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Adsorption and Permeability of Contaminated Clay Soils to Hydrocarbons

Saeid Gitipour, Akbar Baghvand and Saeid Givehchi
Department of Environmental Engineering, Faculty of Environment, University of Tehran, Tehran, Iran

Abstract: This study was focused on the treatment of sites polluted with gasoline through the use of betonies clays. In this research, permeability tests were carried out on both natural and modified (organophilic) bentonites using gasoline (as an organic solution) and water (a base liquid). Moreover, X-rd analysis was performed on the clays to assess the adsorption of hydrocarbons by the soils. Regarding modified clay samples, results of permeability tests showed that the average permeability of the soils decreased from 7.2×10^{-4} to 6.2×10^{-6} cm sec^{-1} as a result of organics adsorption. For natural bentonite samples however, the average permeabilities were increased from 5.45×10^{-9} to 3.4×10^{-4} cm sec^{-1}, as a result of hydrophilic characteristics of the soil. Regarding X-rd analysis, the results showed that the basal spacing (clay particles thickness) of the modified bentonites samples were increased from 27.07' to 39.11' due to the adsorption of gasoline hydrocarbons to the soil. These results demonstrated the efficiency of modified clays as effective barriers for treatment of gasoline contaminated soils.

Key words: Bentonite clay, permeability, gasoline, contaminated sites, adsorption, X-rd analysis

INTRODUCTION

Gasoline becomes an environmental contaminant when it leaks from underground storage tanks (USTs) or petroleum storage facilities. Underground storage tanks installed before 1988 were unprotected steel structures that often leak gasoline into environment. Only in the United States, there are approximately 1-2 million gasoline storage tanks. Out of this number, it is estimated that 100,000 to 400,000 tanks are leaking gasoline into the soil or directly into groundwater. Because over 50% of the drinking water supply in the United States comes from underground wells, gasoline leakage from underground storage tanks is a major source of groundwater and soil contamination (Brauner and Killingstad, 1996).

A typical blend of gasoline is comprised of nearly 200 different hydrocarbons from which 13 chemicals are regulated as hazardous substances under the Comprehensive Environmental Response, Compensation and Reliability Act (CERCLA). These chemicals are comprised of nine hydrocarbons and four additives (Cheremisinoff, 1992).

Studies conducted on clay liners as barrier systems at UST sites indicate that bentonite clays, due to their large surface areas and high cation exchange capacities (CEC), can be used to remove inorganic contaminants (i.e., metallic captions) from leachates generated at contaminated sites (Reddi and Inyang, 2000). Nevertheless, regarding the adsorption of organics (i.e., gasoline hydrocarbons) by clays, researchers (McBride *et al*., 1977; Evans and Pancoski, 1989) indicate that quaternary ammonium cations such as hexa-decyltrimethy ammonium (HDTMA) interact with natural bentonite clays and replace the exchangeable inorganic cations on their particles. As a result of the larger size of the HDTMA cations, the interlaminar distance (or unit particle thickness) of the mineral increases and additional space is produced in the particles, thereby facilitating the attraction of other organic compounds(i.e., hydrocarbons) (Boyd *et al*., 1988).

Coefficient of permeability, a main criterion used to judge whether a compacted clay liner will prevent movement of organic leachates below or adjacent to contaminated sites, is needed to determine the suitability of a liner. Based on the above information, the purpose of conducting this research was to study the permeability and adsorption of gasoline hydrocarbons using modified and ordinary bentonites.

Pervious studies conducted on bentonitic clays have emphasized on quantitative measuring of clay's permeabilities with water and gasoline (Smith *et al*., 2003). In this research, however the bentonite samples have been further evaluated by X-rd analysis to illustrate the effect of increases in their particles interlaminar distance as a result of gasoline adsorption on the pearmability of the soils.

Corresponding Author: Saeid Gitipour, Department of Environmental Engineering, Faculty of Environment, University of Tehran, Tehran, Iran Tel: 009821802-7629 0912-3040090

The objectives of this research are to measure the permeabilities of ordinary and modified bentonites with gasoline hydrocarbons and water and to evaluate the changes that occur in clay particles thickness as a result of their adsorption. To accomplish these objectives, permeability tests and X-rd analysis were carried out on clay samples to assess the efficiency of modified bentonites as liner materials at USTs and gasoline contaminated sites.

MODIFIEDBENTONITES(ORGANOPHILICCLAYS)

Organobentonites are organophilic (high organic affinity) clays synthesized by the ion exchange of quaternary ammonium organic cations (with nonpolar organic functional groups) onto the mineral surfaces of bentonite (Grube *et al.*, 1987). Bentonite is primarily composed of Na+-saturated montmorillonite. Previous studies have shown that these organobentonites strongly sorb nonionic organic pollutants relative to conventional bentonite and the magnitude and mechanism of sorption is related to the molecular structure of the quaternary ammonium cation (Smith and Jaffe, 1994). Unlike conventional bentonite, which swells in the presence of water and desiccates in the presence of nonpolar organic liquids, organobentonites exhibit the reverse behavior. They swell in the presence of nonpolar organic liquids and desiccate in the presence of water (Li *et al.*, 1996).

Due to the above mentioned properties of the clays, they have been studied for use in earthen liners for waste disposal facilities (Smith and Galan, 2000) and their geotechnical engineering properties have been investigated (Soule and Burns, 2001).

Based on the above information and due to the low organic adsorption characteristics of natural clays, modified bentonites are therefore recommended for use at hydrocabon contaminated sites to prevent leaking of the organic contaminants (Smith *et al.*, 2003). Permeability is the major guideline used to evaluate the performance of the liners and because US EPA regulations require that the magnitude of permeability not exceed 10^{-7} cm sec^{-1} during the lifetime of such systems (Grube *et al.*, 1987), therefore, information regarding the permeability and contaminant adsorption characteristics of the clays are investigated in this research.

MATERIALS AND METHODS

Permeability testing of soil samples: The ordinary (natural) and modified bentonite clays used in the tests consisted of montmorillonite (bentonitic clay) minerals. In

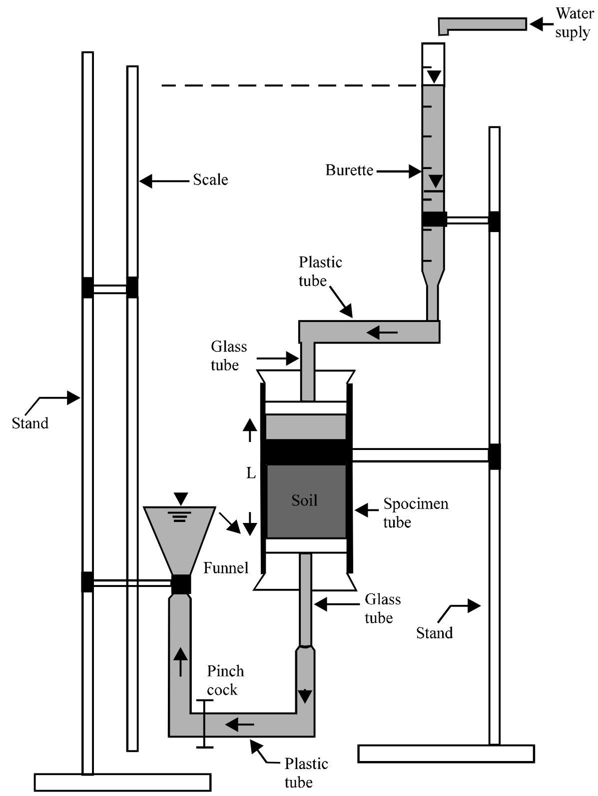

Fig. 1: Schematic diagram of falling head permeability test setup

addition to possessing highly plastic and colloidal characteristics, this clay is very expansive with water, exhibiting a liquid limit of 500% or more (Mitchell, 1992).

The tests were carried out at the environmental engineering laboratory of the University of Tehran. At the beginning of the tests, the soils were homogenized and clay-to-sand ratio of 5:95 (W/W) was applied to prepare the samples (this ratio is generally used in preparing soils used as slurry walls and liner systems).

Rigid wall permeameters were used to perform the permeability tests. To guard against inevitable variations in the preparation and testing of the samples, duplicate samples were prepared for each test. The permeability of the soils was tested by permeating them from the bottom to remove the air in the soil pores. Testing continued until a minimum of 2 pore volumes of flow were passed through each sample and the permeability reached to equilibrium. A total of 8 samples (2 bentonites, 2 permeants (water and gasoline), plus duplicate runs) were prepared for the tests. Figure 1 presents a schematic diagram of permeability test apparatus.

X-Ray diffraction analysis: X-ray diffraction analyses were conducted at X-rd laboratory of Mineral Engineering

Department of The University of Tehran. The soil analysis were carried out by mixing the modified and ordinary (natural) bentonites with gasoline to evaluate the adsorption of gasoline constituents and asses the changes that occur in the interlaminar distance of the clays as a result of their interaction with the hydrocarbons. Adsorption may occur through a physical or chemical bonding between soil particles and the hydrocarbons.

Prior to X-rd analysis, samples of the clays sufficient to fill an aluminum sample holder (approximately 1 g of the clays for each sample) were mixed separately with gasoline and water. The samples were then immediately transferred to the x-ray diffractometer for analysis. A total of 4 samples were analyzed at this stage (2 clays, gasoline and water). In addition, 2 samples of ordinary and modified bentonites were analyzed to measure the initial basal spacing (thickness of bentonite particles). This amounted to a total of 6 samples for the X-rd analyses.

A Siemens D500 X-ray powder diffractometer with a CuKa radiation source was used to analyze the clays. The analyses were performed at a 10 min running period for each sample.

RESULTS

The results of permeability tests are presented in Table 1. For the ordinary bentonite samples the tests showed a significant reduction in the permeability of the ordinary bentonite permeated with water versus those permeated with gasoline.

The average permeabilities of ordinary bentonite samples with water and gasoline were 5.45×10^{-9} and 3.4×10^{-4} cm sec^{-1}, respectively showing almost 4.8 orders of magnitude decrease for the samples permeated with water than with gasoline. The lower permeability with water was due to the strong affinity between the clay and water molecules which caused increases in clay particles thickness thus reducing soil porousity and decreasing its permeability.

For the modified bentonite samples, test results showed a lower permeability with gasoline than with water mainly due to their organophilic and hydrophobic characteristics. The average permeabilities

Table 1: Permeability tests for ordinary and modified clays subjected to gasoline and water

	Coefficient of permeability (cm sec^{-1})			
Leachate type	Ordinary bentonite	Average	Modified bentonite	Average
Water	7.2X10E-9	5.45X10E-9	8.9X10E-4	7.2X10E-4
	3.7X10E-9		5.5X10E-4	
Gasoline	4.5X10E-4	3.4X10E-4	8.2X10E-6	6.2X10E-6
	2.3X10E-4		4.2X10E-6	

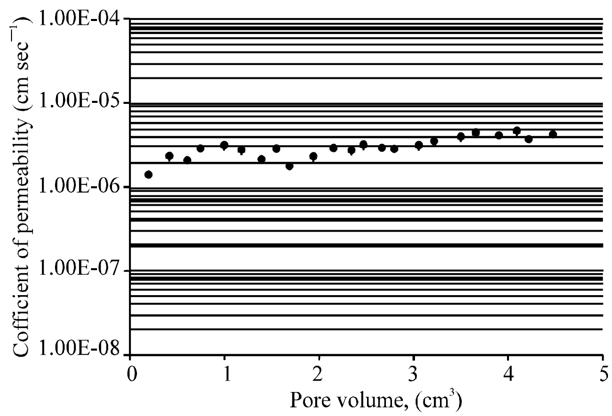

Fig. 2: Plot of coefficient of permeability of modified bentonite samples with gasoline

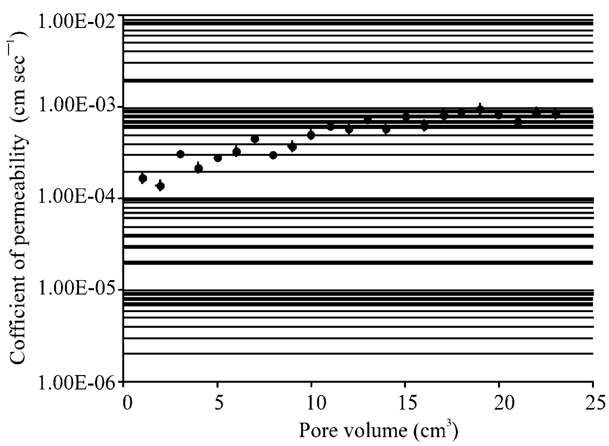

Fig. 3: Plot of coefficient of permeability of modified bentonite samples with water

of the modified bentonite samples with water and gasoline were $7.2\text{x}10^{-4}$ and $6.2\text{x}10^{-6}$ cm sec^{-1}, respectively. This shows almost 2.1 orders of magnitude decrease in the permeability when the permeant was changed from water to gasoline. The lower permeability is attributed to the adsorption and swelling of the modified bentonite with hydrocarbons, thus decreasing its' hydraulic conductivity. Figure 2 and 3 presents the plots of coefficient of permeability of modified bentonite samples with gasoline and water.

As shown in the Table 2, the original thickness of unit cells of ordinary and modified bentonites were 12.44' and 27.07', respectively. The analysis indicate a drastic increase (from 12.44' to 20.47'; a 64.45% change) in the basal spacing of the natural bentonite as a result of its interaction with water. This is a prominent indication of the stationing of water molecules on the ordinary bentonite particles. The results do not show such a profound interlaminar increase for the ordinary bentonite

Table 2: X-rd analyses results for clay soils exposed to gasoline and water

	Thickness of ordinary bentonite particles (Å)			Thickness of modified bentonite particles (Å)		
Compound	Original	After Exposure	Percent of change	Original	After Exposure	Percent of change
Water	12.44	20.47	64.55	27.07	27.85	2.88
Gasoline	12.44	13.38	7.55	27.07	39.11	44.47

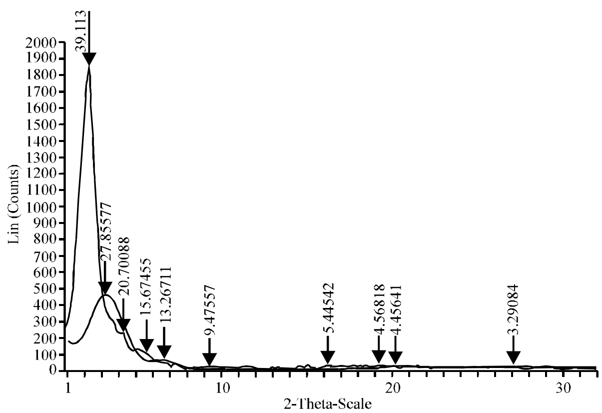

Fig. 4: X Ray Diffraction analysis of modified bentonite subjected to gasoline and water

mixed with gasoline. This suggests a lack of interaction between the bentonite and hydrocarbons.

For modified bentonite samples, moderate increases (44.45%) were observed in the unit cell thickness (basal spacing) of the clay particles. The particles thickness of modified bentonite clay increased from 27.07 to 39.11 Å for the samples subjected to gasoline, thus illustrating the interaction between modified bentonite and the gasoline hydrocarbons. Figure 4 shows the X-rd graphs of the modified clay following its exposure to water and gasoline.

DISCUSSION

This research investigated the adsorption and permeability changes of ordinary and modified bentonites exposed to water and gasoline hydrocarbons due to increases in their unit cells thicknesses. The results of this study support the hypothesis that organobentonites (modified bentonites) effectively intercalate gasoline hydrocarbons into their particles, thus increasing the clay's particles volume and thereby reducing the soil permeability. This is in agreement with the findings of Smith *et al.* (2003) research in which the permeability of modified bentonites were effectively reduced after their exposure to hydrocarbons.

The swelling of modified clay particles would also reduce the effective pore diameter of the soil, thereby decreasing the mobility of hydrocarbons in clay liners. The pore diameter plays a significant role in clay permeability.

In summary the results of this research indicate that modified bentonites, due to their low permeability and high organic adsorption characteristics, could be used as viable materials as liner systems for removing hydrocarbons at USTs and other gasoline contaminated sites .

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