay suspension while being agitated by a magnetic stirrer in a 500mL beaker. After the sample was stirred for four hours, the tailoring agent-clay suspension was centrifuged and washed four times with distilled water to thoroughly remove all the replaced cationic compounds in the clay. The sample was then frozen quickly and freeze-dried for the experiments (Janes &

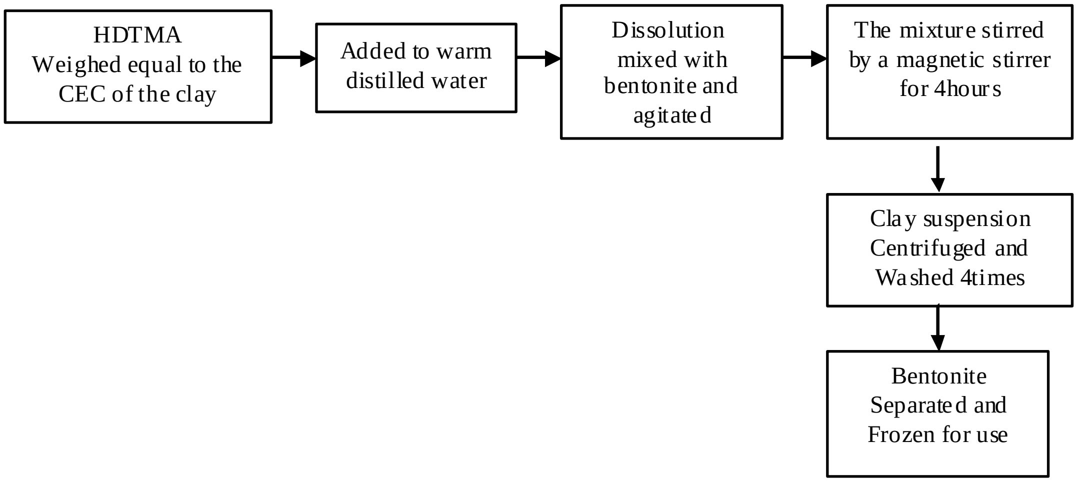


Fig. 2. Schematic diagram of clay modification process (Gitipour *et al.*, 2008)

Boyd, 1991). Fig. 2 presents a schematic diagram of the clay modification process.

The adsorption of organic compounds on bentonites can be studied by X-ray diffraction analysis (XRD). The technique gives data pertinent to basal spacing of minerals and establishes the fact of adsorption and provides information regarding the absorbed molecules into the basal spacing of the clay particles (Gitipour *et al.*, 2006). XRD analysis was carried out by mixing the modified and ordinary bentonites separately with crude oil and water to evaluate the changes occurred in the interlaminar distance of the clays resulting from their interaction with these organics. Prior to the analysis, the clays samples (1 gram of the clays for each sample) were mixed separately with crude oil and water. A porcelain crucible and a spatula were used to mix the samples to help prevent them from shrinkage and to inhibit the formation of cracks. Next, each sample was placed in the sample holder by a glass slide and smoothly leveled to achieve a dispersed horizontal orientation of clay particles. The sample holder was then immediately transferred to the x-ray diffractometer for analysis. X-rays are electromagnetic radiations of wavelength about 1Aæ%, about the same size as an atom. The XRD technique helps measure the size and shape of clay's unit cells. The analyses were conducted at the XRD laboratory of the Mineral Engineering Department of University of Tehran. A Bruker AXS D8 X-ray diffract meter with a Cu-K=1.54 Aæ% radiation source was used to analyze the clay samples. The analyses were performed at a 20-minute running period for each sample.

Free swell tests were carried out to determine the volume changes of modified and ordinary bentonites due to adsorption of crude oil and water. To perform the tests, 2 cm^3 of ordinary and modified bentonite samples were placed in different glass tubes. Then 20 cm^3 of crude oil and water were added slowly to each tube, separately. A total number of 4 samples were tested during the study (two soil–liquid samples, duplicate runs). To evaluate the swellings of the clays, the glass tubes were kept intact in the laboratory for a period of 48 hours (see Fig. 3).

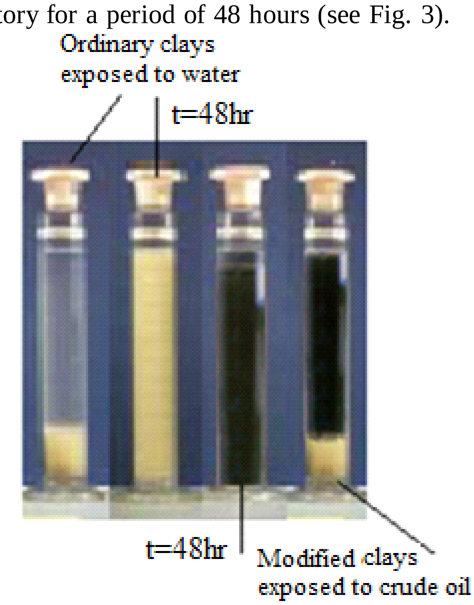


Fig. 3. Free swell tests for ordinary and modified samples exposed to water and crude oil after 48 hours

The objective *Permeability Tests* was to determine the leaching characteristics of ordinary and modified bentonites as materials in GCL systems at UST sites. To accomplish these goals, samples of the ordinary and modified bentonites were separately tested with crude oil and water. For the permeability tests, the original plan was to test two types of the bentonites in their original forms. Water and crude oil were separately applied to the samples. A rigid wall permeameter was used to assess the hydraulic conductivity of the GCL. To guard against inevitable variations in the preparation and testing of the samples, duplicate samples were prepared for each test. To prepare the specimens, ordinary bentonite and modified bentonite were loosely packed in molds with a diameter of 103 mm and height of 7 mm. Next, the prepared specimens were sandwiched between two filter papers attached with the nonwoven geotextiles, and placed in the apparatus. Testing continued until a minimum of two pore volumes of liquid (according to ASTM permeability test method) were passed through each sample and the permeability reached equilibrium. Eight samples (two bentonites, two permeants, plus duplicate runs) were prepared for the tests

RESULTS & DISCUSSION

For free swell test, as presented in Table 1, the crude oil located on the top of modified bentonite samples introduced 410% volume change in the clay particles volume. However, in the case of water, the increase in volume of the particles was only 7.5% due to hydrophobicity of modified bentonites. Nevertheless, ordinary bentonites did not present sufficient volume increase when exposed to crude oil (15 %) as compared with water (542.5 %).The results of the tests support the hypothesis that organobentonites effectively intercalate crude oil constituents into their particles, thus increasing the particles volume, the volume increase would then reduce the permeability of the soil, hence reducing the mobility of hydrocarbons in clay liners.

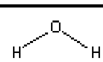
The summary of XRD analysis conducted on ordinary and modified bentonite samples is presented in Table 2. XRD analysis on ordinary and modified bentonites indicated that the basal spacing of the modified bentonite increased 136.4 %. The positioning of QAS on the surface of the clay particles would be the major reason for the basal spacing increase. For ordinary bentonites mixed with water, the basal spacing increased 75.7% while for modified bentonite samples, the basal spacing change was only 4.5 %. This shows the insignificant tendency of modified bentonites to absorb water.

In the case of the modified bentonites exposed to crude oil (Fig. 4), the basal spacing presented a 63.15% of volume increase. Regarding the permeability of GCLs prepared with ordinary and modified bentonites, As shown in Table 3, the average value of the modified clay permeability coefficient exposed to water was 1.94×10^{-6} cm/s. As for the permeability of the samples exposed to crude oil, the tests showed an average value of 5.20×10^{-9} cm/s. This reduction could be attributed to the swelling of modified bentonite particles due to the adsorption of crude oil constituents. For the ordinary bentonite samples, the average permeability of the clay exposed to water was much higher than that of crude oil. The higher permeability could be attributed by the affinity of the ordinary clay with water and the lack of crude oil adsorption by the clay particles.The plots of the Permeability coefficient of modified bentonite samples with water and crude oil are shown in Fig. 5.

Table 1. Changes in volumes of ordinary and modified bentonites exposed to water and crude oil

Test fluid	Dry clay volume (cm^3)	Clay Type					
		Ordinary Bentonite			Modified Bentonite		
		Volume(cm^3)		Average volume change (%)	Volume(cm^3)		Average volume change (%)
Water	2.0	12.9	12.8	542.5	2.1	2.2	7.5
Crude Oil	2.0	2.3	2.3	15.0	10.6	9.8	410.0

Table 2. XRD analysis results for ordinary and modified bentonite samples exposed to crude oil and water

Testing liquids	Molecular Formula	Structure	**Basal Spacing of Ordinary Bentonite, A°**				**Basal Spacing of Modified Bentonite, A°**			
			Original	After Exposure	Amount of change	Percent of change	Original	After Exposure	Amount of change	Percent of change
Water	H_2O		12.1	21.26	9.16	75.7	28.6	29.9	1.3	4.55
Crude Oil	NA	NA	12.1	12.16	0.06	0.50	28.6	46.66	18.06	63.15

NA: Not Applicable

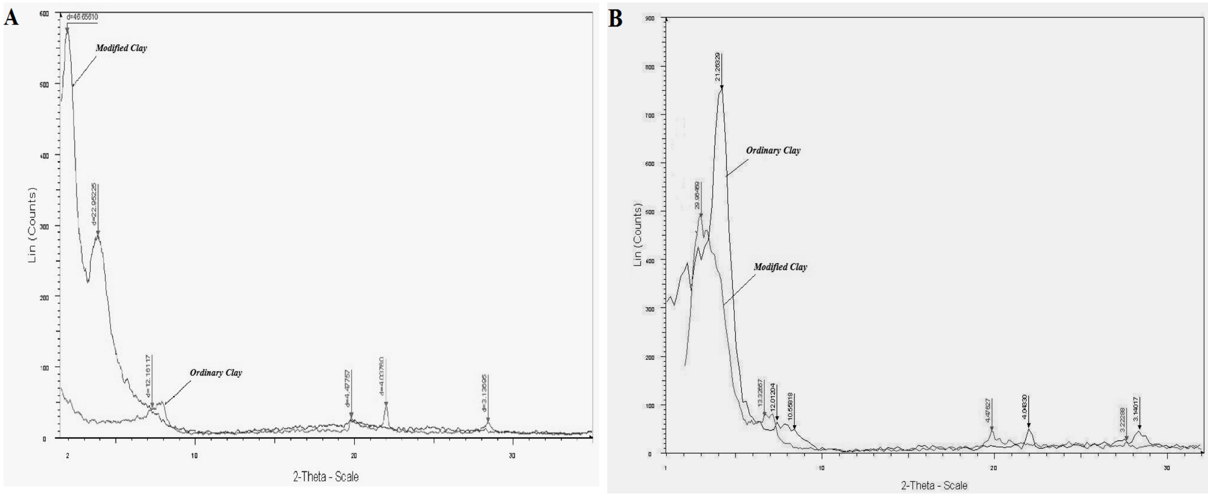


Fig. 4. X-ray diffraction analysis of modified and ordinary clay particles exposed to (a) crude oil (b) water

Table 3. Changes in GCLs permeability coefficient with ordinary and modified bentonites (cm/s)

Permeability coefficient, K [cm/s]						
	Ordinary Bentonite			Modified Bentonite		
Leachate type	1	2	Average	1	2	Average
Water	5.71×10^{-11}	1.34×10^{-10}	9.56×10^{-11}	2.51×10^{-06}	2.4×10^{-06}	1.94×10^{-06}
Crude Oil	1.43×10^{-06}	8.79×10^{-07}	1.15×10^{-06}	3.34×10^{-09}	7.06×10^{-09}	5.20×10^{-09}

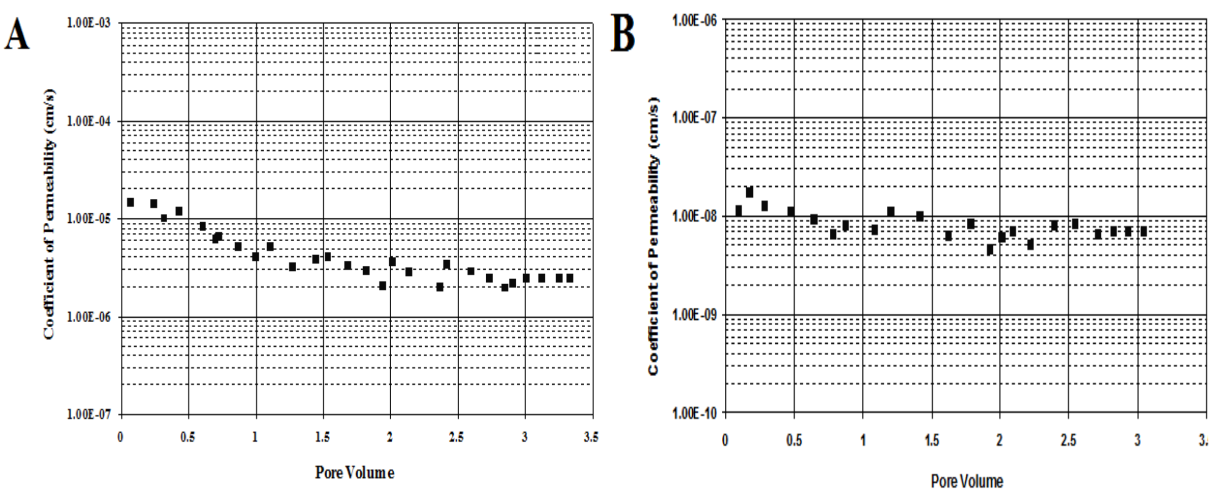


Fig. 5. Plots of permeability coefficient of modified bentonite samples Exposed to (a) water (b) crude oil

CONCLUSION

Underground Storage Tanks (USTs) are typically surrounded by GCLs and berm systems to reduce the fuel oil leakages. As an alternative to conventional containment system, an innovated GCLs system is proposed which equipped with organophilic clays. The system can significantly protect the soil around the USTs against the contaminants leakage more efficiently than the conventional GCLs containing ordinary clays. The organophilic clays will adsorb organic contaminants (i.e. crude oil) and swell, thus forming an impervious layer underneath the leaking areas.

In addition, according to the study results, simultaneous use of ordinary and organophilic bentonites in the composition of GCLs (or any other barrier systems) is also proposed. Adsorption of water molecules by ordinary bentonites causes the increase in clay basal spacing, while modified bentonites adsorb hydrocarbon contaminants instead. As there are different types of contaminants in hazardous waste leachates, application of both ordinary and modified bentonites is proposed to increase the liner efficiency as barrier systems at hazardous waste sites. This method of application can be useful in removing water and hydrocarbon-based contaminants from leachates generated at hazardous waste landfills.

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