ASSESSMENT OF SALINE SOIL STABILIZATION VIA OIL RESIDUE AND ITS GEO-ENVIRONMENTAL IMPLICATIONS

by

Lamya F. Mohammed

Department of
Civil Engineering and Applied Mechanics

McGill University

Montreal, Canada

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Short Title

SALINE SOIL STABILIZATION BY OIL RESIDUE & ITS ENVIRONMENTAL IMPLICATIONS

This thesis is dedicated to my parents

ABSTRACT

Two natural soils from Bahrain were used in this study to investigate the feasibility of using Arabian oil residue as a means to stabilize collapsible saline soils. Since the presence of oil residue in soils can pose an environmental threat, the high oil retention capability of the stabilized soils is critical to its application.

The behavior of the stabilized soils has been experimentally investigated in the laboratory. This study has concentrated on the evaluation of the mechanical properties of the stabilized soils, the oil retention characteristics and its bonding mechanisms, and the leaching and migration behaviors of oil residue from the stabilized soils.

The geotechnical investigation results indicated that the addition of 4% oil residue, by weight, was sufficient to significantly enhance the strength performance of the tested soils. The geochemical tests showed that the bonds formed between the oil and the soil surfaces were predominantly Van der Waal's attraction, weak hydrogen bonding, and cation and water bridging. These bonds were found to be relatively weak but stable and insensitive to leaching forces. The geo-environmental results revealed good oil retention in these samples, with less than 3% of the oil residue by weight leached from the stabilized soils after 40 days of leaching in distilled water.

The migration of oil from the stabilized soils has also been theoretically evaluated. The theoretical study utilizes the model developed by Yong et al. (1992) with a few modifications made to accommodate this particular situation. The model was solved using an explicit finite difference method, Powell's optimization technique, and experimental results. The predicted oil migration profiles were found to be slightly over-estimated as compared to the experimental profiles.

RÉSUMÉ

Deux sols naturels provenant de Bahrein ont été utilisés dans cette étude pour déterminer la faisabilité de l'utilisation de résidus pétroliers arabes pour stabiliser les sols salins instables. Puisque la présence de résidus pétroliers dans les sols peut causer un problème environnemental, une forte capacité de rétention pour ces sols stabilisés est critique.

Le comportement de ces sols stabilisés a été étudié de façon expérimentale en laboratoire. Cette étude a porté sur les propriétés mécaniques des sols stabilisés, les caractéristiques de la rétention du pétrole et les mécanismes de liaisons, ainsi que sur le comportement de lixiviation et de migration de résidus pétroliers dans les sols stabilisés.

Les résultats de l'étude géotechnique indiquent que l'addition de 4% de résidus pétroliers (par masse) est suffisant pour augmenter de façon significative les performances des sols étudiés. Les études géochimiques montrent que les liaisons formées entre les résidus pétroliers et la surface du sol sont principalement des forces d'attraction de Van der Waals, des liaisons hydrogènes faibles, ainsi que des liaisons par "pont" d'eau et de cations. Ces liaisons sont relativement faibles mais stables et non sensibles aux forces de lixiviation. Les résultats géo-environnementaux révèlent une bonne rétention des résidus pétroliers dans ces échantillons, avec moins de 3% des résidus, par masse, lixiviés des sols stabilisés après 40 jours de lixiviation dans l'eau distillée.

La migration des résidus pétroliers dans les sols stabilisés a été évaluée théoriquement. L'étude théorique utilise le modèle développé par Yong et al. (1992) avec quelques modifications adaptées pour ce cas particulier. Le modèle obtenu a été résolu en utilisant une méthode explicite de différences finies, la technique d'optimisation de Powell, et des résultats expérimentaux obtenus des études de lixiviation. Les profils de migration des résidus pétroliers prédits étaient légèrement surestimés par rapport aux profils expérimentaux obtenus.

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PUBLICATIONS

The following papers, produced during the course of this thesis, have been presented at scientific conferences:

(1) Mohammed, L.F., Yong, R.N., and Mohamed, A.M.O., **Assessment of Oil Residue Retention in Soil**. Presented in the First Annual Civil Engineering Graduate Student Society Conference, McGill University, Montreal, Quebec, Canada, February 17, 1994, pp. 6-7.

(2) Yong, R.N., Mohammed, L.F., and Mohamed, A.M.O., **Retention and Transport of Oil Residue in a Sandy Loam Soil**. Presented in the **ASTM** Symposium on Analysis of Soils Contaminated with Petroleum Constituents, Atlanta, Georgia, U.S.A., June 24, 1993. Appeared in Analysis of Soils Contaminated with Petroleum Constituents, ASTM STP 1221, Tracey A. O'Shay and Keith B. Hoddinott, Eds., American Society for Testing and Materials, Philadelphia, May 1994, pp. 89-110.

(3) Mohamed, A.M.O, Yong, R.N., and Mohammed, L.F., **Soil Improvement Using Chemical Treatment**. Appeared in the Proceedings of the First Geotechnical Engineering Conference, Cairo University, Cairo, Egypt, September 30- October 3, 1991, pp. 1-12.

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CHAPTER 1
INTRODUCTION

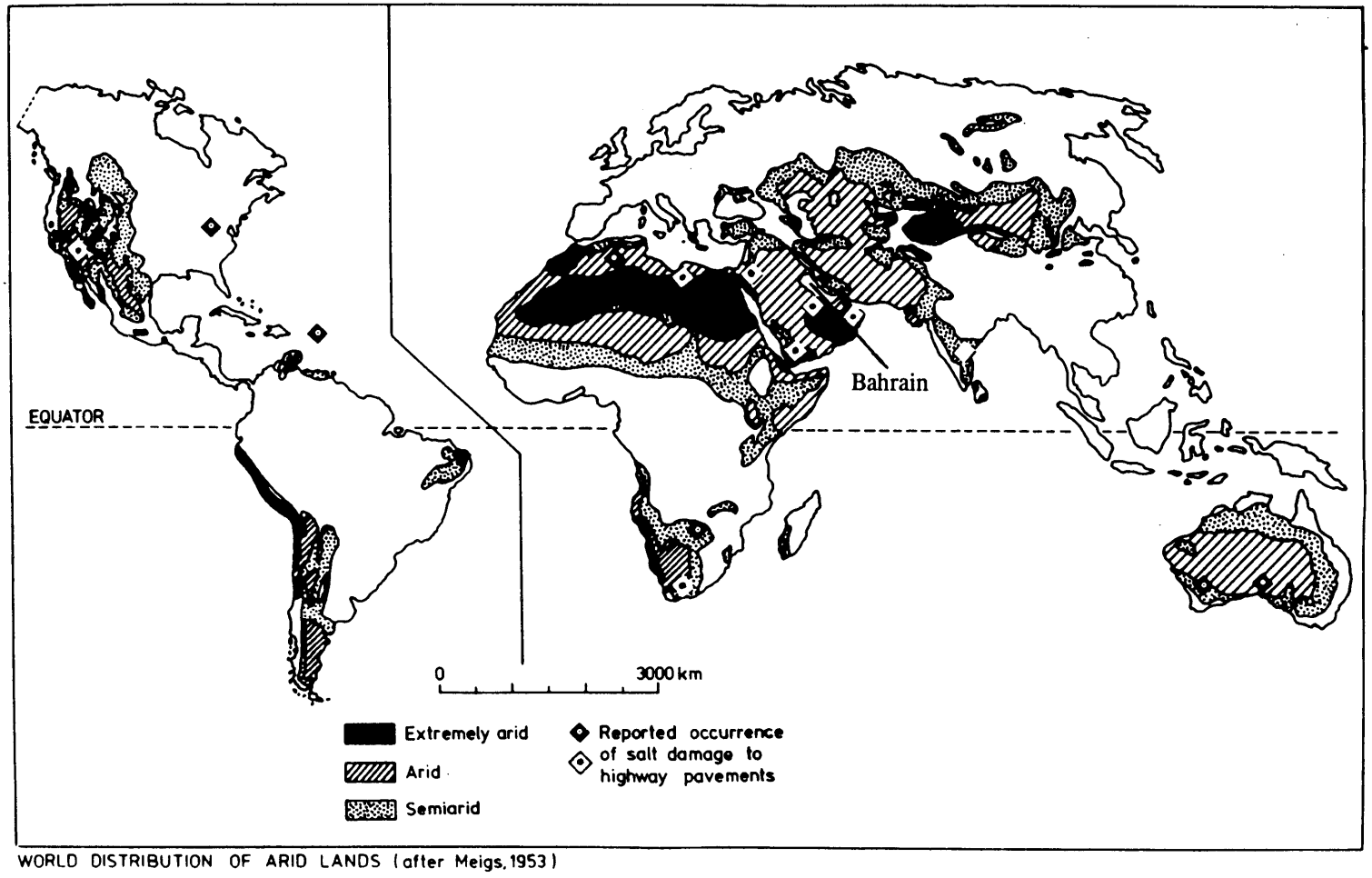
1.1 Salt-affected Soils

Salt-affected soils cover a large part of the earth's surfaces; about 10% of the global land surface is affected by different kinds of salts. The dominant types of salt-affected soils include saline and alkali soils. Salt-affected soils occur in areas where soil type, texture, climate, and regional controls favour the formation and retention of salt (see Figure 1.1). They exist in different soil types, though their appearance is most frequent in soils originated from limestone and dolomite bedrocks. The presence of nearby salty surface water, such as shallow brackish water table or sea water, plays another major role in the mechanisms of their formation. Moreover, hot climatic conditions with low rainfall, as in arid regions, also promote salt accumulation.

Many parts of the Middle East possess salty ground conditions. Most of the soils in the Middle East are saline and calcareous within the top 2 meters; alkaline or neutral in the surface horizon; coarse to medium texture on upland sites; fine texture in closed basins; and usually are only weakly developed morphologically. The Arabian Gulf region is one of the areas suffering from such an aggressive environment. The soil in this region consists of medium to fine-sized particles cemented by crystallized salt. The water table in most of the Arabian (Persian) Gulf countries is located at relatively shallow depths and characterized by its high salinity. This is because of the presence of evaporite salts dissolved from local bedrock or from sea waters (Szabolcs ,1989; Dregne, 1990; Szabolcs, 1990).

1.2 Environmental Conditions in Bahrain

Bahrain is an island country located in the Arabian Gulf, just off the coast of Saudi Arabia. It is essentially a desert plain with occasional low hills. The climate is



WORLD DISTRIBUTION OF ARID LANDS (after Meigs, 1953)

Figure 1.1 - World map showing climatic zones and locations where salt damage to structures and roads has been reported in the literature.

very hot in the summer and mild in the winter (18-35°C). Relative humidity is high throughout the year (48-83 %). The average rate of rainfall is very low (75 mm/year), whereas the annual rate of evaporation is very high (20 mm/day during the summer) (Doornkamp et al., 1980).

Despite low precipitation, brackish groundwater is generally encountered at shallow depths throughout Bahrain, ranging from 10 m in central areas to less than 1 m near the coasts. Analyses of groundwater from several areas in the country reveal its high salinity. Studies by Doornkamp et al. (1980) have shown that the groundwater in Bahrain has salinities of 5 to 150 gm/l, sulphate contents of 100 to 10 000 ppm and chloride contents from 1000 to 150 000 ppm.

Several studies on salt-affected soils reveal a great deal about their geological formation and composition (Bush, 1973; Fookes and Higginbottom, 1975; Fookes, 1978; Akili, 1981a). Most salt-affected soils along the Arabian Gulf coast consist of loose to dense silty sand cemented by crystallized salt, primarily calcite, dolomite, and halite. Depending upon the location, salt-affected soils can be called either coastal or inland soils. Coastal soils are common in Bahrain, and are locally known as Sabkha soils.

Coastal Sabkha soils (see Figure 1.2) are supertidal surfaces which have developed as a result of a sedimentation sequence that appears to have started over several thousand years ago with seawater transgressing over sand dunes. Following this transgression, the depositional environment was shifted from subaerial to subaqueous, causing carbonate sedimentation. Through diagenetic processes, the primary marine sediments were transformed to new minerals (ie. calcite, dolomite, gypsum, and halite). Thus, the main coastal Sabkha sediments are composed of: (1) aeolian sands mixed with marine carbonate sediments; (2) muddy carbonate sands and silts; (3) diagenetic minerals (calcite, dolomite, gypsum and halite); and (4) wind-blown sand.

A typical profile of coastal Sabkha soil in Bahrain can be described as follows: (1) upper zone, which represents the top 1 meter, comprises of poorly cemented fine sand and silt with occasional lenses of gravel; (2) intermediate zone consists of cemented silty sand mixed with muds and may contain shells and marine sediments; (3) lower zone, which is usually located below 10 meters, contains strongly cemented dense sand

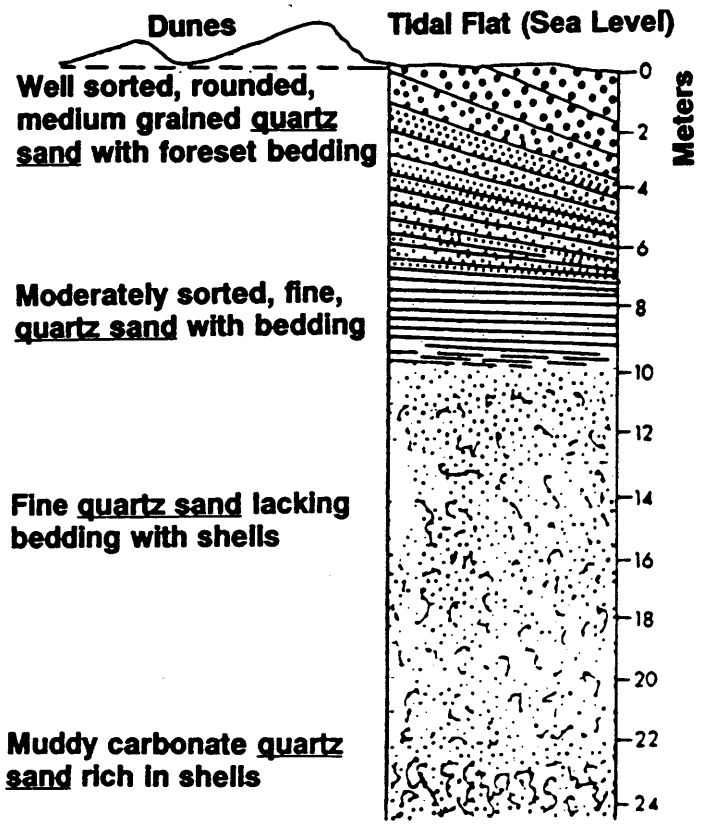


Figure 1.2 - Vertical sequence from a coastal Sabkha sand deposit in the Arabian Gulf (after Shinn, 1973).

and silt or bedrock, which is dominated by limestone and sandstone type (Doornkamp et al., 1980 ;Akili, 1989).

1.3 Geotechnical Properties of Sabkha Soils

The geotechnical properties of Sabkha soil have been discussed in several studies (Akili, 1981b; Stipho, 1985; Al-Sanad et al., 1989). Studies have shown that most Sabkha soils possess a collapsible behavior. They exhibit considerable strength in their dry condition but have a strong potential for loss in strength upon wetting. The geotechnical properties of Sabkha soils can vary widely with moisture content, fines content, salt type and quantities. Due to similarities of ground conditions in the Gulf region, examples given in any Gulf state are usually applicable to Bahrain.

Variation in soil moisture may result from fluctuation of brackish groundwater or a change in climatic conditions, as previously described. Akili (1981b) has studied the influence of moisture content on the strength of some soils in eastern Saudi Arabia. He concluded that the maximum CBR (California bearing ratio) values of the soils occur just to the drier side of the optimum moisture content.

The effect of leaching forces on some geotechnical properties of collapsible soils from Kuwait was investigated by Ismael (1993). He recorded a reduction in soil shear strength and preconsolidation pressure and an increase in soil permeability and void ratio as a result of leaching. Similar observations were noted by Lamb (1990) on examining the effect of leaching on the geotechnical properties of collapsible soils from the east-central part of Iowa, USA. These two studies attribute the mechanical instability of the collapsible soils to the removal of a "cementing substance", primarily salts. The implication is that this substance acts as a binder which imparts cohesion to the soil, and that leaching of this material leads, in the presence of water, to the formation of a weak collapsible soil mass.

The effect of soil type was examined by Doornkamp et al. (1980) and Qahwash (1989). Doornkamp has reported that the soil in Bahrain is dominated by sand with fines contents varying from 5 to 30 % , organic contents of 0.1 to 2 % and traces of shells

near the coastal areas. Common types of clay minerals include palygorskite and montmorillonite; such minerals are characterized by large surface areas and high ionic exchange capacities. Qahwash (1989) has discussed the influence of sand content on the performance of Sabkha soils obtained from eastern Saudi Arabia. He recorded a significant increase in soil strength (CBR values) and a dramatic reduction in swelling and plasticity potential as the sand content increased.

Basma and Tuncer (1992) investigated the effect of soil type, compaction, water content, initial dry unit weight, and applied pressure on the collapse potential of Jordanian soils upon wetting. They reported that well graded soils tend to collapse more than poorly graded ones. Their study also concluded that the collapse potential decreases with an increase in : (1) the difference between the sand and clay percentages; (2) compaction water content; and (3) initial dry unit weight, while it increases with pressure on wetting.

The influence of salt content and type on the behavior of Sabkha soil was investigated by Akili and Torrance (1981), Stipho (1985) and Al-Sanad et al. (1989). Salt content in Sabkha soil is dominated by sulphates, chlorides and carbonate of sodium, calcium and magnesium as described by Akili and Torrance (1981). Salt has been found either dissolved in soil pore fluids or as salt crusts (in crystallized form) on the surface. Stipho (1985), in testing such effects on soils in eastern Saudi Arabia, reported that an increase in salt content of undisturbed soil samples would increase cohesive strength but reduce the angle of shearing resistance. Also, cementation with sodium chloride showed higher shear strength as compared with calcium carbonate.

1.4 **Statement of the Problem**

From the previous literature review, one can see the strong potential for Sabkha soils to create a chemically aggressive environment and lead to a structurally unstable soil condition. The presence of high contents of soluble salts (e.g. sulfate) and alkaline salts (e.g. carbonate) in these soils is most likely responsible for such behavior. In addition, in an environment where the level of a salty water table is high and climatic conditions

are hot, salt accumulation near the ground surface will be expected. Because of rapid evaporation, water moves through the soil by capillary fringe into the atmosphere. The movement of water accelerates solution and precipitation of soluble salts. The salt crystals are highly corrosive to construction materials, such as steel and concrete. Therefore, such salt attack can cause damage to concrete slabs and foundations and can lead to deterioration of bases and sub-bases of highways.

The other major problem associated with Sabkha soils is that they have the potential to collapse upon wetting with or without an applied load. Most Sabkha soils exhibit considerable strength in their natural state due to the presence of chemical cementation bonds, e.g. precipitation of salts, clay bonds, clay bridges, and capillary suction formed between soil grains as the soil dries after deposition (Karakouzian, et al., 1992). However, when such soils are wetted (due to an infiltrating rainfall, percolation of surface water, or a rise in the level of a nearby water table), the cementation bonds, bridges and/or capillary suction are partially destroyed. Consequently, the cohesive component of the shear strength is reduced and collapse may occur.

The amount of strength reduction and/or collapse depends on the degree of saturation, load and soil density, and chemical composition of the percolating fluid. The source of the initial shear strength affects the rate of the strength reduction because the strength is instantaneously reduced when capillary suction provides the shear strength. However, strength reduction may be considerably slower when clays are involved in bonding and/or bridging. In addition, the dissolution of salt bonds are found to be more profound in the presence of fresh water as compared to saline water (Rocca, et al., 1992). A schematic picture illustrating the nature of the problems associated with Sabkha soils is shown in Figure 1.3.

Both problems can result in distress and damage to structures and highways. However, the second problem, i.e. low structural and/or chemical stability of Sabkha soils, is more severe from the standpoint of geotechnical engineers. This is due to the expected rapid and extensive damage associated with construction on these soils. Therefore, in this study, special emphasis is placed on enhancing the mechanical properties of these soils under wetting conditions.

Sabkha soil is very heterogeneous and is a generally unstable material, as

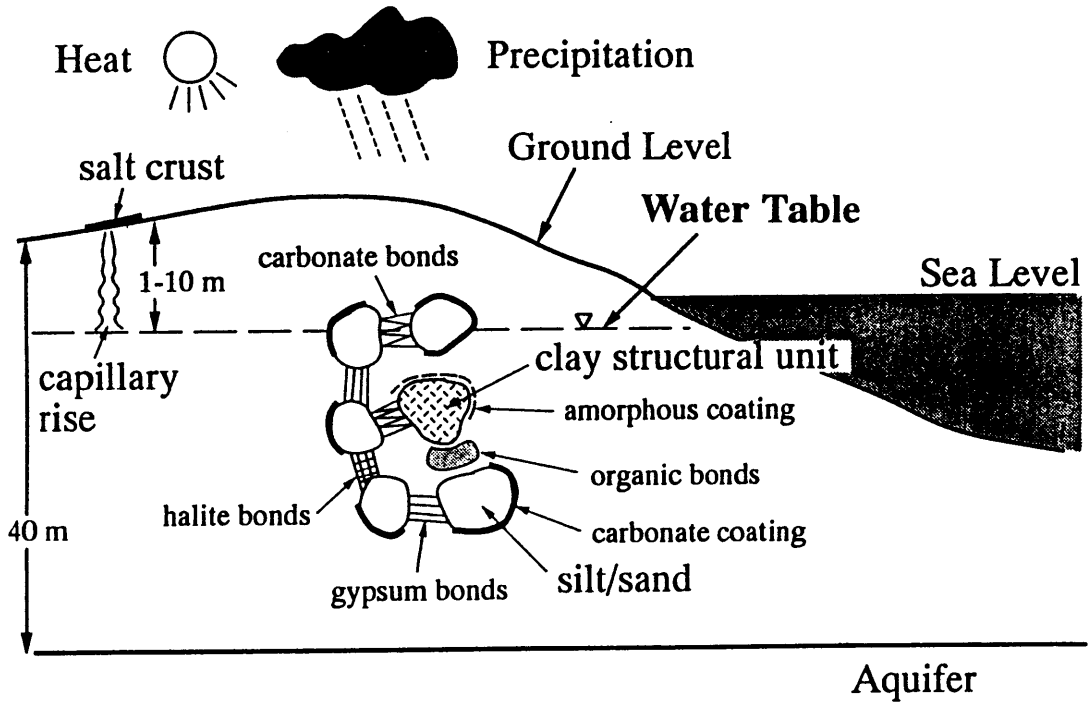


Figure 1.3 - Schematic representation of ground condition in Bahrain showing problems associated with Sabkha soil.

described previously. Studies have shown that the poor performance of Sabkha soil can be attributed to the following (Stipho, 1985; Akili, 1989; Qahwash, 1989):

(1) Variation in cementation bonds which causes a decrease in soil strength under wet conditions.

(2) Potential variation of compressibility characteristics and low bearing resistance leading to excessive differential settlement.

(3) Evaporative pumping mechanism moving soluble salts towards the surface creating a salt encrusted surface.

(4) Alternate hydration and dehydration of salt deposits, especially gypsum and anhydrite, due to hot and humid conditions causing volume changes (i.e. heave or settlement).

(5) Presence of cavities in the dolomitic formation can contribute to subsequent failures.

The potential engineering problems associated with Sabkha soils have been discussed in several studies (Fookes, 1978; Akili and Torrance, 1981). The major problems with reference to engineering works on Sabkha soil include:

(1) Salt attack on sub-structure materials promotes deterioration of concrete and its reinforcements.

(2) Formation of salt crusts near the ground surface initiates surface cracking, particularly in pavements.

(3) Presence of salt in soil affects the nature and physical behavior of foundations.

(4) Salt in soil acts as a corroding agent on embedded metallic structures, pipes, etc.

In order to overcome the problems associated with Sabkha soils, various soil improvement techniques have been considered. The selection of an appropriate soil improvement technique depends mainly upon the objectives of the improvement, ground conditions, and improvement cost. The objectives of the improvement in this study are: (1) to enhance the mechanical properties of the soil by binding soil particles together (increasing its strength); and (2) to protect sub-bases of highways and small structures from the deteriorative attacks of salt by providing an impermeable horizontal barrier.

To meet these objectives, improvement techniques such as stabilization, reinforcement, and grouting have been proposed. The stabilization technique is considered for particular study herein. Among the numerous stabilizer agents commonly used are: cement, lime, bitumen, organic polymers, and fly ashes.

The stabilization technique was utilized here for its effectiveness to treat the upper portion of the soils which is dominated by silts and sands. Since the desired depths of treatment in this case are predominantly near the top surface, stabilization was considered very feasible. This technique was also found to be very suitable for sandy soils since their high permeability permits the medium easier access to the stabilizer.

Because of the presence of a very active petroleum industry in the Arabian Gulf, the use of oil residue for stabilization appears as a very propitious application of a "native" product. Oil residue (residuum) is the bottoms remaining undistilled fraction of crude oil. Moreover, the use of oil residue can be advantageous in the Arabian Gulf region where the soils are mostly very dry. In these circumstances the oil residue is anticipated to strongly adhere to dry soil surfaces and be substantially retained within the soil matrix.

Since oil residue can pose a threat to the surrounding environment, considerable research is undertaken to examine the long-term stability of such material. It is expected that the effects of rainfall and groundwater fluctuation would provide the opportunity for migration of oil residue from the stabilized soils. This can cause environmental problems in the form of groundwater and surface water contamination. Therefore, this form of soil improvement requires proper retention of the additive and bondings achieved.

1.5 **Objectives of the Study**

This research deals with the feasibility of using oil residue as a means to stabilize and neutralize Sabkha soils (collapsible soil), and also examines the long-term behavior associated with such a material. The objectives of this research programme are:

(1) To investigate the feasibility of using oil residue to modify beneficially the mechanical properties of Sabkha soil. This study assesses the influence of

different parameters, such as oil residue content, leaching forces, saline condition, and soil washing, on the strength performance.

(2) To examine the interaction and bonding mechanisms between the oil residue and soil surfaces in terms of:
   (a) mode of interaction.
   (b) energy status of the entire system.

(3) To investigate the environmental impacts associated with the application of oil residue. This study includes the investigation of the following:
   (a) retention characteristic of the oil residue in the stabilized system.
   (b) desorption potential of the oil residue from the stabilized soil.
   (c) leaching and migration behaviors of the oil residue from the stabilized system under different environmental conditions (i.e. infiltrating rainfall and fluctuation of groundwater).

(4) To predict the long-term migration behavior of the oil residue in soils with the aid of a transport model.

1.6 Approach

The objectives are implemented through experimental and theoretical studies. All the necessary details involved in the experimental studies will be explained in Chapter 3. The laboratory experimental studies include the following:

(1) Various physical and chemical tests, to determine the composition and properties of the tested soils and oil residue (e.g. x-ray diffraction, infrared spectroscopy, geotechnical testing, surface activity of soil, and physico-chemical characteristic of oil). To simplify this study, two natural soils from Bahrain, and one type of oil residue, i.e. atmospheric Arabian oil residue, are used.

(2) Unconfined compression, California bearing ratio, and direct shear tests, to determine the mechanical properties of the soils under the effect of various oil residue content, soil washing, and leaching forces.

(3) Infrared spectroscopy and soil suction tests, to obtain the nature of interaction and

bonding between oil residue and soil surfaces and the energy state of the soil fluids, respectively. The contribution of the above influencing parameters are also considered.

(4) Soil leaching tests, to examine the leaching and migration behavior of the oil residue from the soils. In these tests, only the optimum oil content for maximum strength, obtained from geotechnical testing, is used to prepare the stabilized samples. Each stabilized sample is separately leached in distilled water and saline water, and the concentration of the leached oil residue from the stabilized soils is measured using the partition-infrared method. However, the amount of oil retained in these soils is determined using the Soxhlet extraction technique.

The theoretical study involves the application of an existing transport model developed by Yong et al. (1992), modified to accommodate this particular situation. The model applies concepts from irreversible thermodynamic, Fick's laws, Darcy's law, and equilibrium mass transfer principles. The resulting model is solved using explicit finite difference method. All the unknown material parameters generated from the model are computed using Powell's optimization technique and the experimental results obtained from the soil leaching test.

1.7 Organization of the Thesis

The thesis consists of nine chapters, the contents of which are as follows:

Chapter 1: an introductory chapter which gives a background of the ground conditions in Bahrain and presents the problem, objectives, and approach of the present study.

Chapter 2: summarizes the published literature concerning soil improvement techniques and the overall behavior of petroleum hydrocarbons in soils. The latter includes reviews relating to geotechnical performance, geochemical characteristic, and transport behavior of petroleum

hydrocarbons in soils.

Chapter 3: describes the experimental methods, materials, and testing procedures employed in this study.

Chapter 4: presents the results and discussion of the laboratory program concerning the geotechnical performance of the soil-oil mixtures.

Chapter 5: presents the results and discussion of the laboratory studies on the geochemical characteristics of the soil-oil mixtures.

Chapter 6: presents the results and discussion of the experimental study on oil leaching behavior, with special emphasis on the various transport processes of oil in a soil-oil system.

Chapter 7: summarizes an overall assessment of the experimental results obtained from this study, i.e. the results of geotechnical, geochemical, and environmental testing.

Chapter 8: contains the development of an oil transport model in a soil system and its calibration and prediction for this particular situation under a given set of conditions.

Chapter 9: gives the summaries and conclusions, suggestions for future research in the same field, and scientific contributions.

CHAPTER 2
LITERATURE REVIEW

2.1 Soil Improvement Techniques

The use of soil improvement techniques has been one of the greatest challenges for the geotechnical engineer for more than half a century. Soil improvement techniques are useful in solving problems related to stability, deformation, and seepage. The feasibility of a particular technique is strongly related to the type of problem. To improve the hydraulic properties of soils, vertical drains or geosynthetics are recommended. However, to enhance the mechanical properties of the soil, stabilization, grouting, and reinforcement are considered feasible solutions (Evstatiev, 1988; Fleming, 1991).

Ground condition and cost of improvement are also important factors in selecting the adequate improvement technique. In Sabkha soils, long-term stability of grouting materials, metallic reinforcement, and geosynthetics can be questionable. The presence of salt can result in a significant loss in the stability of these materials. Salt attacks such materials and can lead to deterioration of concrete, corrosion of metals and degradation of synthetics. In addition, the costs of these soil improvement techniques can be very high (Vanimpe, 1989; Hausmann, 1990).

Studies on the improvement of Sabkha soils associated with engineering practice are limited. Oweis and Bowman (1981), Stipho (1985) and Obika et al. (1989) have suggested some remedial techniques to reduce the salt attack on foundations and roads. Oweis and Bowman (1981) proposed the use of asphalt coatings and wrapping techniques to protect foundations against salt attack. Obika et al. (1989) recommended the use of thick asphalt surface pavements to protect roads in saline environments.

After reviewing the existing soil improvement techniques, the selection of stabilization was considered to be a feasible solution for this problem. Stabilization techniques include mechanical and chemical approaches. Mechanical approaches ensure soil stability by compacting it, whereas chemical approaches involve the use of additives

(stabilizing agents) to enhance the soil performance. Common stabilizing agents that are presently used include: cement, lime, bitumen, organic polymers, and fly ashes. Special emphasis on selecting the proper type of additive and methods of application should be considered.

Experience with construction on Sabkha soils has shown the applicability of mechanical stabilization to densify the soil if shells are not prevalent (Juillie and Sherwood, 1983; Akili, 1989). The most widely used techniques include surface densification by vibratory rollers (with and without fill on top), deep compaction by vibroflotation, and dynamic compaction. Akili (1989) has reported some difficulties in compacting deep soil. The presence of high fines contents, shells, undetectable cemented layers, and cemented zones at a high depth could retard deep compaction.

The performance of Sabkha soils stabilized with Portland cement was studied by Stipho (1989) and Ahmed (1989). Stipho (1989) showed that a ratio of 5% (by weight) of cement was sufficient to substantially increase the shearing strength of the stabilized soil. Ahmad (1989) has suggested a ratio of 8% (by weight) of cement to improve the strength and durability characteristics and reduce the degradation effects. The applicability of cement to stabilize Sabkha soils has been described by Ingles and Metcalf (1973). They reported that the presence of excess soluble salts (especially sulphates) in a soil-cement mixture could retard or prevent a proper hydration process. Furthermore, the feasibility of using lime or other salt additives to stabilize Sabkha soils was not considered since such soils are already rich in salt.

To enhance the performance of the traditional stabilizers (i.e. cement, lime, bitumen), the addition of fly ash has been recommended. Fly ash acts primarily as a filler, improving the binding effect of the stabilizers. Natt and Joshi (1984) investigated the performance of sandy soils mixed with a combination of cement and fly ash. Their study showed that the maximum values of both densities and unconfined compressive strengths of the tested soils had been achieved with the addition of 20% fly ash. Although negative environmental impacts associated with the application of fly ash are not reported, considerable research towards the chemical composition of its leachate, its corrosiveness on buried structural elements, and its radioactivity and toxicity should be undertaken (Hausmann, 1990). Also, the economical feasibility of using fly ash in

Bahrain can be questionable.

A variety of organic compounds (i.e. polymers, resins) has been tried as soil stabilizers. Their main functions are to retard water adsorption and enhance soil hardening. The effectiveness of using most organic compounds as stabilizers is still in the testing stages. Cost, toxicity, and method of application of these stabilizers are the major factors in retarding their applications (Nelson and Miller, 1992).

Bitumen is another type of additive which is widely used as a stabilizing agent, especially for the sub-base of roads and highways. Bitumen is a product obtained after processing oil residue. Bituminous stabilization can add significant cohesion to soils and reduce their water absorption capacities. When bitumen is added to soils, a strong and insoluble gel is formed, which coats the particles and fills the soil pores. Bituminous stabilization is best utilized for well-graded sands with a fines content in the range 8 to 20%. Increasing the fines content within this range can improve the strength of soil but reduce its water resistance. However, lack of fines can cause a significant loss of adhesion between soil and bitumen (Ingles and Metcalf, 1973; Hausmann, 1990).

Bitumen is commonly applied to soils in emulsion form. The use of cationic emulsions to stabilize soils has been preferred over other types of emulsions. This is because the adhesion of cationic emulsion to soils is relatively high, since most naturally occurring soils possess negatively charged surfaces (Hausmann, 1990). However, bitumen can be relatively costly because of the additional processing required in its preparation. On the other hand, oil residue is relatively cheap and can be a satisfactory soil stabilizer. To ensure the feasibility of oil residue, the stabilized soils must be properly tested for mechanical stability and long-term performance. Bitumen is composed mainly of resin and asphaltene, whereas oil residue contains mostly saturates and aromatic hydrocarbons and to a lesser extent resins and asphaltenes (Ali and Saleem, 1988; Kircher, 1989).

2.2 Behavior of Oil in Soil

The behavior of various derivatives of petroleum hydrocarbons in soils was examined previously by different researchers. A summary of their findings in relation

to geotechnical, geo-chemical, and transport aspects is presented herein.

2.2.1 Geotechnical Performance

Several studies have discussed the engineering characteristics of soil mixed with petroleum derivatives, especially with respect to compaction, strength, and water absorption. Kezdi (1979) as well as Ingles and Metcalf (1973) investigated the geotechnical performance of bitumen-stabilized soils. They quoted results indicating that: (1) the maximum dry density achieved with a constant compactive effort falls with increasing bitumen content; (2) the optimum amount of water necessary for reaching maximum density decreases with increasing bitumen content, whereas the corresponding total amount of liquid added (water and bitumen) actually rises; (3) the unconfined compressive strength initially increases with increasing bitumen content until maximum mechanical stability is reached, beyond which a reduction in the strength is recorded; (4) the adsorption of water leads to a reduction in soil strength; (5) the strength of unsoaked samples generally peaks at a lower bitumen content than the soaked ones; this effect diminishes as the bitumen content increases.

Ola (1978) investigated the strength characteristics of sand-bitumen mixtures. Ola's study reported an initial increase in the maximum dry density, bearing capacity (CBR value), and unconfined compressive strength up to a bitumen content of 3 percent, with a subsequent decrease. Moreover, Al-Balbissi (1989) obtained similar strength results for sand mixed with a combination stabilizer (e.g. lime-bitumen, cement-bitumen ;both prepared at a ratio of 1 to 4). He recorded an increase in soil strength with bitumen content until it reached the maximum followed by a reduction.

The geotechnical performance of sand mixed with various contents of crude oil was examined by Puri et al.(1994). The study reported a decrease in the maximum dry density, internal angle of friction, and coefficient of permeability of the sand in the presence of crude oil.

2.2.2 Geo-chemical Characteristic

Understanding the various mechanisms of interaction between oil and soil surfaces are important in predicting the oil retention capacity of the soil, and also the long term

behavior of the oil. Interaction mechanisms are influenced by soil constituents, the type of oil, and the presence of water. Previous studies (Theng, 1974; Clementz, 1976; Rausell-Colom and Serratosa, 1987; Schnitzer and Kodama, 1992) have shown that the existence of surface active constituents in the soil matrix, such as organic, amorphous materials and clays, can significantly enhance oil retention in soils. This is because such active constituents possess large surface areas and high surface charges which give them the ability to adsorb high quantities of oil. However, the presence of water on soil surfaces, prior to the introduction of oil, interferes with soil-oil bonding. As the amount of water in association with soil increases, adsorption of oil decreases. This is explained by the fact that oil has low aqueous solubility and large molecular size, and thus cannot easily penetrate adsorbed water layers to approach the surface. The effective diameter of various hydrocarbon molecules varies from 1 to 3 nm for a complex hydrocarbon type and from 5 to 10 nm for an asphaltene. However, water molecules have a much smaller diameter than hydrocarbons, approximately 0.3 nm (Welte, 1972).

Various studies (Ali et al., 1989; Yong and Rao, 1991) have shown that oil is composed mainly of weakly polar (resin) to non-polar compounds (saturates and aromatic hydrocarbons). The weakly polar compounds have higher adsorption capacity onto soil surfaces than the non-polar compounds. The adsorption of non-polar compounds onto soil surfaces is dominated by weak bonding, i.e. Van der Waals attraction, and is restricted to external soil surfaces since most of the oil fractions possess low dipole moments (less than 1) and also low dielectric constants (less than 3) (Yong, 1973; Yong and Rao, 1991). In addition, the aqueous solubility and partition coefficient of the oil (i.e. organic carbon partition coefficient, octanol-water ratio) play major roles during interactions. Most hydrocarbon molecules are hydrophobic and have low aqueous solubilities and thus they partition to a greater extent onto the soil phase than the aqueous phase. The high partitioning of the oil onto soils is expected to reduce oil mobility and thus improves its retention in soils (Meyers and Oas, 1978; Dzombak and Luthy, 1984; Hassett and Banwart, 1989).

A proper knowledge of the various behaviors of bituminous materials in soils is very critical to this study. The adsorption of bitumen onto surfaces of different soils and aggregates has been examined by several researchers (Jeong and Kobylinski, 1983; Curtis

et al. 1989). Curtis et al. (1989) investigated the adsorption of asphalt and its oxidized form onto different types of aggregates (silica, alumina, sandstone, and limestone). The study showed that the aggregate ranking of adsorbed asphalt was alumina > silica > limestone > sandstone. Moreover, the oxidized asphalt had a higher adsorption to aggregate surfaces. The percent difference between the adsorption of asphalt and its oxidized form gave a ranking of: silica (50%) > alumina (38%) > sandstone (10%) > limestone (3%). Similar results were obtained from a study conducted by Jeong and Kobylinski (1983). They found that the association of bitumen to silicate minerals was four times greater than its association with carbonate minerals. This reflects the high surface activity of the silicate minerals as compared with the carbonate ones.

There have been a number of studies examining different behavioral aspects of bitumen in soils (Ensley, 1975; Salem et al.,1985). Ensley (1975) has pointed out that orientation of asphalt molecules together with the type of functional groups involved plays a major role during the adsorption of asphalt on mineral aggregate. Furthermore, Salem et al. (1985) studied the effect of bitumen on the retention and release of some chemical elements (e.g. nutrients and heavy metals) in sandy soils. The study reported that the addition of bitumen to sand increases aggregation and stability of soil, and decreases the extractable amounts of chemical elements.

Desorption of various hydrocarbons from different soil surfaces has been the subject of a limited number of studies (Yaron, 1989). Yaron (1989) studied the desorption behavior of selected petroleum hydrocarbons (m-xylene, n-decane, t-butylbenzene) from soils with different clay and organic matter (OM) contents (BetDagan- clay 12%, OM 0.5%; Gilat- clay 16%, OM 0.6%; Oxford- clay 35%, OM 7.2%). The desorption of these hydrocarbons from the studied soil surfaces was found to be strongly affected by the type of soil and hydrocarbon. The study showed that the rate of desorption occurred in the following order: m-xylene > n-decane > t-butylbenzene. Moreover, the desorption rate of these hydrocarbons from soils were in this order: BetDagan > Gilat > Oxford. *From the above study, one can expect that the light hydrocarbons will have higher desorption rates than the heavier fractions. Also, the desorption rate of hydrocarbons increases as the contents of active constituents in the soil matrix reduces.*

2.2.3 Transport Behavior

In an oil-soil-water mixture, oil has the potential to co-exist in at least three different situations: (1) adsorb onto the soil surfaces; (2) link some of the soil particles; and (3) exist separately in soil pore fluid. In turn, one expects that within the pore fluid of soil, oil can exist in three separate phases: dissolved, non-aqueous or gaseous. The persistence of oil to co-exist in the above three situations depends on its composition and concentration, soil constituents, environmental conditions (e.g. temperature and rainfall), and nature and rate of various natural processes (e.g. adsorption, leaching, volatilization, and degradation). The presence of low oil concentration, high content of heavy constituents of oil, and active soil constituents in the soil-oil media together with the low rate of leaching are expected to enhance the oil retention in soils (Sims and Overcash, 1983; ; Hillel, 1989; Warren et al.,1992).

The contribution of the natural processes in transporting the oil from oil-soil-water media has been examined by various researchers. A study by Eastcott et al. (1989) on the persistence of a particular mass of crude oil in a marine environment over a period of one year showed that: 30% had been lost by biodegradation, 20% by volatilization, 3% by photolysis, and 2% by dissolution. Therefore, one can speculate that the transport processes of oil in soils will be dominated by: leaching, volatilization and biodegradation. Moreover, since oil residue possesses low volatility potential and high molecular weight (Ali et al., 1989), the volatilization and biodegradation rates are expected to be low. However, the process of leaching oil from soils is the most critical one since oil may pose a threat to groundwater supplies. The leached oil can be either in an aqueous or in a separate liquid phase (non-aqueous phase liquid; NAPL). The leaching behavior of the aqueous phase of oil is controlled by its water solubility, whereas the leaching of the liquid phase is governed by its viscosity and surface wetting properties. Moreover, the permeability of soil and the rate of water flow, due to rainfall or fluctuation of surface water, can also influence the oil leaching processes from the soil-oil matrix (Jury and Valentine, 1986; Thomas et al., 1991; Yong et al, 1992).

The literature addresses a wide range of studies on the environmental fate of various types of hydrocarbons in soils. Special emphasis will be given here on the leachability behavior of some hydrocarbons from soils. Pamukcu and Hijazi (1992)

studied the leachability of fuel oil mixed with kaolinite clay at 10 % by weight using a triaxial permeability apparatus. The study showed that the oil content in the leachate, at a flow rate of $9x10^{-10}$ m/sec, was approximately 380 ppm. This study also reported that the addition of a small percent of additives, such as organoclay, cement, fly ash, and lime, can significantly reduce the oil migration from soil-oil mixtures. Furthermore, the migration and biodegradation of petroleum residue in loamy soils, contaminated up to 6 % by weight, were investigated by Loehr et al. (1992). The study indicated that over a span of eight months, there was no significant biodegradation and the oil concentrations in the collected leachates were below the detection limits.

The leachability of oil from contaminated soils mixed with bituminous materials has been discussed by several investigators. Eklund (1989) examined the leaching behavior of oil from petroleum contaminated soils incorporated into bituminous concrete. After 1 week of continuous leaching with distilled water, the study reported oil contents of 2 ppm in their leachates. Moreover, a study by Sciarrotta (1991) on the oil leachability from sand, contaminated with residual fuel oil and mixed with asphalt paving materials, revealed that the concentration of oil in the leachates was below the detection limits. *From the above literature review, one can conclude that light hydrocarbons (e,g., gasoline, fuel oil) are more likely to volatilize and leach out, while the heavier constituents (i.e. oil residue, bitumen) have a higher retention in soils.*

In order to predict the long-term behavior of hydrocarbons in soils, a subsurface transport model should be developed and calibrated. Most subsurface transport models developed have dealt with two major processes: (1) dissolution, which allows the transport by advection, diffusion, and dispersion; and (2) sorption onto soil surfaces, which retards transport. Moreover, in modelling the transport of organics (i.e. hydrocarbons), volatilization and biodegradation processes as well as the behavior of non-aqueous liquid phase should be incorporated (Bouchard et al., 1989; Bonazountas, 1991; Luckner and Schestakow, 1991).

Previous studies on the transport modelling of hydrocarbons in soils reveal that there is no well-developed model (Donigian and Rao, 1986; Jury and Ghodrati, 1989; Guven et al., 1990). The application of most of the present models are simplified and

calibrated for a specific site under certain conditions. Moreover, although the various transport processes are highly complex and often linked, such models usually consider their effect separately and treat them as single first order processes.

2.3 General Remarks

From the review of the existing literature, several comments can be made concerning the behavior of oil in soils with respect to: soil improvement techniques, bituminous stabilization, differences between various forms of oil and oil residue, oil retention characteristics in soils, and environmental fate and transport of oil in soil-oil systems.

Most researchers have discussed the various soil improvement techniques, with limited suggestions on their applicability to Sabkha soils. In general, they pointed out that the major problems associated with Sabkha soils include their aggressive attack on construction materials (concrete) and their interference with the stabilization processes of some additives (cement).

Bituminous stabilization is a very effective technique for improving the engineering performance of sandy soils. It has been shown that bituminous stabilization can significantly enhance the mechanical stability and water resistivity of soils. Moreover, a bitumen content of 3 to 5% has been recommended as an optimum range for stabilizing sandy soils (Lambe, 1962; Hausmann, 1990). However, Ingles and Metcalf (1973) have pointed out that the presence of high contents of salt in soils may reduce the effectiveness of bituminous stabilization. Therefore, the present study investigates the effect of salt on the stabilization processes of a similar additive (oil residue).

Researchers have examined the behavior of bitumen and various petroleum hydrocarbons in soils. Bitumen is the processed fraction of oil residue, and consists of mainly resins and asphaltenes. Petroleum hydrocarbons contains mostly saturates and aromatic types. Oil residue is the "bottoms" remaining undistilled in the fractionation process of crude oil. Thus, oil residue contains saturates, aromatic hydrocarbons, resins, and asphaltenes (Petrakis et al., 1980; Kircher, 1989).

A proper knowledge of the various mechanisms of interaction between oil and soil surfaces is important in predicting the oil retention capacity of the soil. The extent of

interactions between oil and soil surfaces is strongly dependent on the amount and properties of both soil and oil. Previous studies have shown that the association of various oil constituents on silicate minerals are higher than carbonate minerals. Also, the presence of surface-active constituents in the soil matrix can significantly enhance its interaction with oil. In the case of oil, the major properties that affect its mode of interaction with soil include: water solubility, volatility, partitioning behavior, charge distribution, polarizability, and molecular size and weight. Moreover, due to low volatility and water solubility and high partitioning of heavy oil, studies have shown that they exhibit a better retention in soils than the lighter fractions of oil. In addition, since most fractions within heavy oil possess non-polar behavior and consist of large molecular sizes and weights, it is expected that Van der Waal's interaction will dominate (Clementz, 1976; Yaron, 1989; Yong et al., 1992).

Understanding the environmental fate and transport of oil is essential to properly characterize its hazard potential in a soil-oil system. Within an oil-soil-water system, oil can co-exist in four phases: adsorbed, dissolved, gaseous, and liquid (non-aqueous phase liquid; NAPL). The co-existence of each phase is influenced with various natural processes. Such processes include: adsorption, leaching, volatilization, biodegradation, and photolysis. The leaching process is the most critical one since leached oil may cause contamination of groundwater. The leaching process can be affected by soil permeability and texture, oil properties, and amount and intensity of rainfall. Moveover, studies have shown that the heavy fractions of oil possess low transport potential. Several researchers have tried to combine the above processes in one model in order to simulate the environmental transport. However, most of the existing transport models of oil in soils lack certain flexibilities in their applications (Hunt et al., 1988; Rubin and Mecherz, 1989; Ostendorf, 1990; Erickson et al. 1991).

This study attempts to present an overall behavior of oil residue in sandy loam soils. Special emphasis has been placed on the evaluation of the geotechnical, geochemical, environmental aspects of oil residue in soils, as indicated previously in Section 1.5 on objectives of the study. The details of the materials, experimental methods, experimental results, and theoretical work required to accomplish this study are presented in the following chapters.

CHAPTER 3
MATERIALS AND METHODS

The presentation of the laboratory testing program is divided into two parts. The first deals with materials characterization and sample preparation. The second part presents the experiments and testing procedures involved in this study. The experimental work focuses attention on the investigation of: (1) the mechanical stability of soil-oil mixtures, (2) the interaction and bonding mechanisms between soil and oil, and (3) the oil leachability potential from soils.

3.1 Material Properties

The materials used in this study are: two Bahraini natural soils, Arabian oil residue, and two solutions (distilled and saline water). Summarized below are the key points for characterizing these materials, and the corresponding results of their compositions and properties.

3.1.1 Soil Samples

Various disturbed soil samples, obtained from different sites in Bahrain (Al Manama, Karbabad, Muharraq, Sanabis, and Sanad) were initially characterized. In all these sites, the soil samples were collected from the surface to a depth of about 3m. The sampling of these soils was conducted by the Ministry of Works (Geotechnical Engineering Division) in Bahrain. Due to the similarities in their textures and mineralogical compositions as revealed by gradation and X-ray diffraction analyses, two representative soil samples were used in this study. The first type of soil was obtained from the northern part of the country (Muharraq) at a depth of 0.2 - 1m. The second type of soil was collected from the eastern area (Sanad) at a depth of 1.5 - 2.5m. A highway project and an industrial area are expected to be located within the coming few years in the Muharraq and Sanad areas, respectively. The soil profile at the Sanad site,

as provided by the Ministry of Works (Geotechnical Engineering Division) in Bahrain, is shown in Figure 3.1.

The composition and properties of the two tested soils, obtained from the Sanad and Muharraq sites, are given in Table 3.1. The selected analyses are conducted on triplicate samples and their average values were reported. The analyses were carried out following procedures described by ASTM standards and various techniques reported by different researchers as described below. Measurement of specific gravity and consistency limits were performed according to ASTM D854, test method for specific gravity of soils, and ASTM D4318, test method for liquid limit, plastic limit, and plasticity index of soils, respectively, and particle size analysis was conducted using the method described in ASTM D422, method for particle-size analysis of soils. Determinations of compaction parameters and permeability coefficients (at maximum dry density) were carried out following ASTM D698, test methods for moisture-density relations of soils and soil-aggregate mixtures using 5.5-lb (2.49-kg) rammer and 12-in. (305-mm) drop, and ASTM D2434, test method for permeability of granular soils, respectively.

pH and conductivity measurements of 1:10 soil-water extract were conducted according to ASTM D1293, test methods for pH of water, and ASTM D1125, test methods for electrical conductivity and resistivity of water, respectively. Cation exchange capacity (C.E.C.) of soils was determined at natural soil pH using the silver thiourea method (Chhabra et al., 1975). The ethylene glycol-monoethyl ether (EGME) method without sample pretreatment (Carter, et al., 1986) was used for determination of specific surface area, and the rapid titration method (Hesse, 1971) was used for determination of carbonate content. Organic content determination involved the wet oxidation method (Nelson and Sommers, 1986), and amorphous material determination was performed using the method described by Segalen (1968). Sample preparation for X-ray diffraction and analysis was performed following the procedures described by Moore and Reynolds (Moore and Reynolds, 1989).

The presence of high salt content in the natural soils, as in this case (Section 3.1.3.a), makes it important to assess their effect on the performance of the stabilized soils. In addition, it is reported by Ingles and Metcalf (1973) that the presence of salt

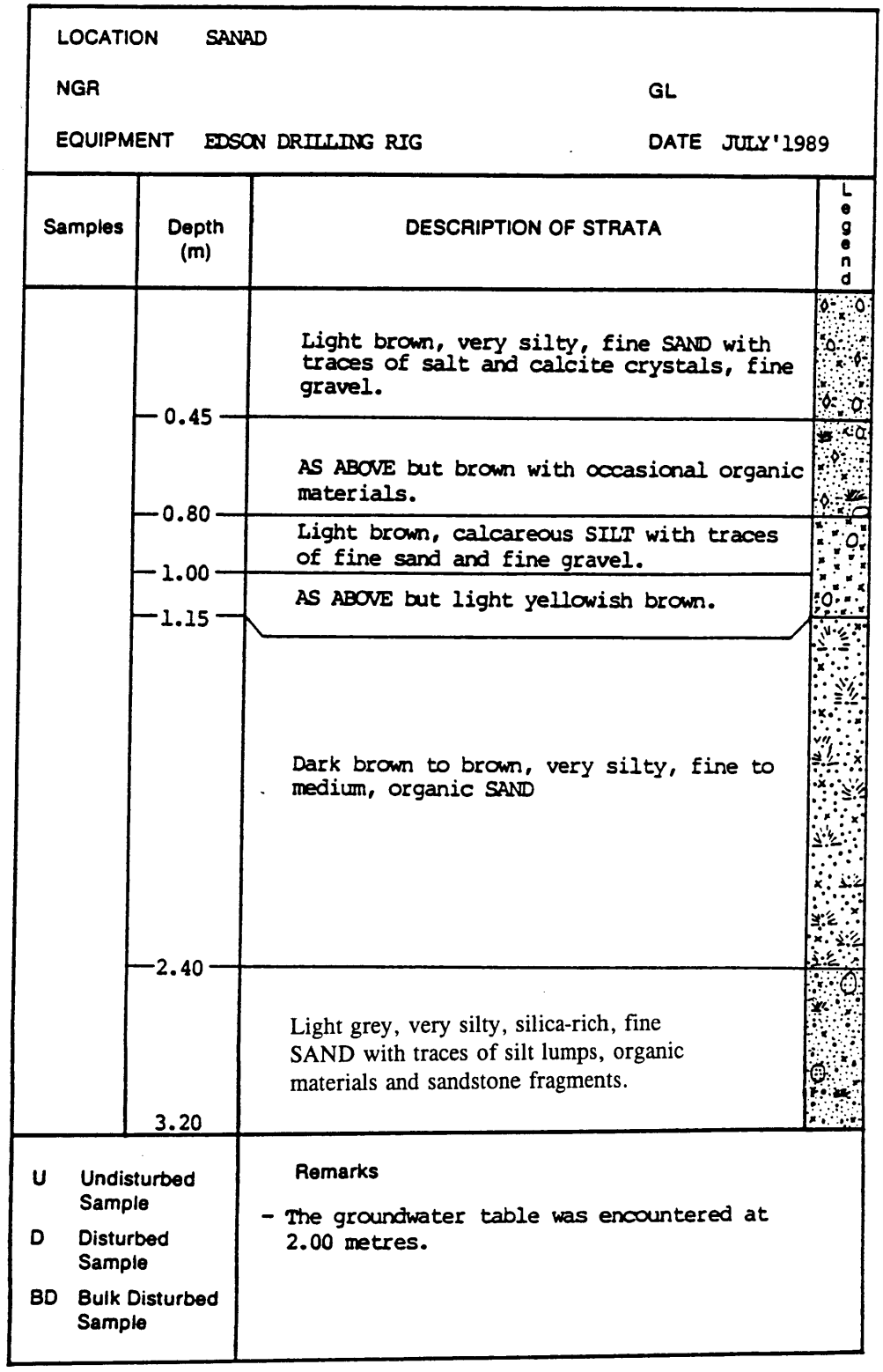


Figure 3.1 - Soil profile at the Sanad site.

Table 3.1 - Selected properties and composition of tested soils from Bahrain.

Properties	Locations in Bahrain			Variation Range in Bahrain (Doornkamp)
	Muharraq	Sanad	Sanad washed	
Geotechnical				
Specific gravity	2.68	2.7	....	....
Consistency limits				
liquid limit (%)	NP	21.0	41.0	....
plastic limit (%)	NP	16.0	28.0	....
Soil Gradation				
sand (w%)	70.0	63.0	60.0	50 - 90
silt (w%)	23.0	25.0	27.0	5 - 35
clay (w%)	7.0	12.0	13.0	0 - 20
effective diameter D_{10} (μm)	35.0	20.0	20.0	....
D_{50} (μm)	170.0	95.0	90.0	....
Soil Texture	Silty sand	Sandy loam	Sandy loam	Sandy to loamy soils
Compaction				
maximum dry density (Mg/m^3)	1.82	1.78	1.35	....
optimum moisture content (%)	12.5	14.0	29.0	....
Permeability (m/sec)	8.5×10^{-7}	2×10^{-7}	5×10^{-6}	....
Chemical				
Soil pH (1:10 soil/water)	8.0	7.8	8.2	7.2 - 8.5
Soil Conductivity (1:10 soil/water;ds/m)	0.93	1.5	0.47	0.25 - 20
C.E.C. (cmol/kg)	19.0	24.0	....	....
Surface Area (m^2/kg)	35×10^{-3}	40×10^{-3}	62×10^{-3}	....
Organic Content (w%)	0.84	1.3	1.25	0 - 4
Carbonate Content (w%)	37.0	28.0	26.0	4 - 50
Amorphous Silica (w%)	3.2	0.3	0.3	....
Mineralogical Composition (by X-ray analysis)	Quartz, Calcite, Dolomite, Feldspar, Palygorskite, Montmorillonite, Illite, Kaolinite.			Quartz, Calcite Dolomite, Feldspar, Halite, Gypsum Palygorskite, Smectite.

may interfere with the adsorption of oil onto soil surfaces. Therefore, the effect of the soil washing process, which is partial removal of the soluble salt initially present in soils, will be considered in this study. To examine such effects, a natural soil sample from the Sanad site is washed in distilled water prior to its application in this study. The properties of the washed soil is presented in Table 3.1. The procedures for analyzing the washed soil followed the methods mentioned earlier in this section. In this study, the natural soil was first placed in a large bucket and mixed with distilled water a 1:1 ratio. The washing process was then started, which involved stirring for few minutes, settling overnight, discharging the supernatant and then continuing until the salt content in the supernatant reached an acceptable level. Finally, the washed soil was dried, ground, sieved to finer than 4.75 mm mesh, and stored for further testing.

From soil gradation analyses, the soil samples from the Sanad and Muharraq sites were classified as a sandy loam and silty sand, respectively. The soils are composed of predominantly sand and silt particles, with minor proportions of clay. The clay fraction represents 7% and 12% (w/w) of the soil particles for the Muharraq and Sanad sites, respectively. The Atterberg limit tests reveal that these soils possess relatively low plasticity potentials.

The X-ray diffraction analyses of the tested soils show a great similarity in their composition. The test results indicate that the main mineral constituents are quartz, feldspar and carbonate, and to a lesser extent clays. The X-ray diffraction analysis of the fine fraction, i.e. less than 0.002 mm, of the tested soils, shows the major types of clays identified in Figure 3.2. This figure displays the peak intensities versus diffraction angles for an air-dry sample from the Sanad site. A qualitative estimate, based on peak intensities, reveals that montmorillonite and palygorskite are the predominant clay minerals present in these samples. These clay minerals are known to possess high surface activities, which are mainly responsible for the activity of these soils. However, the absence of measurable carbonate peaks in the X-ray diffraction patterns, presented in Figure 3.2, suggests that the carbonates occur primarily in the sand and silt-size fractions.

Results of the soil chemical testing, shown in Table 3.1, indicate that from the relatively high values of pH and conductivity of the examined soils, they can be

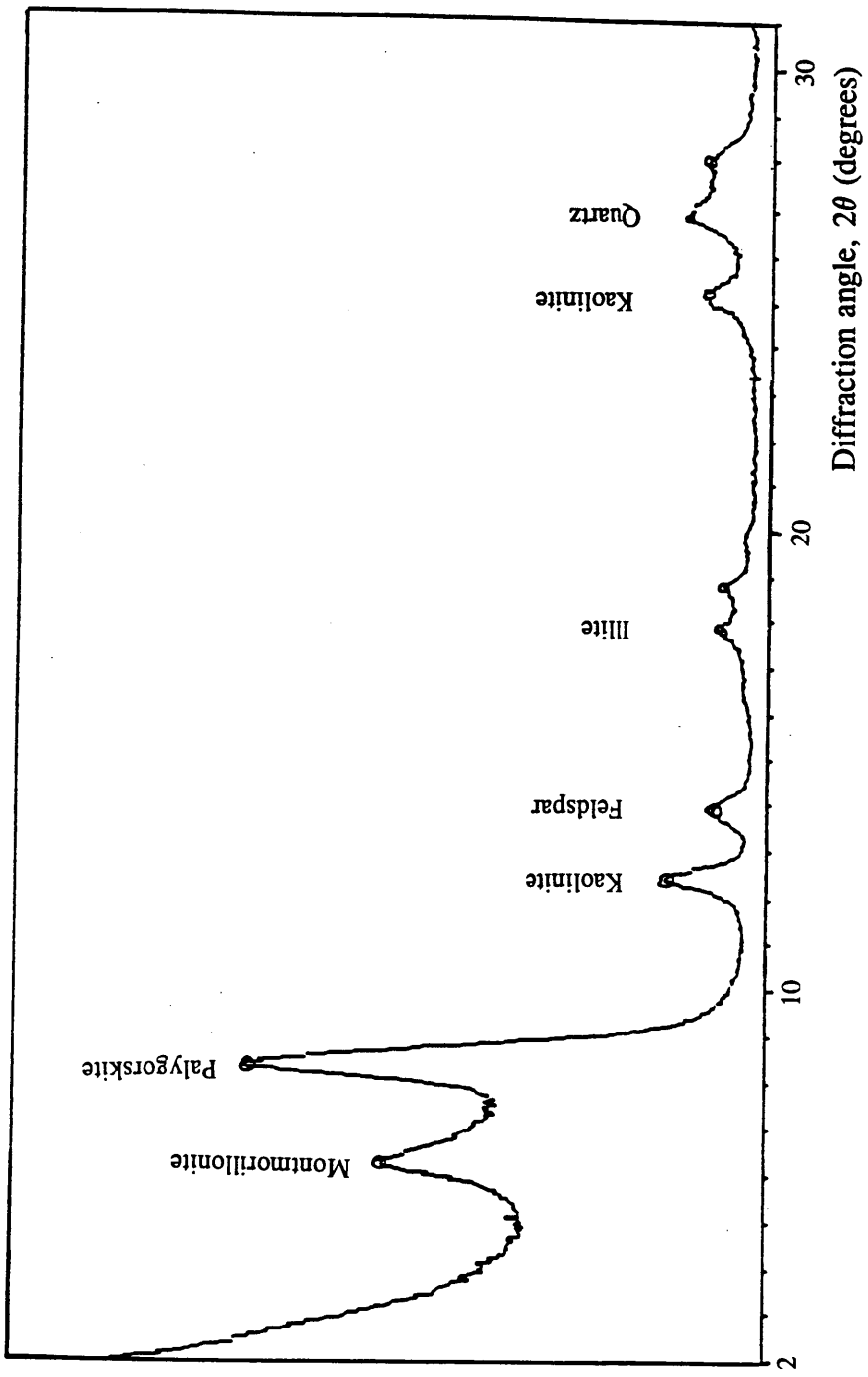


Figure 3.2 - X-ray diffraction pattern of fine fraction of the Sanad soil.

characterized as saline-alkali soils. The values of cation exchange capacity (C.E.C.) and specific surface area of the soils are representative of the presence of a high carbonate content. The surface properties of these soils (C.E.C and surface area) lie in the range between the surface activity of kaolinite and illite. The soil organic content and amorphous materials content are considered to be low. Moreover, surface properties and plasticity of the natural washed soil from the Sanad site are shown to be substantially higher as compared to the unwashed one. The composition and soil properties results share great similarities with other studies conducted on the properties of Bahraini soils (Doornkamp et al., 1980).

3.1.2 Oil Residue Sample

The oil residue used for the study was provided by the Bahrain Petroleum Company (BAPCO), and is classified as atmospheric Arabian oil residue (residuum). Oil residue is the "bottoms" remaining from the fractional distillation of crude oil, and is a complex mixture consisting mostly of heavy forms of saturates and aromatic hydrocarbons, and to a lesser extent, resins and asphaltenes. The saturated groups consist of long chains and branched paraffins and cycloparaffins. Most of the aromatic hydrocarbons present in oil residue are dominated by polyaromatic types and may contain alkyl substituents. The resins consist of fused aromatic rings with alkyl and other polar substituents (i.e., pyridines, quinolines). Asphaltenes are composed of highly condensed polycyclic aromatic rings that may contain metallo-organics such as porphyrins, which can form chelated complexes with metals, e.g. vanadium and nickel (Petrakis et al., 1980; Kircher, 1989). The typical composition and properties of Arabian oil residue are presented in Table 3.2.

Previous studies on the composition and properties of Arabian oil residue (Ali and Bukhari, 1989; Ali et al., 1989; Kircher, 1989) indicated that the typical oil residue has a high boiling point, high viscosity, a specific gravity close to 1, a high molecular weight, and a complex structure. These studies also revealed that the structure of oil residue comprises polyaromatic nuclei linked by saturated chains or rings and bears heteroatoms such as nitrogen, oxygen, and sulfur scattered throughout the structure.

For this study, the tests on the oil residue sample received from BAPCO which

Table 3.2 - Composition and properties of Arabian oil residue.

Properties	Value	Variation Range*
Physical		
Specific Gravity	0.97[1]	0.94-0.99
Viscosity at 100 °C (cs)	20[1]	20-90
Boiling Point (°C)	> 370	370+
Chemical		
Elemental Composition (w%)		
Carbon	82	82-84
Hydrogen	11	11-12
Sulfur	4	2.5-5
Oxygen	2	1- 2
Nitrogen	< 1	< 1
Metal Concentration (ppm)		
Vanadium	40	20-110
Nickel	15	6- 28
Iron	10	6- 20
Hydrocarbon Types (w%)		
Saturate	26	15-35
Aromatic	49	45-53
Resin	15	13-18
Asphaltene	10	3-12
Hydrocarbon Conc. (w%)	93[1]	
Molecular Weight (g/mole)	> 900	
Physico-chemical		
Water Solubility (ppm)	< 10[1]	Low Solubility
Organic Carbon partition coefficient (log)	3.6[2]	
Octanol-water Ratio (log)	4.3[2]	High Partitioning
Volatilization Ratio (w%)	5[1]	
Vapor Pressure (mm Hg)	3E-3[2]	Low Volatility
Henry's Law Constant (atm-m^3/mole)	4E-4[2]	

[1] : Experimentally measured values at room temperature of 22±2°C.

[2] : Estimated values based on empirical relations.

* : Other values and variation range were obtained from studies conducted on oil residue by Ali et al. (1989) and Ali and Bukhari (1989).

were conducted at room temperature (22±2°C), included determination of specific gravity, viscosity, hydrocarbon concentration, volatility ratio, and water solubility. The specific gravity was measured in a pycnometer following the method described in ASTM D891, test methods for specific gravity, apparent, of liquid industrial chemicals by pycnometer method. Oil viscosity was determined using a Contraves Rheomat 15 viscometer and the method described by the British Institute of Petroleum (Method IP 72, 1983). Total petroleum hydrocarbon present in the oil residue was measured using the Soxhlet extraction method (Greenberg et al., 1992). The procedures for the last two tests is summarized in later sections where the subject of rheology (Section 3.4) and measurement of oil concentration in soil (Section 3.9.1) are discussed. Determination of the volatility ratio, i.e. the ratio of the volatilized fraction weight to the oil residue weight, is discussed in Section 6.3.1, where the problem of oil volatilization is addressed.

Solubility of oil residue in water was determined in accordance with the methods described by ASTM E1148, test methods for measurement of aqueous solubility, and Mackay and Shiu (1977). In this test, saturated aqueous solutions were prepared by adding excess quantities of oil residue to distilled water and stirring vigorously for at least 24 hours. The saturated aqueous solutions were then decanted and filtered to remove suspended particles. Following filtration, the oil was extracted from these solutions and analyzed using infrared spectrophotometry, described in Section 3.9.2 on the partition-infrared method. A similar procedure was used to measure the solubility of oil residue in saline (brackish) solution. However, the measured solubility of oil in saline solutions were below the detection level ($<$ 1 ppm). The organic carbon partition coefficient (K_{oc}) and octanol-water ratio (K_{ow}) were estimated from empirical relations described by Means et al. (1980), and Chiou et al. (1977), respectively. Vapor pressure (P_v) and Henry's law constant (K_h) were both estimated from Mackay (1981). The above estimations were made based on a knowledge of the values of water solubility, boiling temperature, and molecular weight of oil residue.

The results shown in Table 3.2 indicate that the oil residue has a low water solubility, low volatility ratio, a high octanol-water ratio, and a density slightly less than that of water. This indicates that the behavior of oil residue is akin to a non-polar and

light non-aqueous phase liquid (LNAPL) organic compound in soil. The dominating non-polar fractions, which include saturates and aromatic hydrocarbons, represent about 75% of oil residue by weight. The low polarity of oil residue is attributed to the low dipole moments (less than 1) and low dielectric constants (less than 3) of most of its constituents (Yong and Rao, 1991). In addition, there is a limited percentage of oxygen, nitrogen, and sulfur present in the oil residue (totalling about 7% by weight).

Several studies (Mackenzie, 1970; Neumann et al., 1981; Tuck et al., 1988) have also shown that the behavior of oil in soil, especially the non-aqueous phase liquid, is strongly affected by its viscosity, density, dielectric constant and surface wetting properties (i.e., interfacial tension, and contact angle). The results of this study have shown that oil residue has a relatively high viscosity. However, the interfacial tensions of oil residue is expected to be low due to its high partitioning behavior. This speculation is backed by Elmonayeri (1983) who stated that the interfacial tension of bitumen can be less than 20 dynes/cm. Furthermore, the surface wetting properties in an oil-soil-water system is influenced by the properties of both oil and soil. Studies have reported that lighter hydrocarbons have higher wetting capabilities onto soil surfaces than the heavier fractions. Also, hydrocarbons have slightly higher wetting capabilities onto limestone soil surfaces than sandstone surfaces (Hoiberg, 1965).

Oil residue contains various individual constituents of several different chemical classes. Each of these compounds occurs in adsorbed, dissolved, liquid (non-aqueous phase liquid; NAPL), or gaseous phases according to its physico-chemical properties. The types of the chemical classes present in oil residue have been reported in several studies (Ali et al., 1989; Changming et al., 1989; Malhotra et al., 1989). The major classes include: (1) paraffinic (e.g. n-hexadecane), (2) cycloparaffinic (e.g. methylcyclohexane), (3) mono-aromatic (e.g. butylbenzene), (4) polycyclic aromatic (e.g. naphthalene, pyrene), (5) heterocyclic which includes nitrogen compounds (e.g. pyridine, quinoline); oxygen compounds (e.g. dibenzofuran); and sulfur compounds (e.g. benzothiophene).

To provide a basis for understanding the environmental behavior (transport and fate) of oil residue in soil, the physico-chemical properties of its constituents are important. The properties of selected major compounds present in oil residue are

summarized in Table 3.3 and include: molecular formula and weight (MWt), specific gravity (S.G), water solubility (S_w), organic carbon partition coefficient (sorption coefficient, K_{oc}), octanol-water ratio (K_{ow}), vapor pressure (P_v), Henry's Law constant (K_h), and half-life periods ($t_{½}$).

Most of the compounds present in the oil residue possesses low solubility in water resulting in low aqueous mobility in the environment. Despite the high water solubility of heterocyclic nitrogen compounds, their presence in the oil residue were limited (see Table 3.2). The organic carbon partition coefficient, K_{oc}, and octanol-water ratio, K_{ow}, of each compound (often expressed in logarithm form) are indicators of oil affinity to organic materials. Since most of the oil residue compounds have high values of K_{oc} and K_{ow}, they are expected to have high retention capacities, thus reducing their environmental mobilities.

Vapor pressure and Henry's Law constant are also significant parameters in evaluating the volatility of oil from the soil pore space into the atmosphere. Most oil residue compounds have relatively low vapor pressures and Henry's law constants, reflecting their low volatility. However, the high volatility of saturated compounds are most likely responsible for the volatilized portion of the oil residue.

The degradation potential of the oil residue compounds in soil is expressed in terms of their half-life period. The degradation of oil in soils results from various processes including volatilization, photolysis, and chemical and biological reactions. The half-life period represents the combined effect of the various degradation forms. The half-life of oil residue compounds varies from one day to five years. Since the predominant fraction of oil residue contains polyaromatic compounds with high half-lives (see Table 3.2 & 3.3), its degradation rate is expected to be low (Gilbert et al. 1989; Bonazountas 1991).

3.1.3 Fluid Samples

Soil pore fluid and groundwater analyses were employed to complete the chemical characterization of the two tested sites in Bahrain. From these analyses, the type and concentration of various ions present in soil and groundwater samples can be determined. The soil pore fluids for both the Sanad and Muharraq sites were obtained using the

Table 3.3 - Physico-chemical properties of selected compounds present in Arabian oil residue at 22±2°C.

Compound[1]	Formula[1]	MWt[1]	S.G[2]	S_w[2] (ppm)	K_{oc}[2] (log)	K_{ow}[2] (log)	P_v[2] (mm Hg)	K_h[2] $\frac{atm.m^3}{mole}$	Half-Life[3] (days)
n-hexadecane	$C_{16}H_{22}$	226.5	...	0.9	...	...	...	...	15-19
n-decane	$C_{10}H_{22}$	142.3	0.73	0.052	...	4.86	1.35	0.187	...
Methylcyclohexane	C_7H_{14}	98.2	0.77	14	...	2.86	37	0.435	...
Cyclohexane	C_6H_{12}	84.2	0.78	55	...	3.44	77	0.190	28-182
Butylbenzene	$C_{10}H_{14}$	134.2	0.86	11.8	3.4	4.28	1	1.25E-2	...
Naphthalene	$C_{10}H_8$	128.2	1.16	31.7	3.11	3.36	0.23	4.6E-4	17- 48
Phenanthrene	$C_{14}H_{10}$	178.2	1.18	1.28	4.36	4.57	8.6E-4	5.48E-5	28-126
Pyrene	$C_{16}H_{10}$	202.3	1.27	0.135	4.88	5.18	2.5E-6	1.09E-5	238-630
Chrysene	$C_{18}H_{12}$	228.3	1.28	0.006	5.39	5.60	7.5E-9	7.26E-9	371- 990
Dibenzanthracene	$C_{22}H_{14}$	278.4	1.28	0.0005	6.22	6.36	1.E-10	7.33E-9	361- 940
Dibenzofuran	$C_{12}H_8O$	168.2	1.09	10	3.91	4.17	...	...	7- 28
Methylbenzodithophene	$C_{11}H_8S_2$	204.3	...	...	...	...	...	...	...
Benzothiophene	C_8H_6S	134.2	1.15	140	...	1.80	...	...	...
Pyridine	C_5H_5N	79.1	0.98	233400	...	0.65	14	1.2E-5	1- 7
Idole	C_8H_7N	117.2	1.22	3558	1.69	2.14	2.7	...	...
Quinoline	C_9H_7N	129.2	1.09	5995	...	2.04	0.084	2.38E-6	3-10
Acridine	$C_{13}H_9N$	179.2	1.01	57.34	...	3.40	...	...	...

. MWt: Molecular weight; S.G : Specific gravity; S_w : Water solubility; P_v : Vapor pressure; K_h : Henry's Law Constant; log K_{oc} : logarithm of organic carbon partition coefficient; log K_{ow} :Logarithm of octanol/water ratio.

. [1] Ali et al. (1989), [2] Montgomery and Welkom (1989), [3] Howard et al. (1991).

saturation extract method (Hesse, 1971). In this method, the soil is mixed with distilled water until the saturation point is reached, which is just above the liquid limit condition. The soil-water mixture is then left to equilibrate overnight and finally filtered to obtain the pore fluid (saturation extract).

Since the groundwater in both the Sanad and Muharraq sites are encountered at relatively shallow depths, the chemical composition of the groundwater was determined. Two groundwater samples obtained from two different sites in Bahrain were analyzed in this study. The first water sample was collected from the eastern part of Bahrain (Sanad) at a depth of about 2 m. The second water sample was obtained from the northern part of the country (Karbabad) at a depth of 1m. The latter site was chosen due to difficulties in collecting groundwater samples from the Muharraq site.

Both the soil pore fluids and groundwater samples were subjected to various chemical analyses. These analyses included the determination of pH, electrical conductivity, soluble and exchangeable cations (Na, K, Ca, and Mg), and soluble anions (Cl, SO_4, HCO_3, and CO_3). The analyses were performed following procedures described by ASTM standards (1992), and standard methods for the examination of water and wastewater (Greenberg, et al., 1992).

pH and conductivity parameters were measured according to ASTM D1293, test methods for pH of water, and ASTM D1125, test methods for electrical conductivity and resistivity of water, respectively. Determination of exchangeable cations in soils were achieved using the silver thiourea method of Chhabra et al. (1975). Soluble calcium and magnesium were determined using ASTM D511, test method for calcium and magnesium in water, and sodium and potassium were carried out according to ASTM D4191, test method for sodium in water by atomic absorption spectrophotometry, and ASTM D4192, test method for potassium in water by atomic absorption spectrophotometry, respectively. The measurement of both soluble and exchangeable cations was carried out using Atomic Absorption Spectrophotometry.

Chloride was measured in accordance with the titration method described in ASTM D4458 (test method for chloride ions in brackish water, seawater, and brines). Determination of both carbonate and bicarbonate was based on the acid titration method presented in ASTM D3875 (standard test for alkalinity in brackish water, seawater, and

brines). The sulphate measurement was conducted using the turbidimetric method (ASTM D4130, test method for sulfate ion in brackish water, seawater, and brines).

3.1.3.a *Soil pore fluids*

The results of the chemical analyses of soil pore fluid are presented in Table 3.4. The reported results are based on average values obtained from analyses on replicate samples. These results reveal that the two soils are rich in soluble ions, especially chloride, sulfate, calcium, and sodium. The values of exchangeable cations are reflective of the soil's C.E.C. measured in the previous section. From these analyses, both soils can be classified as saline-calcareous soils. The study shows that the salinity content of the Sanad soil is higher than that of the Muharraq soil, whereas the alkalinity of the Muharraq soil is higher than that of the Sanad soil. The results of the chemical analyses of these tested soils lie within the range of values obtained from various analyses conducted by Doornkamp et al. (1980) on more than 100 soil samples from different sites in Bahrain. Moreover, Doornkamp's analyses reported a decrease in the salinity (electrical conductivity) and a slight increase in the soil pH with depth.

3.1.3.b *Groundwater samples*

The chemical compositions of the two tested groundwater samples, as well as the range of several chemical analyses conducted on more than 100 groundwater samples from different sites in Bahrain (Doornkamp et al., 1980), are presented in Table 3.5. A high concentration level of chloride, sulphate, sodium, and calcium are recorded for the tested water samples. The salinity of the tested groundwater samples are representative of the high salinity of the existing soils and nearby surface water, Arabian Gulf seawater.

3.1.3.c *Synthetic saline (brackish) water*

The experimental program involved the application of two solutions, distilled water and saline (brackish) water. Distilled water was used as a "reference". The pH of the distilled water used in this study varied between 5.5 and 6.5. Reported studies on the rainwater in Bahrain (Doornkamp et al., 1980) revealed that the pH of the rainwater

Table 3.4 - Chemical analyses of soil pore fluid samples.

Parameters	Locations in Bahrain		Expected Range in Bahrain (Doornkamp)
	Muharraq	Sanad	
Saturation Percentage	34.6	30.7	
Soil pH	7.8	7.5	6.5 - 8.5
Conductivity (ds/m)	6.0	21.0	3 - 100
Soluble Ions (meq/100g)			
HCO_3^-	2.6	2.7	1 - 7
Cl^-	1.5	17.0	2 - 100
SO_4^{-2}	7.3	13.0	5 - 100
Ca^{+2}	7.2	11.8	5 - 50
Mg^{+2}	1.7	3.7	2 - 30
Na^+	3.0	15.3	2 - 100
K^+	0.3	2.8	1 - 10
Exchangeable Cations (meq/100g)			
Ca^{+2}	13.5	16.2	
Mg^{+2}	5.6	3.0	
Na^+	1.7	5.0	
K^+	0.4	1.5	
Exchangeable Na (%)	9.0	20.0	

Table 3.5 - Chemical analyses of tested groundwater samples.

Parameters	ASTM Test	Locations in Bahrain		Concentration Range in Bahrain (Doornkamp)
		Karbabad	Sanad	
pH*	D 1293	7.7	7.85	....
Conductivity (ds/m)	D 1125	3.4	22.00	5 - 200
Soluble Ions (ppm)				
CO_3^{-2}	D 3875	135	68	....
HCO_3^-	D 3875	275	140	....
Cl^-	D 4458	4150	22 130	1000 - 150 000
SO_4^{-2}	D 4130	2450	4 140	1000 - 10 000
Ca^{+2}	D 511	820	2 810	500 - 3 000
Mg^{+2}	D 511	380	1 500	300 - 4 000
Na^+	D 4191	2700	10 500	1000 - 50 000
K^+	D 4192	250	580	100 - 2 000

* pH units

lies within the pH range of the used distilled water. Therefore, distilled water can be used as an indication to examine the effect of the rainfall infiltration on the stabilized soil behavior. However, brackish water was employed to simulate the effect of rise in groundwater on the stabilized soil performance. The potential for groundwater rise was attributed to over-irrigation and leakage from sewage lines.

In this study, a synthetic saline water was prepared based on the chemical analysis results of the tested groundwater samples (Section 3.1.3.b). The preparation of this brackish water followed the procedure described in the preparation of standard Canadian shield saline solution (Abry, et al., 1982), with a few modifications made to account for the high salinity of this water. For example, to prepare 1 litre of brackish water used herein, two major steps were involved. The first step required preparation of a stock solution by mixing 100 ml distilled water with 1000 mg potassium chloride (KCl), 30 mg strontium chloride ($SrCl_2.6H_2O$), 210 mg sodium bicarbonate ($NaHCO_3$), and 14 mg sodium nitrate ($NaNO_3$). The second step involved the dilution of the same 100 ml stock solution into 1 litre of distilled water, and then mixing with these dry chemicals: 7.35 g calcium chloride ($CaCl_2.2H_2O$), 12 g magnesium sulfate ($MgSO_2.7H_2O$), 33 g sodium chloride (NaCl), and 0.15 g Sodium silicate ($NaSiO_3.9H_2O$). The chemical composition of the prepared brackish water based on both calculated and measured values are presented in Table 3.6. This saline water is expected to be a representative of the in-situ brackish groundwater existing in Bahrain.

3.2 **Sample Preparation**

To ensure that the soil samples to be tested were as close to uniform as possible, the two natural soils were air dried, ground, and sieved to finer than 4.75 mm mesh. These two soils, together with the washed soil prepared earlier, constituted the source batches from which all samples were derived. One batch from each soil was used to determine the "natural" soil properties and behavior. The other soil batch was mixed with oil residue and its behavior was examined.

The soil-oil mixtures were prepared according to the method described in ASTM

Table 3.6 - Chemical composition of synthetic Bahrainian groundwater.

Parameters	Local Ground-water (Sanad)	Synthetic Brackish Groundwater (ppm)		Arabian Gulf Sea Water (ppm) (Fookes,1985)
		Calculated	Measured	
pH[1]	7.85	....	8	....
Conductivity (ds/m)[2]	22.00	....	25	....
Soluble Ions (ppm)				
HCO_3^-	140	152	130	170
Cl^-	22 130	24 048	23 870	35 000
SO_4^{-2}	4 140	4 679	4 050	3 300
NO_3^-		10		
Ca^{+2}	2 810	2 004	1 820	420
Mg^{+2}	1 500	1 183	1 160	1 550
Na^+	10 500	13 066	12 600	20 650
K^+	580	524	500	660
Sr^{+2}		10		
Si^{+3}		15		

[1] pH units
[2] ds/m (decisiemens per meter)= mmhos/cm (millimhos per centimetre)

D4223, standard practice for preparation of test specimens of asphalt-stabilized soils, with the following modifications. Each stock mixture of soil and oil was prepared by first mixing a specified content of the oil residue with soil, and then adding water until its optimum moisture content was reached. In each case, the mixture was blended by hand for about 5 minutes to obtain a homogenous mixture. The addition of oil residue to dry soils simulates actual field conditions in most arid regions and is expected to enhance oil adsorption onto soil surfaces (Theng, 1974; Clementz, 1976). However, the presence of water in soil-oil mixtures is needed to facilitate mixing, distribution, and compaction processes. The range of added amounts of oil residue was assessed by previous studies on stabilization of various soils with asphalt (Lambe, 1962; Rico Rodriguez et al., 1988). These studies indicated that at least 4% of asphalt by weight was required to adequately stabilize soils with fines contents greater than 25% by soil weight, as in this case. Therefore, 4% of oil residue was the minimum amount used to prepare soil-oil mixtures for all the tests conducted in this study.

Several soil batches from the Sanad and Muharraq sites mixed with different oil residue and water contents were initially prepared. Soil samples from the Sanad site were first mixed separately with 0%, 4%, 6%, 8%, and 12% (w/w) oil residue; water was then added to the soil-oil mixtures at percentages of 14%, 13.5%, 13%, 12.5%, and 12% (w/w), respectively, resulting in five different batches. Similarly, five different batches of oil-soil-water mixtures were prepared for the soil from the Muharraq site. However, the added water in this case (Muharraq soil) was reduced to 12.5%, 12%, 11.75%, 11.5%, and 11% (w/w), instead of the water content range of 12% to 14% (w/w) used for the Sanad soil. In a similar procedure, washed samples from the Sanad site were also prepared. The variation in the percentage of added water to the soil-oil mixtures was to accommodate the presence of oil residue in maintaining consistent moisture content within each sample (Dunn and Salem, 1971). All additions of oil residue and water were calculated as percentages of the weight of the dried soil with which they were mixed. For each tested soil, the above batches were tested to obtain optimum results with measured properties. However, only the optimum percentage of oil residue, based on geotechnical testing, was used to investigate the environmental impact of oil residue.

Following the preparation process, each stock mixture (i.e., soil-water and oil-soil-water mixtures) was left to equilibrate at room temperature in sealed glass containers for 24 hours. In the case of oil-soil-water mixtures, volatilization of oil during this equilibration period was negligible since oil residue contained mainly heavy forms of hydrocarbons. In experiments where the use of specimens was required, specimens were molded by compacting the samples at their maximum dry densities. To account for variability in reproduction and repeatability, preparation and testing of the samples were strictly controlled. All experiments were performed at a room temperature of 22 ± 2°C. This allows for good comparisons between the tested samples. Moreover, replicate sample testing was used, and the results reported consists of the average value obtained.

3.3 Geotechnical Testing

The geotechnical testing program was conducted to investigate how much improvement could be accomplished in the mechanical stability (strength and mode of deformation) of the tested soils by the addition of oil residue. Various contents of oil residue were used to determine the optimum content that will maximize the soil strength.

The unconfined compression test (UC) was selected as a main indicator for the soil strength improvement. The optimum oil residue content that gives the highest unconfined compressive strength under a defined set of conditions may not necessarily be the content at which the greatest stiffness or least permeable system can be achieved. Other geotechnical testing such as direct shear and California bearing ratio (CBR) tests were also involved to examine the effect of oil residue at the optimum content on various parameters of soil strength. A summary of the key points in evaluating the strength characteristics of both natural and stabilized soils is described below. In each test, duplicate sample testing was used, and the results reported consists of the average value obtained.

For a given soil, stabilized with a particular percentage weight of oil residue, the measured strength can vary significantly depending on the type of test used to measure this strength. Factors such as rate of loading; efficiency of mixing; density to which the

sample is compacted; moisture content; temperature at which it is mixed, cured, and tested; and age of specimen (Dunn and Salem, 1971) contribute to measurement variations. To counter the effects of these factors, all specimens, within each tested soil, were prepared at consistent dry density, moisture content, and temperature and subjected to constant mixing, curing, and loading conditions.

3.3.1 Unconfined Compression Test

The addition of oil residue to soils, especially sandy soils, is expected to enhance their cohesive properties, and thus increases their compressive strengths. Based on this analogy, the unconfined compression test was used in this study to measure the change in the soil strength upon the addition of oil residue. Unconfined compressive strength refers to the sample's resistance to compression with increasing strain, measured under unconsolidated undrained conditions. In this study, the compression tests were performed in accordance with the ASTM D2166 procedure, test method for unconfined compressive strength of cohesive soil.

To measure the compressive strength of the tested samples, cylindrical specimens of 1:2 diameter to height ratio were prepared at their maximum dry densities. Two different specimen preparation techniques were involved in this study. The first preparation technique was used in the determination of (a) influence of water presence on unconfined compressive strength of soil-oil mixtures, in which the oil was added separately to dry and moist soils; and (b) optimum oil residue content based on the unconfined compression test, in which various contents of oil residue (4%, 6%, 8%, and 12% (w/w)) were added to dry soils and then mixed with sufficient water to attain its optimum water content. These sample preparation techniques were described earlier in Section 3.2. The prepared samples were statically compacted into cylindrical molds of 36 mm diameter and 80 mm height using the Instron testing machine. Each specimen was prepared in five equal lifts of 16 mm thickness until its maximum density was attained. The compacted dry densities were 1.71 ± 0.11 Mg/m^3, 1.67 ± 0.11 Mg/m^3, and 1.27 ± 0.08 Mg/m^3 for the Muharraq soil, the Sanad soil, and the washed Sanad soil, respectively.

The second preparation technique was used to measure the long-term strength behavior of the leached samples. These samples included natural and stabilized soils (containing the optimum oil residue content), each leached in distilled and saline water and tested at the end of the leaching process (i.e., 10 pore volumes). Specimens under saturated conditions were extracted in this case by pushing a 16.5 mm diameter thin-walled tube into the soil placed in the leaching cells.

In each case, the specimens were extruded from the mold or tube, trimmed at both sides and measured for diameter, height, weight, and moisture content. All specimens were then compressed to failure at a constant strain rate of 0.5% per minute and the stress-strain responses were recorded.

3.3.2 Direct Shear Test

Stabilization with oil residue is expected to affect the values of soil shear strength components,i.e. cohesion and angle of friction (Dunn and Salem, 1971; Ola, 1978). A direct shear test was conducted on the natural and stabilized samples (containing the optimum oil residue content) from the Muharraq and Sanad soils to examine the change in the strength components upon the addition of oil residue. Testing was performed in accordance with the procedure described in ASTM D3080, method for direct shear test of soils under consolidated drained conditions.

All specimens were prepared by subsequently compacting a predetermined quantity of sample (containing the optimum water content) in a circular ring, having 63.5 mm diameter and 22.9 mm height, until their maximum dry densities were attained (i.e. 1.78 ± 0.03 Mg/m^3 and 1.75 ± 0.03 Mg/m^3 for the Muharraq and Sanad soil, respectively). After preparation, each specimen was pushed into a cylindrical shearing box and tested under drained conditions. During testing, specimens were first consolidated under compressive stresses of 34.5 KPa, 69 KPa, and 103.5 KPa, respectively. Specimens were then horizontally sheared to failure at a constant strain rate of 0.8% per minute. The normal stress-shear stress relationship of each specimen was then reported.

3.3.3 California Bearing Ratio Test (CBR)

Since stabilization with oil residue is expected to be utilized in subgrade soils, especially for highways, CBR can be a useful test as an indicator for the strength of soils. In this test, the resistance of soil to penetration was recorded and plotted against deflection. The strength of the soil was expressed in terms of CBR value at 5.08 mm penetration. CBR testing was performed in accordance with ASTM D1883, test method for CBR (California bearing ratio) of laboratory compacted soils, although a few changes were made to accommodate the limited amount of soil present during testing. These changes included a reduction in the standard sizes of some parts of CBR apparatus, e.g. specimen mold and penetration piston, to one-third their actual sizes. The specimen mold was reduced to 50 mm diameter and 50 mm height and the penetration piston was reduced to 16.5 mm diameter. The diameter of the mold should be at least three times greater than the piston diameter in order to overcome any interferences between the mold's boundaries and the soil failure planes created during penetration (Das, 1984).

The CBR test was conducted on unsoaked, soaked, and leached specimens. In each case, natural and stabilized samples (at the optimum water and oil residue contents) from the Sanad and Muharraq sites were tested. Each specimen was prepared by subsequently compacting the sample in the above specified mold until its optimum dry density was attained (i.e. 1.78 ± 0.03 Mg/m^3 and 1.75 ± 0.03 Mg/m^3 for the Muharraq and Sanad soil, respectively). The CBR values of the unsoaked specimens were measured directly after preparation. However, the CBR values of the soaked samples were measured after immersing the specimens in distilled water for a period of 4 days at 20°C temperature. Soaking in distilled water is expected to lead to higher water absorption than saline water. This is partially attributed to the osmotic effects. Measurement of the CBR values of the leached samples, permeated with distilled and saline water, were conducted at the end of leaching period (i.e. 10 pore volumes).

Following preparation, the specimens were tested on both sides (i.e. top and bottom) to failure at a penetration rate of 1% per minute (0.5 mm per minute) and load-penetration responses were recorded. The load-penetration curves for the two tested natural soils were also obtained from a standard CBR apparatus and their results were compared with the results of the reduced CBR apparatus used in this study.

3.4 Rheological Behavior/ Viscosity

Since oil residue is expected to possess a thermoplastic property, the variation of its physical behavior with temperature can be significant (Ingles and Metcalf, 1973). A direct measurement of such variation can be expressed in terms of the change in its rheological behavior (viscosity). The change in the rheological properties of oil residue can affect the behavior of soil-oil mixtures.

In this study, two series of viscosity tests were carried out. The first series examines the influence of temperature on the viscosity performance of oil residue. The second series investigates the effect of oil residue content on the viscosity of its mixture with soil. The latter series of viscosity testing is expected to provide information about the fabric arrangement of the soil-oil mixture in a water suspension system, which is useful in explaining the change in the physical properties of soil-oil mixtures.

Viscosity measurements for the first series were conducted on four duplicate oil residue samples, each tested at a different temperature. Since the ambient temperature in Bahrain can vary from 20°C in winter to 40°C during the summer months, the viscosity measurement were performed at 22°C, 30°C, 40°C, and 50°C, respectively.

In the second series of viscosity tests, viscosity measurements were made on suspensions prepared from soil-oil mixtures, where the Sanad soil was used. The mixtures were separately prepared by mixing the soil with various oil residue contents (i.e. 0%, 4%, 8%, and 12% by dry weight of soil). Each soil-oil mixture was dispersed in distilled water at 10% (w/w) solids concentration. The soil-oil suspensions were well shaken to ensure uniformity and allowed to equilibrate for a period of 24 hours prior to testing.

The viscosity of the tested samples was measured using a rotating cylindrical viscometer (Contraves Rheomat 15) capable of 15 different shear rates increasing in geometric progression. For each shear rate, the corresponding shear stress was computed by measuring the torque required to maintain that rate.

3.5 Interaction and Bonding

In order to understand the behavior of the system under consideration, interaction (i.e. physical and/or chemical) between oil residue and soil surfaces must be examined. Infrared spectrophotometry was used to evaluate the possible interactions and bonding mechanisms. Preparation and interpretation of infrared analysis were performed according to the methods described by White and Roth (1986) and ASTM E204, practice for identification of material by Infrared Absorption Spectroscopy using the ASTM code band and chemical classification index.

Three series of samples were tested in this study. The first series was performed on individual samples, i.e. oil sample, natural soils from the Sanad and Muharraq sites and washed soil from the Sanad site. The second series was conducted on oil-soil mixtures containing 4%, 8%, and 12% of the oil residue on a dry weight basis. The third series was carried out on leached oil-soil mixtures containing the optimum oil residue content. In all the above samples, only the fine portion of the soil, i.e. finer than 0.075 mm mesh, was used.

The infrared test was conducted on dried soil samples using the pressed-pellet method. The pellets were prepared by mixing 2% of the sample (by weight) with buffering material (potassium bromide, KBr). The sample-KBr mixture was then ground into a homogenous fine powder. Approximately 200 mg of the mixture powder was placed in an evacuated cell. With a pressure of 670 MPa applied to the evacuated cell and maintained for 10 minutes, a clear thin film (pellet) of 13 mm diameter and 1 mm thickness was formed (3 mg/cm^2). This pellet was then placed in a suitable sample holder and analyzed by infrared spectrophotometry using a model Michelson-100, manufactured by Bomem. A similar procedure was used for determining the infrared spectra of oil residue. Only 0.5% of the oil by weight was used in the preparation of oil-KBr pellet (0.75 mg/cm^2). A blank sample of pure KBr was also tested as "background" along with the other samples. The resulting spectra represent the average of at least five scans.

3.6 Retention of Soil Fluids/ Soil Suction

Retention of pore fluids by the soil (soil suction) was determined using a pressure plate apparatus. The test was conducted on natural and stabilized soil samples obtained from two different sites in Bahrain (i.e Sanad and Muharraq). Each soil sample was subjected to two sets of testing. The first set investigated the effect of oil residue content (i.e. 0%, 4%, 6%, 8%, and 12%, by dry weight of soil) on the fluid-retention characteristics of the soil. The second set examined the influence of leaching forces on the fluid retention behavior of the natural and stabilized soils (at the optimum oil residue content). In the second set, distilled water and saline water were used as permeating solutions, and the samples were tested after 10 pore volumes.

The test procedure followed the method described by Yong and Warkentin (1975). In the preparation of the first set, the samples were compacted in lucite rings of 38.1 mm diameter and between 10 to 20 mm height until their desired dry densities were achieved. These densities were 1.71 ± 0.11 Mg/m^3, 1.67 ± 0.11 Mg/m^3, and 1.27 ± 0.08 Mg/m^3 for the Muharraq soil, the Sanad soil, and the washed Sanad soil, respectively. However, in the second set, saturated samples were extracted directly from the leaching cells.

Following preparation, the samples were placed in an enclosed chamber on a water-saturated ceramic plate. The bottom of the plate was in contact with atmospheric pressure. As air pressure in the chamber was increased, water moved out of the samples through the ceramic plate. This continued until equilibrium was reached between the applied air pressure and the energy at which liquid was retained in the soil sample. The change in moisture content of the tested samples was monitored under various suctions (applied pressures). Each sample was subjected to two cycles (desorption and absorption) in the suction range between pF 0.0 and pF 3.8 (where suction pF is the logarithm value of the water head in cm; for engineering purposes, the pF unit is preferred). For each pF stage, a minimum period of about 3 days was required to reach the equilibrium state. Since these samples have small heights (i.e. 10 to 20 mm) and are dominated by sandy soils, gravitational and osmotic effects are neglected in this analysis. Furthermore, all results reported are the mean values of duplicates.

3.7 Soil Suspension

The maximum removal capacity of oil residue from the stabilized soils and oil retention potential under severe conditions were examined with the help of the batch shaker method (soil suspension). Two sets of batch experiments were performed in this study. In the first set, the influence of different contents of oil residue present in soils from the Muharraq and Sanad sites, each containing 4, 6, and 8%, by weight, under the effect of distilled water was considered.

In the second set of experiments, the influence of the batch equilibrated solution was examined. Two different solutions were used: distilled water and synthetic saline water. For this set of batch experiments, stabilized samples from the Muharraq, Sanad, and washed soil from the Sanad site, each containing the optimum oil residue content, were used. A schematic representation of the soil batch study is presented in Figure 3.3.

The batch experiments were carried out in 100 ml screw-cap glass bottles at a room temperature of $22 \pm 2°C$. Duplicate suspension samples consisting of a ratio of 1:10 soil weight to solution volume were used. This ratio was recommended by the United States Environmental Protection Agency (EPA, 1987) for estimating soil attenuation of chemicals from batch tests.

For each batch test, a 50 ml solution was added to 5 g of soil-oil mixture and shaken on a platform shaker for 24 hours. It is expected that the equilibrium time for the above soil suspensions will be reached after 24 hours of shaking (Ball and Roberts, 1991). The samples were then centrifuged at 10,000 rpm for 20 minutes. After centrifuging, the supernatant was carefully extracted (decanted) and kept in a tight-cap glass flask for oil (total petroleum hydrocarbon) analysis, using infrared spectrophotometry. The soil sample remaining after liquid extraction was oven dried and its oil content was determined by the Soxhlet extraction method. Determination of oil concentration in the above liquid and soil samples is described in Section 3.9. The results reported consist of the average values obtained.

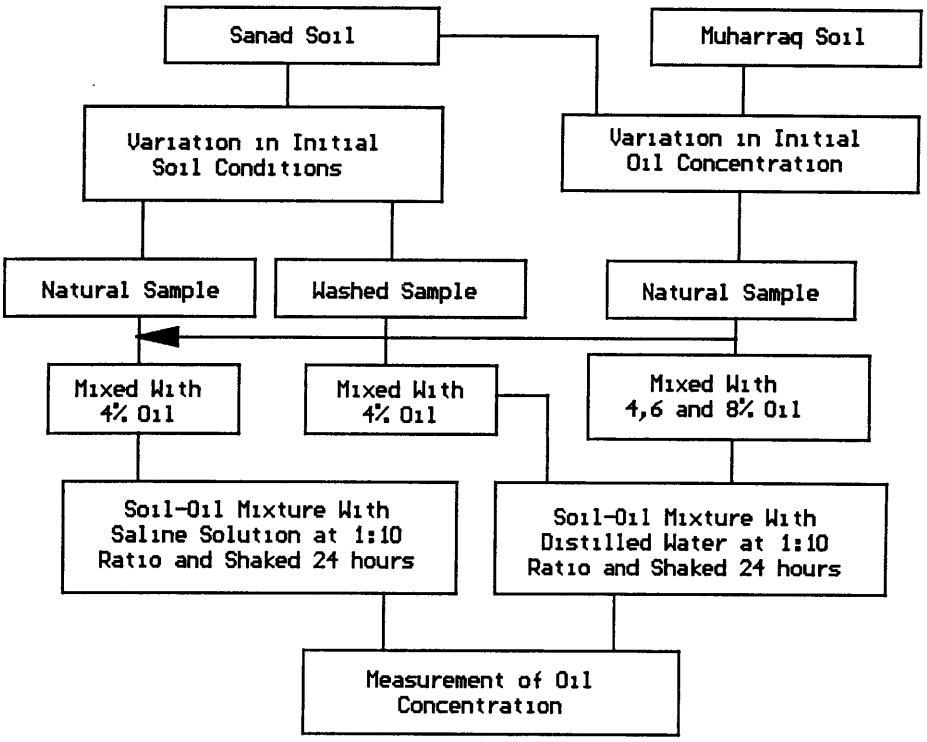


Figure 3.3 - Experimental representation of soil suspension test.

3.8 Soil leaching Study

Oil residue in the stabilized soils are subjected to environmental factors which may influence its migration. Climatic stress can alter soil fabric and oil retaining properties in soil and thus can influence oil migration. Leaching cells are used here to describe the migration of oil from the stabilized soils. The test procedure follows the methods described by Fuller (1982) and Yong et al. (1986). The experiments were conducted at a room temperature of 22±2°C.

The objectives of this test are to determine: (a) the leaching potential of oil constituents and other contaminants such as heavy metals and soluble salts from the stabilized soils, and (b) the migration profile of oil along the stabilized soil, which will be used for a transport model to predict oil migration. The model development and testing will be discussed later in Chapter 8.

3.8.1 Leaching Potential

To achieve the first objective, 10 leaching cells were assembled in three separate sets. The first two sets of leaching cells, each consisting of 4 cells, contained samples from the Muharraq and Sanad sites. The third set, consisting of 2 cells, contained washed samples from the Sanad site. Within each set, the cells were divided into two groups: one group contained the natural soil, whereas the other group contained the soil stabilized with the optimum oil residue content. The natural sample from each soil was used as a "reference" to establish a basis of comparison between the natural soil and stabilized sample.

Each of the above samples was subsequently compacted in a cylindrical plexiglass cell of 50 mm diameter and 50 mm height until its maximum dry density was reached. The compacted dry densities were 1.78±0.03 Mg/m^3, 1.75±0.03 Mg/m^3, and 1.32±0.03 Mg/m^3 for the Muharraq soil, the Sanad soil, and the washed Sanad soil, respectively. Following cell preparation, each cell was connected to a pressure gauge at one end (controlling flow rates) and an effluent collector at the other end. A schematic diagram of the laboratory leaching cell is presented in Figure 3.4.

The compacted samples were first saturated with distilled water. One pore volume

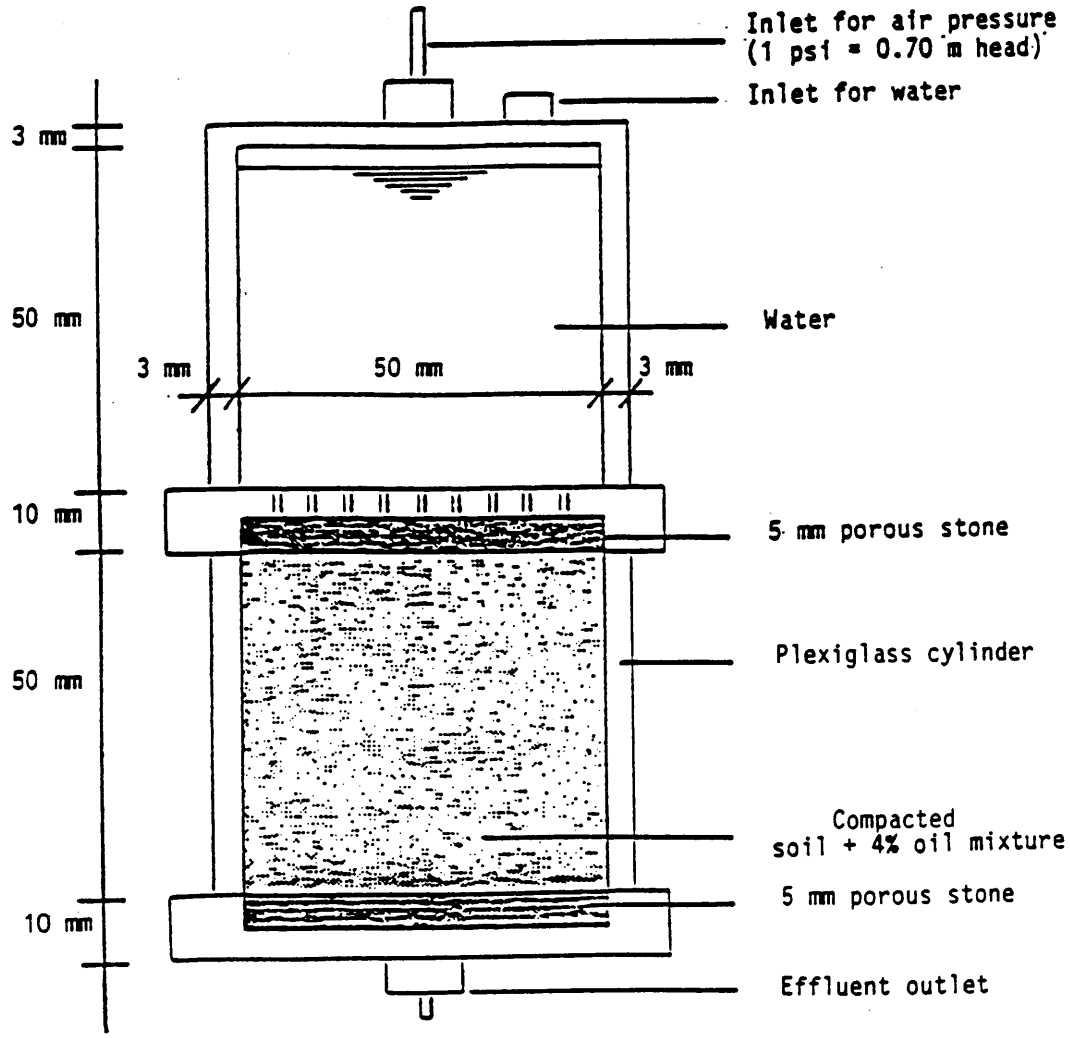


Figure 3.4 - Schematic representation of laboratory leaching cell used in this study.

of distilled water was then passed through the sample, and separated into two series. One series consisted of 6 cells, 2 cells from each of the aforementioned sets, and continued leaching with distilled water (having a pH of 6 and an electrical conductivity of 0.025 ds/m). The other series consisted of 4 cells, the remaining cells from the first two sets, leached with saline water (having a pH of 8 and an electrical conductivity of 25 ds/m). Within each series, half of the cells contained natural soils and the other half contained stabilized soils.

Each cell was leached at a constant flow rate under a hydraulic gradient of 14. During the leaching period, effluents were collected until 10 pore volumes of effluent were recovered. A pore volume of approximately 50 ml was estimated in this case based on the values of compacted soil density and cell volume. A schematic representation of the experimental work involved in determining oil leaching potential is shown in Figure 3.5.

Concentration of oil, some heavy metals, and soluble salt were measured in each collected pore volume. Changes of these concentrations in the leaching effluents were used to evaluate the degree of leaching of the specimens. Leaching was assumed to have ceased when the concentrations of these contaminants showed no further changes. It took about 40 days to achieve complete leaching in this case under the above specified conditions. Laboratory leaching was conducted in the absence of a lateral stress field (confining pressure). For each pore volume, duplicate fluid samples were analyzed and the reported results consist of the average values obtained. Concentration of the leached oil detected in the collected effluents was determined using the partition-infrared method (section 3.9.2).

Typical heavy metals present in this oil residue include vanadium, nickel, iron, and lead. Concentrations of these heavy metals in the collected effluents were determined by atomic absorption spectrophotometry. However, salt concentrations in the collected effluents were estimated from their electrical conductivities based on an empirical relationship given by Jurinak et al. (1987). Measurement of the electrical conductivity was performed according to the test methods for electrical conductivity and resistivity of water, ASTM D1125. Concentration of leached sulfate in the leached effluents was also measured. Sulfate measurements were conducted using the

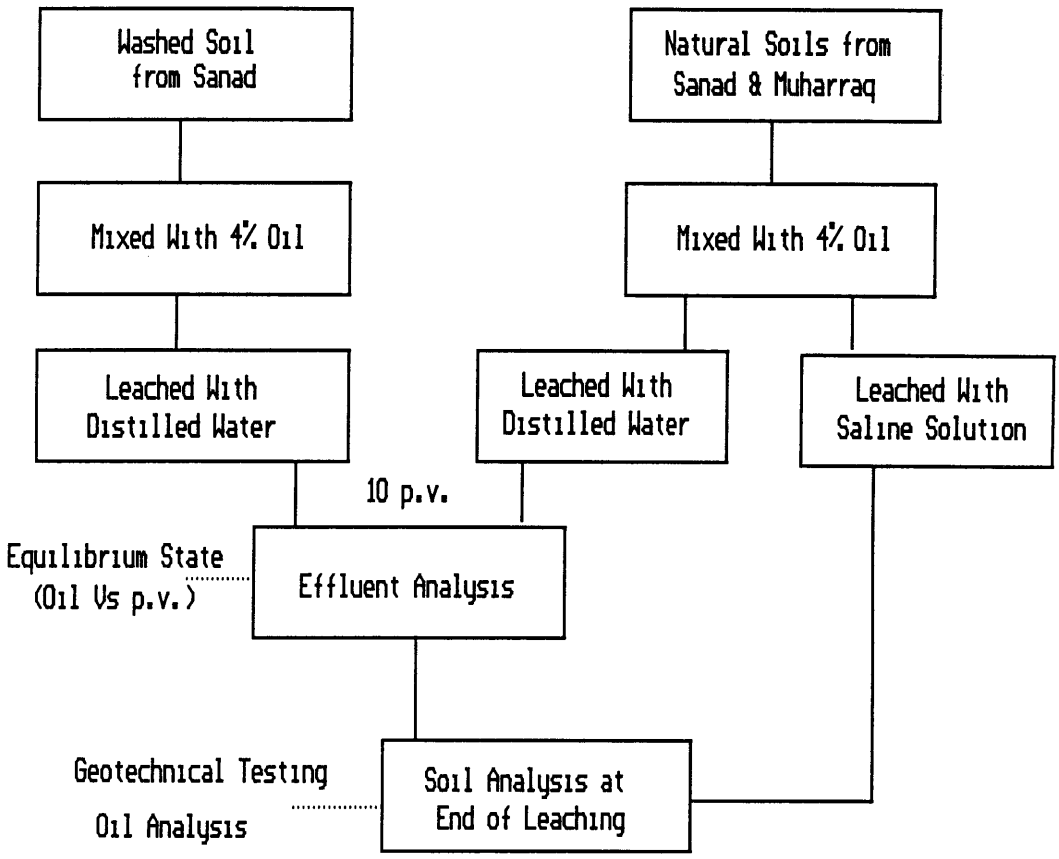


Figure 3.5 - Test scheme used in soil leaching study.

turbidimetric method described in ASTM D4130, test method for sulfate ion in brackish water, seawater, and brines.

After completion of leaching, the reservoir water and air-pressure device were disconnected. The specimens placed in the cells were directly tested on the top and bottom sides in the "reduced" CBR apparatus. Following CBR testing, two samples of 38.1 mm diameter and 12 mm height were directly extracted from each cell for the soil suction test. A small cylindrical sample of 1:2 diameter to height ratio was also extracted from each cell for the unconfined compression test. After extraction, the remaining sample in each cell, containing the stabilized soil, was mixed and duplicate grab samples were taken for oil analysis. Determination of oil content retained in these soil samples was conducted using the Soxhlet extraction method (Section 3.9.1).

3.8.2 Oil Migration Profile

To determine the migration profile of oil residue, three identical leaching cells were assembled. The leaching cells used in this test were 50 mm diameter and 100 mm height plexiglass columns. The test was performed on stabilized soil, containing 4% oil residue by dry weight, obtained from the Sanad site. During the preparation of each cell, the sample was compacted in five lifts, of about 20 mm thickness, until a dry density of 1.5 Mg/m^3 was reached.

The compacted samples were leached with distilled water (pH = 6) under a hydraulic gradient of 14. A pore volume of approximately 100 ml was estimated for this test. The test scheme involved here is shown in Figure 3.6. In each cell, prescribed pore volumes of effluents were recovered before terminating the test. The prescribed pore volumes of effluents were one, five, and ten, respectively. For instance, in the first cell, after completion of passage of one pore volume of distilled water, the test sample was removed and sectioned into different layers for analyses.

During the leaching period, oil concentration in the collected effluents was measured using the partition-infrared method (Section 3.9.2). Following termination of each leaching cell, the sample was sliced into four equal sections of approximately 25 mm thickness. From each section, at least two grab samples were taken for oil analyses.

To determine the amount of oil retained on soil surfaces and the concentration of

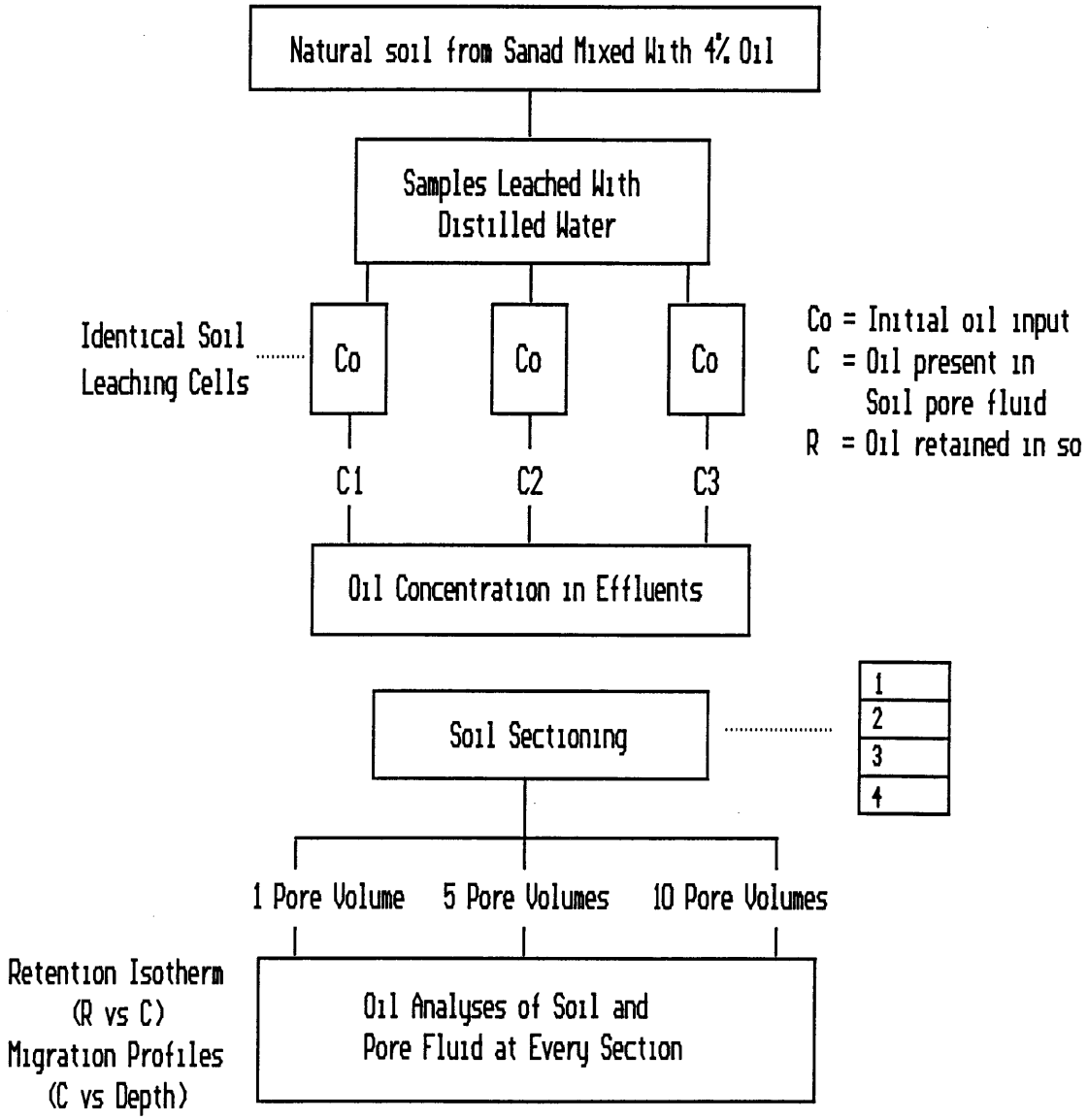


Figure 3.6 - Schematic diagram showing test procedure involved in determining oil migration profiles in soil-oil mixture.

oil present in pore fluid of soil, the soil suspension test was conducted on each extracted soil sample. The soil sample was mixed with distilled water at a 1:10 weight to volume ratio and shaken for 24 hours. Concentration of oil in the supernatant was measured using the partition-infrared method and oil retained in the soil was determined by the Soxhlet extraction method. The results for each sectioned sample is expressed in terms of the average value of the two soil samples.

3.9 **Determination of Oil Concentration**

Two different tests were employed in this study to determine the concentration of oil in the soil and fluid samples. The Soxhlet extraction test was used to measure oil concentration in the soil samples, whereas the partition infrared test was used to measure oil concentration in the fluid samples. The procedure involved in both tests is explained hereafter.

3.9.1 Soxhlet Extraction

The amount of oil retained onto (adsorbed to) the soil at the end of leaching was measured by the Soxhlet extraction method (Greenberg et al., 1992; Martin and Loehr, 1986). Approximately 10 g of the soil or oil-soil mixture was oven dried at a low temperature ($< 60°C$), ground, weighed, and placed in a pre-weighed cellulose thimble. The thimble was placed in a Soxhlet extraction tube and washed several times with trichlorotrifluoroethane (Freon) for at least 2 hours at a rate of 20 cycle/hour. The low polarity of Freon and its low boiling point enhances and speeds the extraction process. After extraction, the sample was drained and left in a desiccator for at least 30 minutes prior to weight measurement. The oil content was then determined as the ratio of the difference between the weight of the sample before and after extraction to the weight of the dry soil. These tests were also conducted on at least one duplicate sample, and the results recorded in terms of the mean values obtained for all the samples.

3.9.2 Partition Infrared

Each liquid sample was subjected to liquid-liquid extraction using carbon tetrachloride and analyzed for total petroleum hydrocarbon by infrared spectrophotometry. The concentration of oil in a given fluid sample is expressed in terms of the total petroleum hydrocarbon. Preparation and analysis were performed according to the Partition-Infrared Method (ASTM D3921, petroleum hydrocarbons (oil/grease) content of water/wastewater).

In this test, all liquid samples were preserved with the addition of few drops of hydrochloric acid, refrigerated, and extracted within 30 hours after being collected. The sample was then poured into a separatory funnel and mixed with carbon tetrachloride (CCl_4) at a volume ratio of 1:10 solvent to solution. Carbon tetrachloride has been found to be a good extraction reagent for oil since it effectively dissolves most hydrocarbons and has no C-H bonds to interfere with the analysis. After CCl_4 addition, the sample was vigorously shaken for 10 minutes and left to separate into two layers. The lower extraction layer (which contains the CCl_4 sample) was drained, placed in a 10 mm path-length cell, and analyzed for concentration of oil using an infrared spectrophotometer.

The infrared technique utilizes a narrow frequency peak present at 2930 cm^{-1}. This frequency corresponds to carbon-hydrogen (C-H) stretching which is a typical bond in all hydrocarbons. The absorbance of the C-H bond in a given sample is directly proportional to the concentration of hydrocarbons in that sample. In order to measure the oil concentration, a blank sample of pure CCl_4 as well as standards, with a known oil concentration, were tested along with the other samples. The concentration of oil in the samples was determined by comparing the absorbance of the samples at 2930 cm^{-1} to the absorbance of the standards at the same frequency.

CHAPTER 4
RESULTS AND DISCUSSION
- GEOTECHNICAL ASPECTS -

4.1 Strength Performance

The variation of in-situ soil strength with depth for the Sanad site, where one of the soils used in this study was obtained, is shown in Figure 4.1. Measurement of the in-situ strength was carried out by the Ministry of Works (Geotechnical Engineering Division) in Bahrain using the Mackintosh probe test. The Mackintosh test result revealed that the top 3 meters possesses very low strength performance. In this section, the results of three geotechnical tests (unconfined compression test, direct shear test, and California bearing ratio) conducted on both natural soil samples and stabilized samples are presented for the three sets of soils characterised in Section 3.1.1.

4.1.1 Unconfined Compression (UC)

The unconfined compression test results of four groups of testing are presented herein. The first group examines the effect of the order of water addition on the initial strength performance of the soil-oil mixtures (i.e. the effect of adding water prior and subsequent to oil addition). The second group determines the influence of oil residue content on the initial soil strength. The third group investigates the effect of soil washing on the strength behavior. The last group studies the effect of leaching forces on the long-term strength performance.

4.1.1.a *Effect of order of water addition*

Figures 4.2 (a & b) and 4.3 (a & b) demonstrate the variation of unconfined compressive strengths (q_u) for soil samples containing 0%, 4%, and 8% oil residue, by dry weight of soil (w/w), obtained for the Sanad and Muharraq sites, respectively. In each of these figures, part (a) represents the variation in the stress-strain relations for the tested samples and part (b) shows the values of unconfined compressive strengths for the

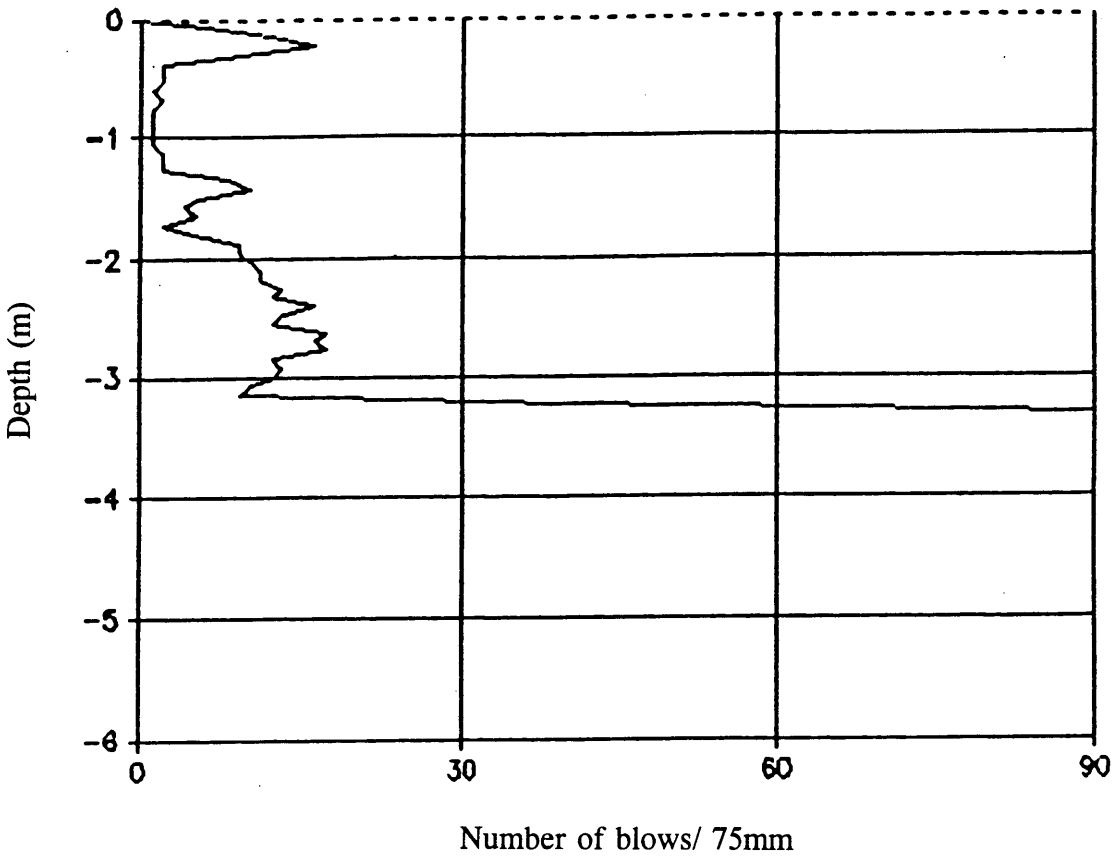


Figure 4.1 - Mackintosh probe test results for the Sanad site.

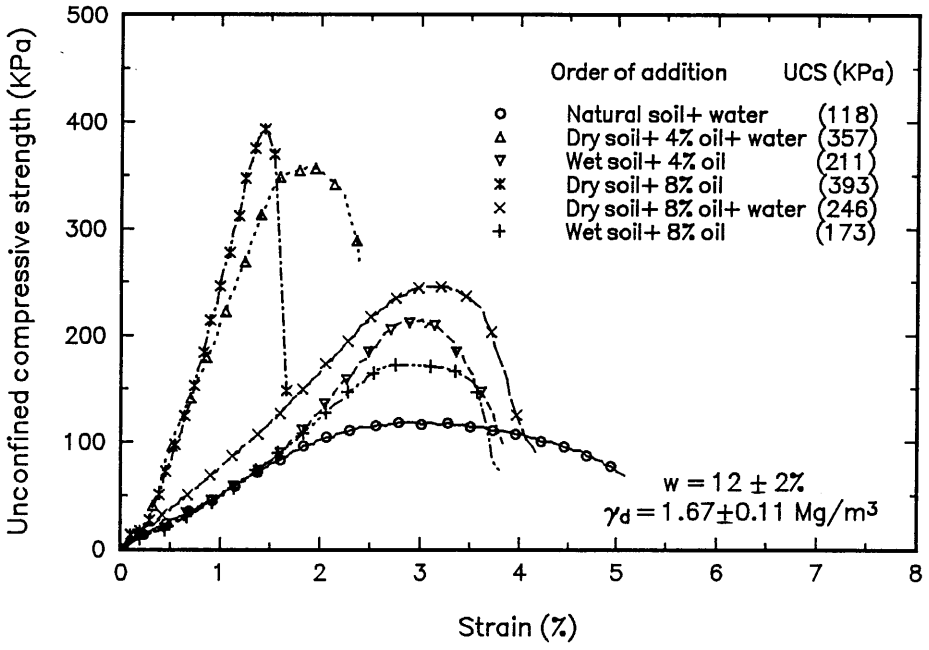


Figure 4.2a - Influence of order of water addition on the stress-strain behavior of stabilized samples from the Sanad soil.

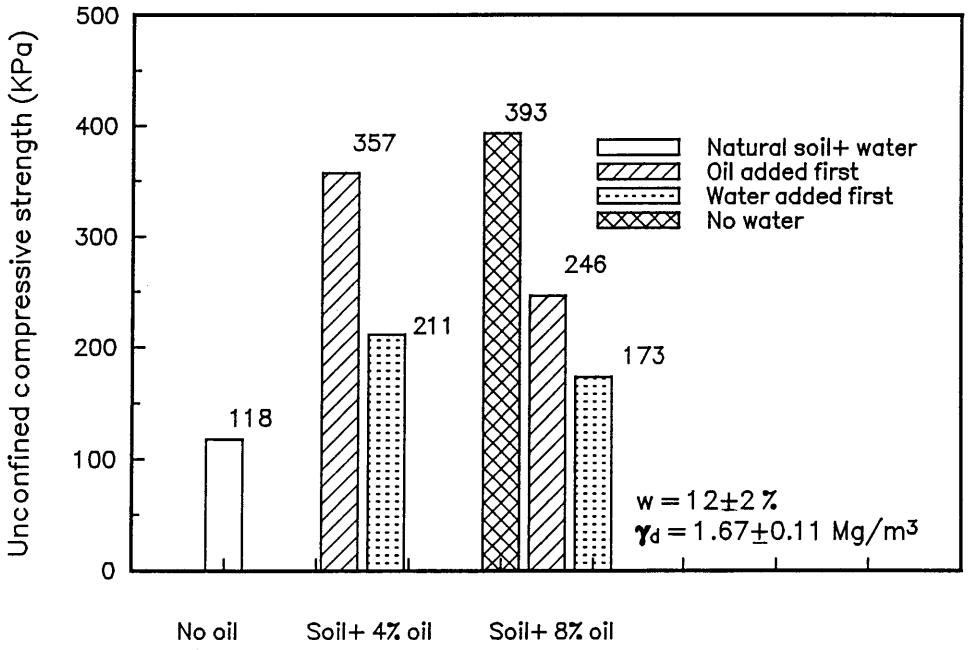


Figure 4.2b - Influence of order of water addition on unconfined compressive strength of stabilized samples from the Sanad soil .

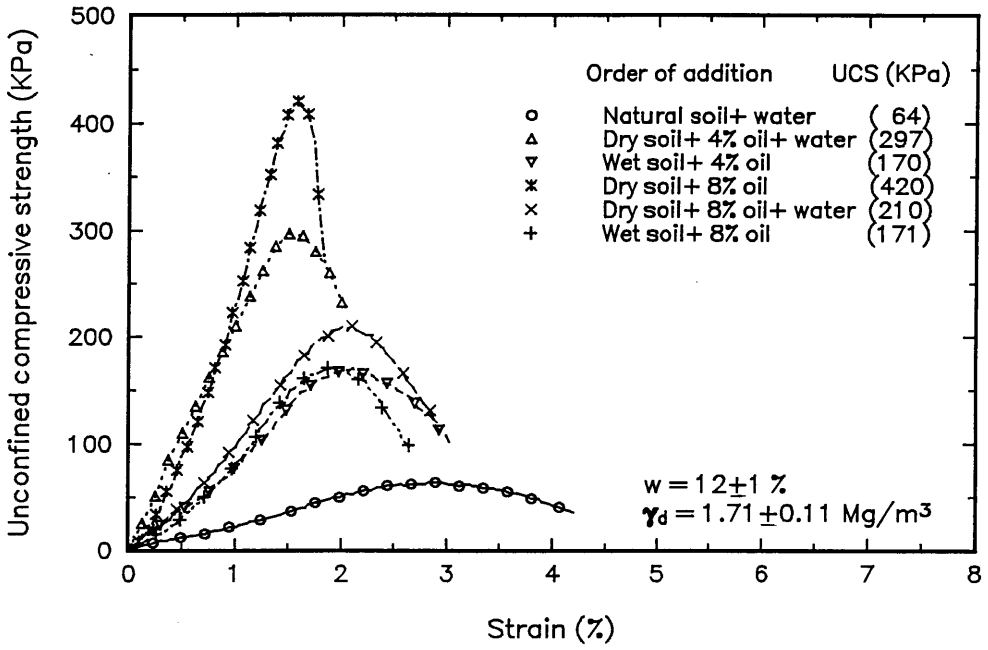


Figure 4.3a - Influence of order of water addition on the stress-strain behavior of stabilized samples from the Muharraq soil.

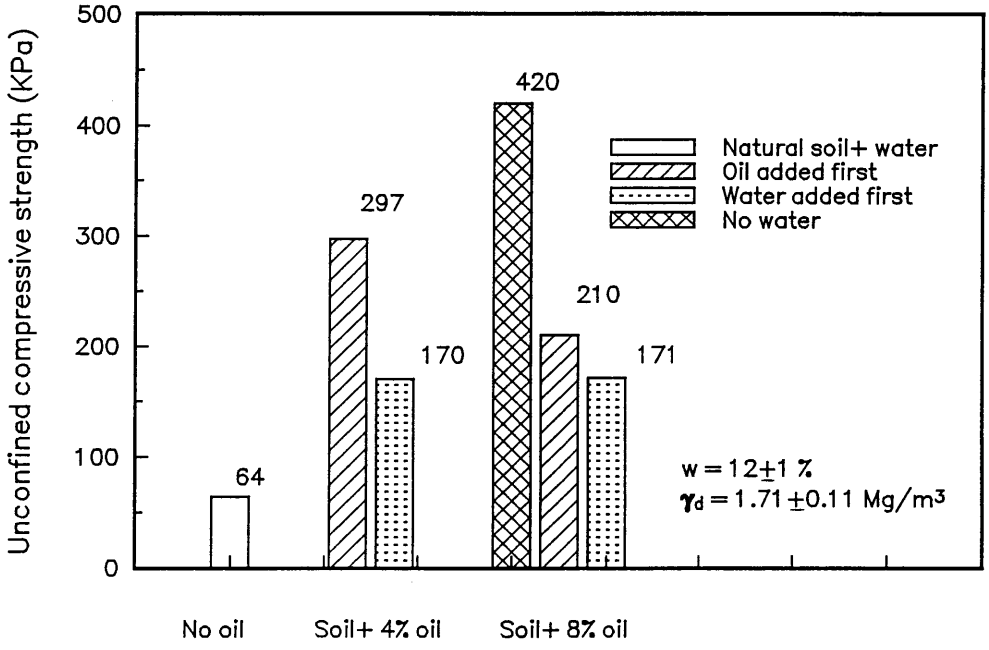


Figure 4.3b - Influence of order of water addition on unconfined compressive strength of stabilized samples from the Muharraq soil.

same samples. For each soil set, two groups of oil-soil-water mixtures were separately prepared and tested. The first group is prepared by first mixing the dry soil with oil residue and then with water. However, the second group was prepared by first mixing the soil with water and then with oil residue. The order of oil and/or water addition is indicated in these figures. Within each of the tested groups, the values of the initial dry densities and initial water contents were maintained within narrow limits of variation. The values of the initial dry densities and the water contents were 1.67 ± 0.11 Mg/m^3 and 12 ± 2 %, respectively for the Sanad soil samples and 1.71 ± 0.11 Mg/m^3 and 12 ± 1%, respectively for the Muharraq soil samples.

The results of Figures 4.2 and 4.3 indicate that the addition of water prior to the addition of oil residue substantially reduces the unconfined compressive strengths of the tested soils. These results show, for instance, that the presence of water prior to the addition of 4% oil residue to these soils reduces their strengths by about 40%. This is because wet surfaces have lower adhesion potential to oil residue than dry surfaces (Yaron, 1989). The presence of water in the soils prior to oil addition is expected to interfere with the formation of the cohesive bonds (e.g. adhesion and interparticle) between the soil particles, thus resulting in a reduction in the soil strength (Theng, 1974).

It can be seen in Figures 4.2a and 4.3a how the presence of oil affects the stress-strain behavior of the stabilized samples. A comparison of the stress-strain curves of the natural soil samples and stabilized samples shows a great variation in their shapes. Despite the fact that values of the initial dry densities of the tested samples within each soil set lay between narrow ranges, there was significant variation in the stress-strain shapes. This can be attributed to changes in the value of the soil modulus. The stabilized samples possess a steep shaped curve which is likely as a result of the formation of a higher modulus system in the presence of oil residue. However, the flat shaped curve in the case of the natural soils is indicative of the formation of a low modulus system as compared to the stabilized sample.

4.1.1.b *Effect of oil residue content*

In the following unconfined compression results, oil-soil-water mixtures were prepared by first mixing separately the soil with various contents of oil residue, followed

with water (resulting in water contents of about 12±2% for both the Sanad and Muharraq soils and water content of 27±2% for the washed Sanad soil). The immediate effect of the addition of 4%, 6%, 8%, and 12% oil residue (w/w) on the unconfined compressive strengths of the tested samples for the three sets of soils are presented in Figures 4.4, 4.5, and 4.6. For each of the tested soil sets, the initial values of the dry densities and water contents were maintained between narrow ranges of variation for comparison purposes.

The results of Figures 4.4, 4.5, and 4.6 illustrate a significant increase in the unconfined compressive strengths of the tested soils in the presence of oil residue. For instance, the addition of 4% oil residue to these soils leads to an increase of about 120% to 300% in their strength, depending upon soil type. The UC results also show that the strength of mixtures containing 4 % oil residue content peaks at a slightly lower strain as compared to mixtures having higher contents of oil residue, as can be seen from the stress-strain relations presented in Figure 4.4a. This can be attributed to a more brittle reponse in the "elastic" behavior of the mixtures containing lower oil residue content.

Figures 4.4, 4.5, and 4.6 demonstrate that the strengths of the soil samples rise significantly at an oil residue content of 4% by dry weight of soil; thereafter, increasing the oil residue content reduces strength. This suggests that 4% oil residue (w/w) is sufficient to significantly increase the cohesive properties of the tested soils. Such increase is likely attributed to the formation of sufficient cohesive bonds in the presence of 4% oil residue. The nature of the individual formed bonds and the overall bonding of the stabilized soil system as a whole will be discussed later when the subject of soil-oil interactions is addressed (Sections 5.1.2 and 5.1.3). In addition, the presence of 4% oil residue (w/w) is found to adequately cover the entire surfaces of these soils with oil (see Section 4.2). From these results (Figures 4.4 through 4.6), it seems that 4% oil residue content is the optimum for maximum strength.

However, as the oil residue content increases beyond 4% (w/w), a reduction in the soil strength performance is observed (Figures 4.4 through 4.6). A similar observation was reported in a study conducted by Puri, et al. (1994) on the geotechnical properties of sand contaminated with a high content of crude oil. This reduction in

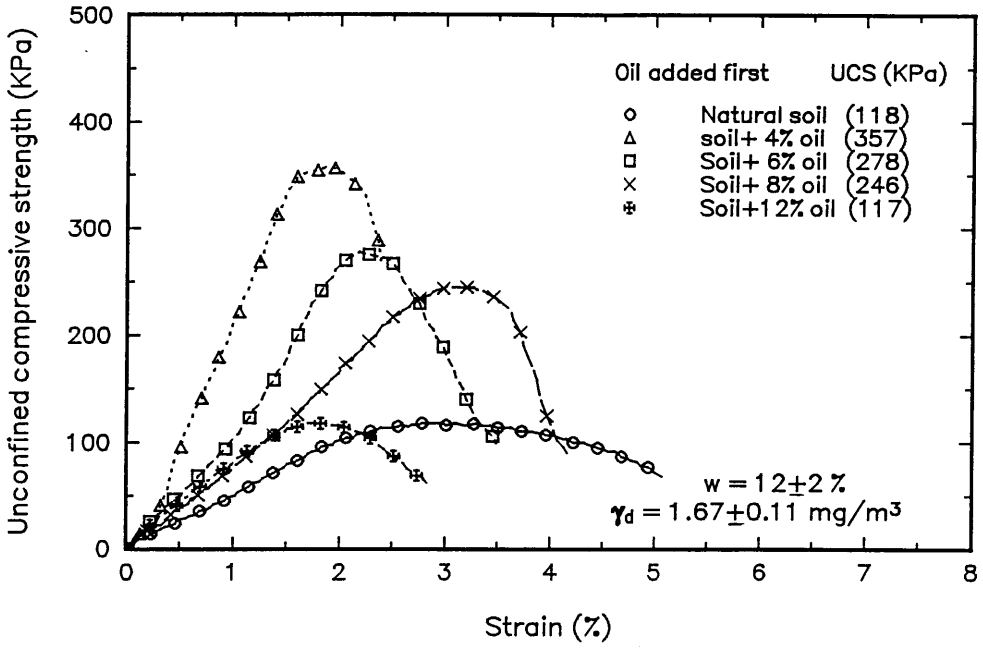


Figure 4.4a - Variation of stress-strain relation with oil residue content for the stabilized samples from the Sanad soil.

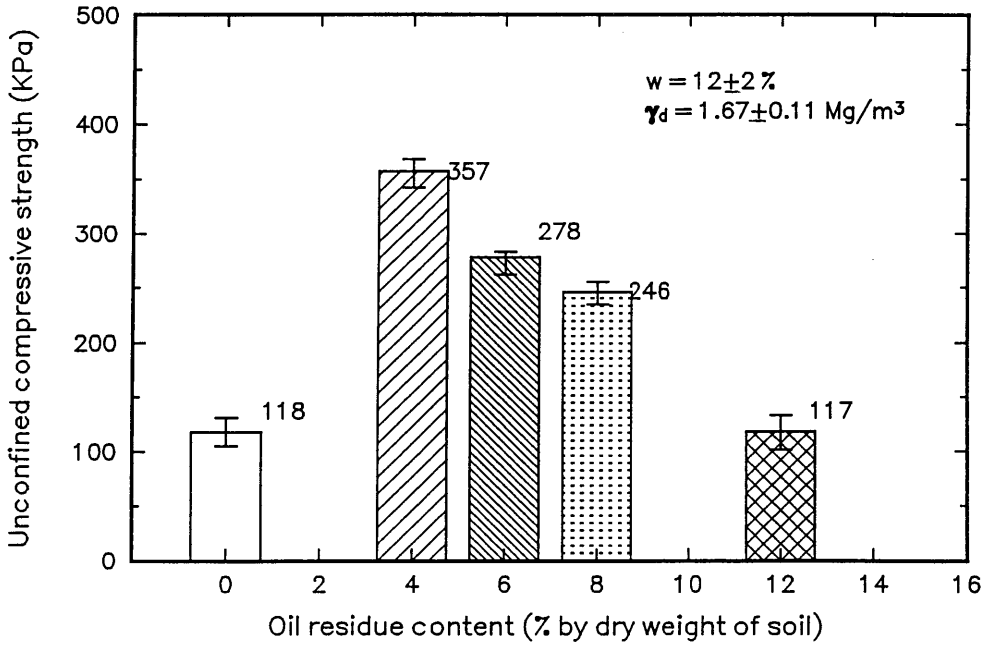


Figure 4.4b - Variation of unconfined compressive strength with oil residue content for stabilized samples from the Sanad soil.

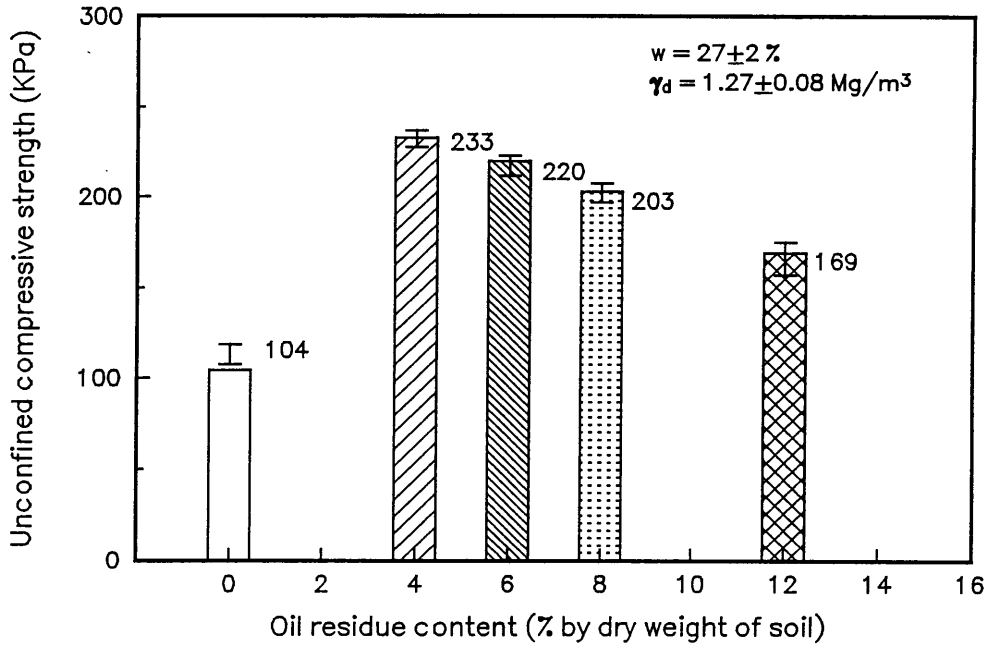


Figure 4.5 - Variation of unconfined compressive strength with oil residue for stabilized washed samples from the Sanad soil.

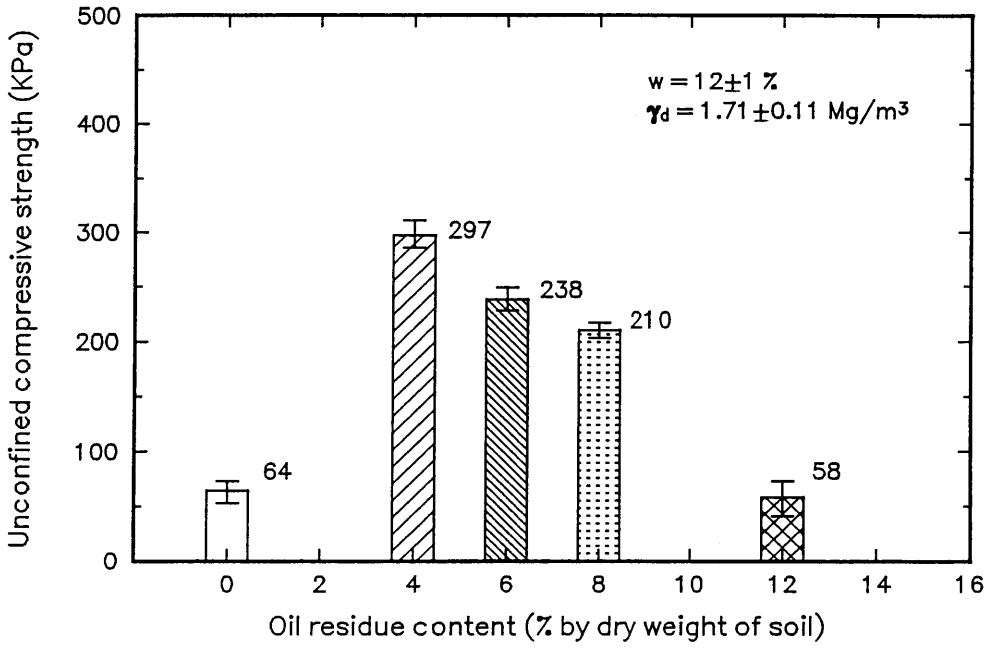


Figure 4.6 - Variation of unconfined compressive strength with oil residue content for the stabilized samples from the Muharraq soil.

strength is likely attributed to the presence of excess oil which tends to fill in the soil pores and may act as a lubricant separating the soil particles. The high content of oil residue in these soils substantially reduces the frictional properties of the soils (Section 4.1.2) and enhances the viscosity and plastic consistency of the mixtures (Section 4.3), resulting in an overall strength reduction. Moreover, the insignificant improvements in the bonding mechanisms associated with high oil residue contents, which will be explained in the infrared results (Section 5.1.2), can be also responsible for such behavior. These strength results are in good agreement with the results reported by Dunn and Salem (1971, 1973) on the stabilization of sand with bitumen.

4.1.1.c *Effect of soil washing*

The washed soil is prepared here by dispersing the natural soil in distilled water in order to reduce its salinity. This soil is used to examine the effect of removing the excess soluble salt (initially present in the natural soil) on the performance of the oil residue in a soil system. Only one washed soil from the Sanad site was used in this study. Soil washing has been shown to significantly increase the plasticity and surface area of the tested soil (above 50% increase in these properties were recorded as compared to the unwashed soil) and to substantially reduce the maximum compacted density of the soil, where about 25% reduction was noted (Table 3.1). In this test, the washed soils (including non-stabilized and stabilized samples) were prepared at constant values of initial dry density (1.27 ± 0.08 Mg/m^3) and water content (27 ± 2 %).

The unconfined compression test results of the washed soil, presented in Figure 4.5, are consistent with the strength results of the tested unwashed soils (Figures 4.4 and 4.6). However, the reduction in their cohesive strength with the increase in oil residue is substantially lower than that of the unwashed soils. As the content of the oil residue increases from 4% to 8% (w/w) in the stabilized soils, for instance, the unconfined compressive strength reduces by about 10% and 30%, for the washed soil and unwashed soil from the Sanad site, respectively. The change in their properties, as explained, is responsible from such variations.

Despite the differences in the initial density, fabric, and bonding between the washed and unwashed soil from the Sanad site, it is of interest to obtain an overall

comparison between their strength performances. The unconfined compression results of the stabilized samples (Figures 4.4 and 4.5) reveal that the strength of the washed soil is substantially lower than the unwashed soil. A reduction of approximately 30% was observed in the unconfined compressive strength of the stabilized washed soil as compared to the stabilized unwashed soil. The decrease in the strength of the stabilized washed soil is primarily attributed to the substantial reduction in the initial density of the stabilized washed soil as compared to the stabilized unwashed soil. The significant increase in the soil fluid potential of the stabilized washed soil as compared to the stabilized unwashed soil, which is explained in the soil suction results (Section 5.1.3), can be another contributing factor in the strength reduction. The increase in the soil fluid potential is associated with an increase in the volume of the soil voids, thus resulting in a reduction in the soil strength.

4.1.1.d *Effect of leaching forces*

The effect of leaching forces on the long-term strength performance of the tested natural soil samples and stabilized samples are examined herein. The stabilized samples were prepared by first mixing 4% of oil residue (w/w) with the dry soil, and then adding water. In order to achieve good comparisons between the obtained results, the initial dry densities (γ_d) of the leached samples were controlled. A summary of the density results for the three tested sets of soils before and after leaching is presented in Table 4.1.

The density results (Table 4.1) suggest that the effect of leaching becomes significant for samples having low initial density. For example, the washed Sanad soil shows 10% reduction in its density after leaching, whereas insignificant reduction (about 2%) in the density of the natural Sanad soil is observed at the end of leaching. This can be mainly attributed to the fact that these samples were well-compacted and possessed low void ratios (less than 0.4).

The results of the unconfined compression tests, presented in terms of the stress-strain relation, for the three sets of soils at the end of the leaching period are shown in Figures 4.7 and 4.8 (a & b), for the Muharraq and Sanad soils, respectively. Part (a) of Figure 4.8 represents the results of the natural soil from the Sanad site and part (b) shows the results of the washed soil from the same site.

Table 4.1 - Comparison of soil density results before and after leaching.

Set / Soil samples	Soil site	Before leaching		After leaching	
		γ_d (Mg/m^3)	w (%)	γ_d (Mg/m^3)	w (%)
1 2 Natural & 2 Stabilized	Muharraq	1.78 ±0.03	12±1	1.75 ±0.02	15±1
2 2 Natural & 2 Stabilized	Sanad	1.75 ±0.03	13±1	1.72 ±0.02	15±2
3 1 Washed & 1 Stabilized	Sanad (washed)	1.32 ±0.03	28±1	1.18 ±0.02	42±2

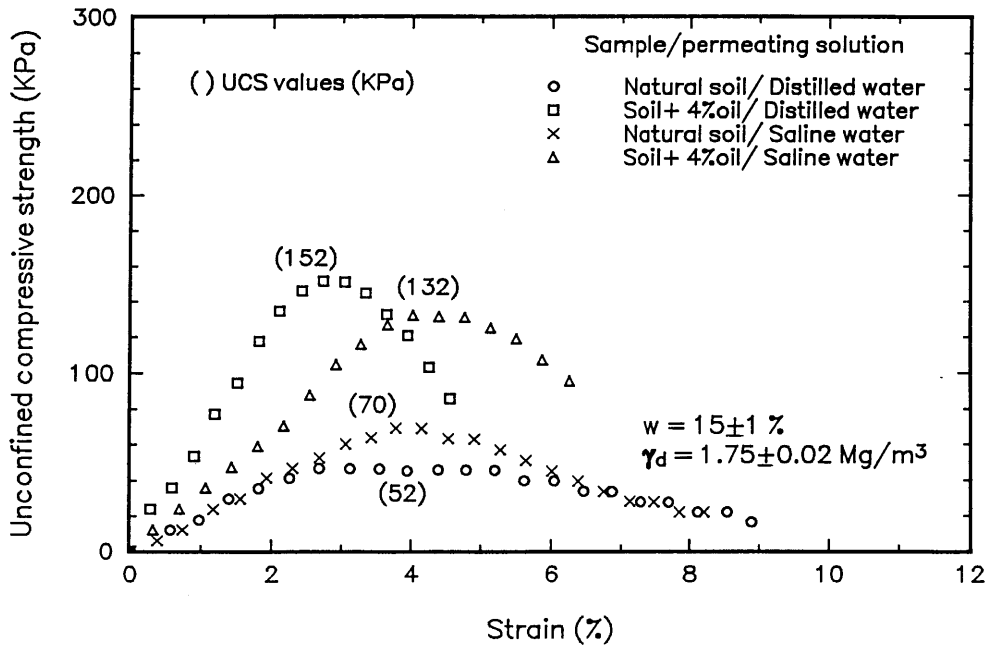


Figure 4.7 - Stress-strain relation for leached samples from the Muharraq soil.

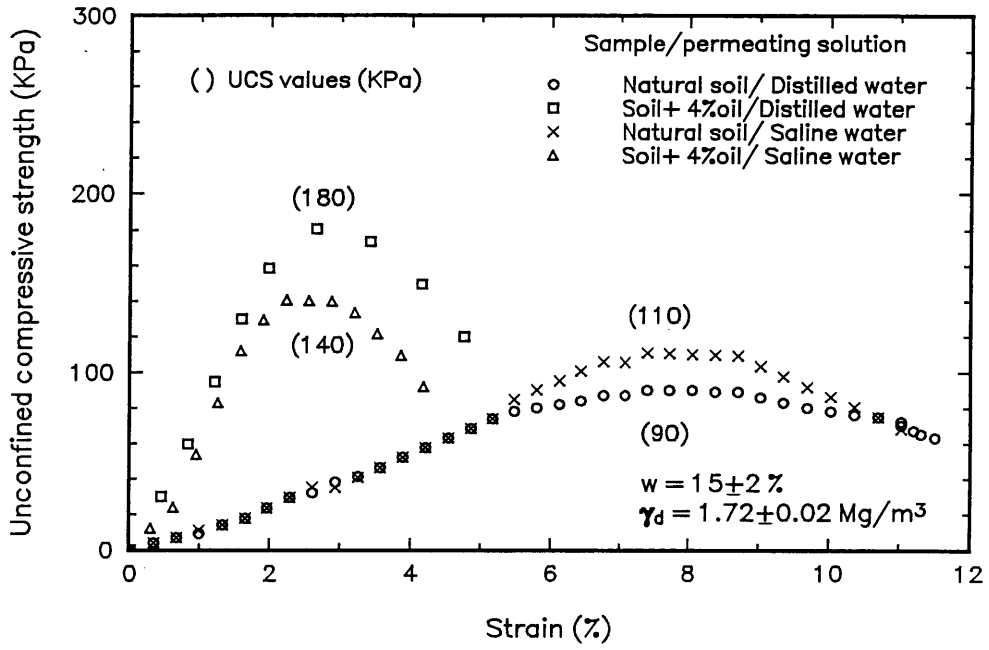


Figure 4.8a - Stress-strain relation for leached samples from the Sanad soil.

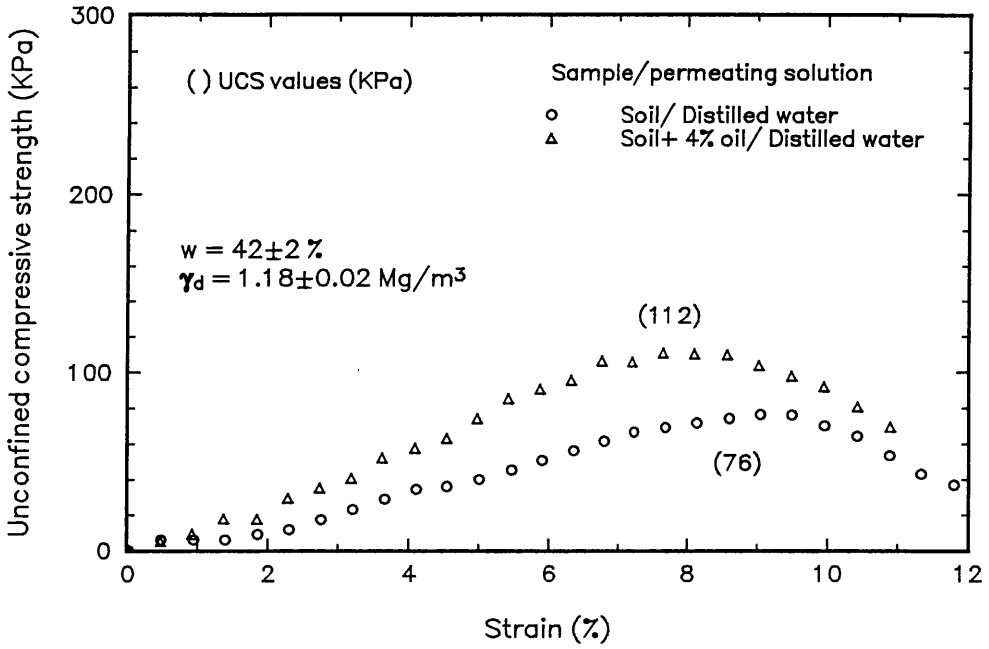


Figure 4.8b - Stress-strain relation for leached samples from the washed Sanad soil.

For each of the tested sets, the natural and stabilized samples were separately permeated with distilled water and saline water and the results after 10 pore volumes of leaching (i.e. 40 days) are presented.

In comparing the results of Figures 4.7 and 4.8 with the strength results obtained in Section 4.1.1.b (Figures 4.4 through 4.6), the leached samples show substantial loss in their strength values as compared to the corresponding unleached samples, despite the fact that the initial density (for each of the tested soil sets) was maintained constant for both cases. These results demonstrate that leaching the samples (both natural and stabilized soil) with distilled water for 40 days, for instance, reduces the soil strength by 20 to 50%, depending upon soil type and condition. This reduction is due to alteration in the internal stability of the soil mass during the leaching process, which directly affects the interparticle bonds and soil density and fabric. The reduction in the interparticle bonds and the increase in the degree of saturation of the leached samples as compared to unleached ones are most likely responsible for the strength reduction of the leached samples.

In examining Figures 4.7 and 4.8, the stabilized leached sample for each soil set showed significantly higher unconfined compressive strength values in comparison with the corresponding natural leached sample. These results show that the stabilized leached samples possess about 50% higher strengths as compared to the natural leached samples. This can be mainly attributed to the contribution of the oil cementation bonds present in the stabilized samples and the insignificant effects of leaching on the performance of these bonds. Most of these bonds seem to be retained in the stabilized soil system after the leaching process, which is discussed in Section 5.1.2.

The strength performance of the leached samples are shown to be influenced by the chemical composition of the permeating solutions. The results of leaching natural soil samples reveal that the samples leached with saline water have slightly higher strength values in comparison with the same samples leached with distilled water (Figures 4.7 and 4.8a). This increase can be partially attributed to the precipitation of additional salt bonds, especially carbonates, developed as a result of the leaching action with saline water containing high carbonate content. These strength results agree with the results reported by Torrence (1974) on the effect of leaching in saline solutions on the strength

performance of Norwegian marine clays. The increase in the strength of Norwegian clays was explained by development of stronger face-to-edge bonds caused by the additional net attractive forces in high salt concentration. However, the slight reduction in the strength of natural soils leached with distilled water is likely as a result of partial removal of the salts present initially in the soil and the cementation associated with it. A similar observation was reported by Ismael (1993) on the geotechnical performance of Kuwaiti soils leached with distilled water.

The leaching of the stabilized samples shows a slight decrease in the unconfined compressive strength of the stabilized samples leached in saline water as compared to the same samples leached with distilled water (Figures 4.7 and 4.8a). This decrease can be attributed to complex physico-chemical effects, such as an exchange potential between various cations present in the saline leaching solution and the oil molecules present in the soil matrix.

4.1.2 Direct Shear

The results of the direct shear tests of the natural and stabilized samples are illustrated in Figures 4.9 and 4.10 for the Sanad and Muharraq soils, respectively. The stabilized samples were prepared by first mixing the soil with 4% oil residue (w/w) and then adding water ($12\pm2\%$). Both natural and stabilized samples were tested within narrow ranges of density values (i.e. 1.75 ± 0.03 Mg/m^3 for the Sanad soil and 1.78 ± 0.03 Mg/m^3 for the Muharraq soil). The components of shear strength (cohesion and friction) for each tested sample are determined from the intercept and slope of the failure envelope obtained from normal stress-shear stress relation. The resulting equations for normal stress-shear stress relation are shown on the figures.

The direct shear results (Figures 4.9 and 4.10) show that the addition of 4% oil residue to the soils has a simultaneous effect of increasing the cohesive strength and slightly reducing the frictional resistance. The cohesive strength of the two tested soils increases by more than 150% in the presence of 4% oil residue, while the angle of frictional resistance decreases by less than 18%. The reduction in the angle of frictional resistance is noted to be much smaller compared with the significant increase in the cohesion, thus resulting in a significant increase in the total shear strength. This increase

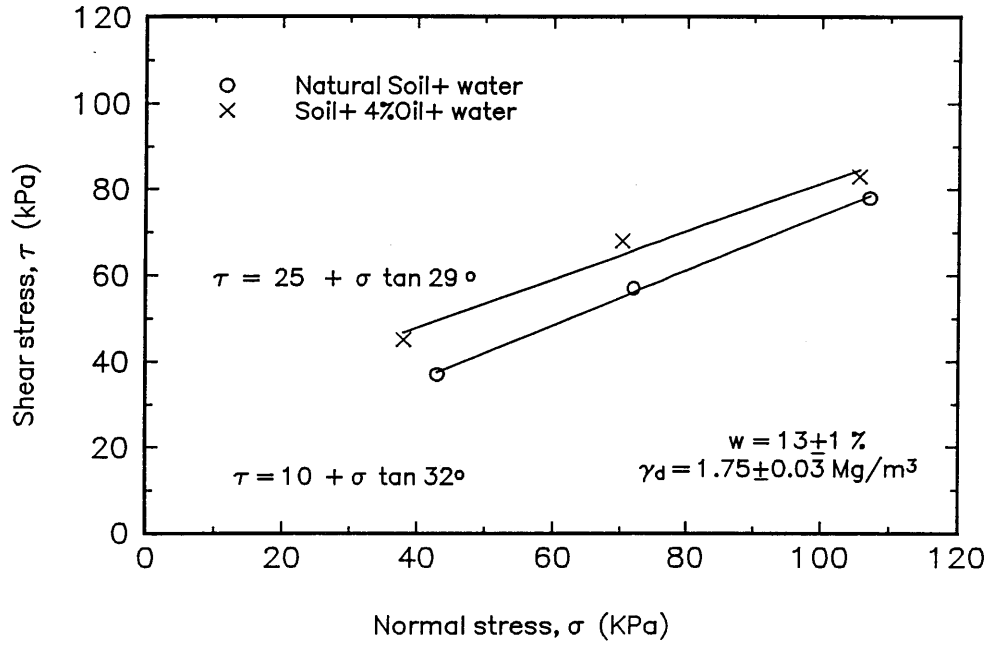


Figure 4.9 - Direct shear test results for the Sanad soil.

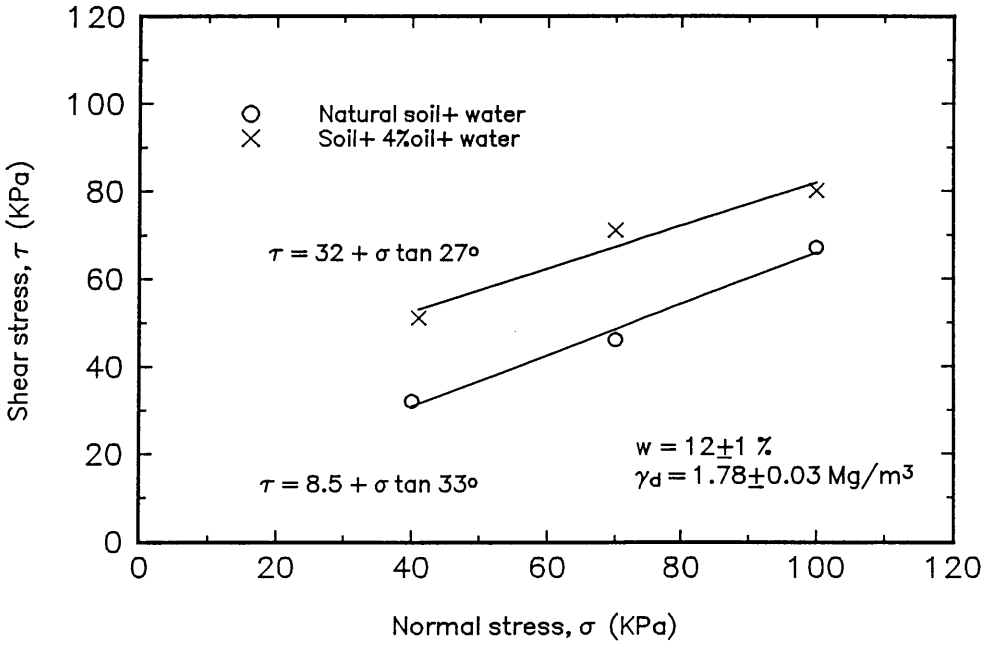


Figure 4.10 - Direct shear test results for the Muharraq soil.

in the cohesive properties of the stabilized soils is likely attributed to an overall increase in the interparticle bondings of the oil-soil-water system. However, the presence of oil in these soils seems to reduce the sliding and interlocking resistance between particles due to its "lubricating" nature, and hence reduces the frictional properties.

Since the initial dry density of the tested samples are constant in both the unconfined compression and direct shear tests, it is of note to compare the increase in the cohesion associated with the presence of 4% oil residue in each test. The unconfined compression results showed an increase of 200% and 350% in the cohesive properties of the Sanad and Muharraq soils, respectively. However, the increase in the values of cohesion obtained from the direct shear test results (i.e. 150% for the Sanad soil and 280% for the Muharraq soil) is found to be lower than its corresponding increase reported in the unconfined compression test results. The variation in the testing technique and testing condition can be partially responsible for such a difference. Nevertheless, these two tests still gave comparable increases in the cohesion values of the tested soils.

4.1.3 California Bearing Ratio

The feasibility of testing the samples in the "reduced" CBR apparatus used in this study is first verified by comparing the load-penetration responses of the natural unsoaked soils, from the Sanad and Muharraq sites, obtained from "standard" CBR and "reduced" CBR apparatus (Figure 4.11). Each of the above samples was tested at a constant density of 1.76 ± 0.04 Mg/m^3 and a water content of $12 \pm 2\%$. The close similarities in the load-penetration behaviors between the "standard" CBR and "reduced" CBR of the tested samples, as shown in Figure 4.11, confirm the applicability of using the "reduced" CBR apparatus for testing.

The results of the load-penetration relations for both natural and stabilized samples, containing 4% oil residue, from the Sanad and Muharraq soils are shown in Figures 4.12 and 4.13, respectively. In each of these figures, part (a) represents the CBR results of the unsoaked and soaked samples, while part (b) illustrates the CBR results of the leached samples. The preparation techniques of these samples, and their specimens, were kept identical to the previous sets of samples used in the unconfined

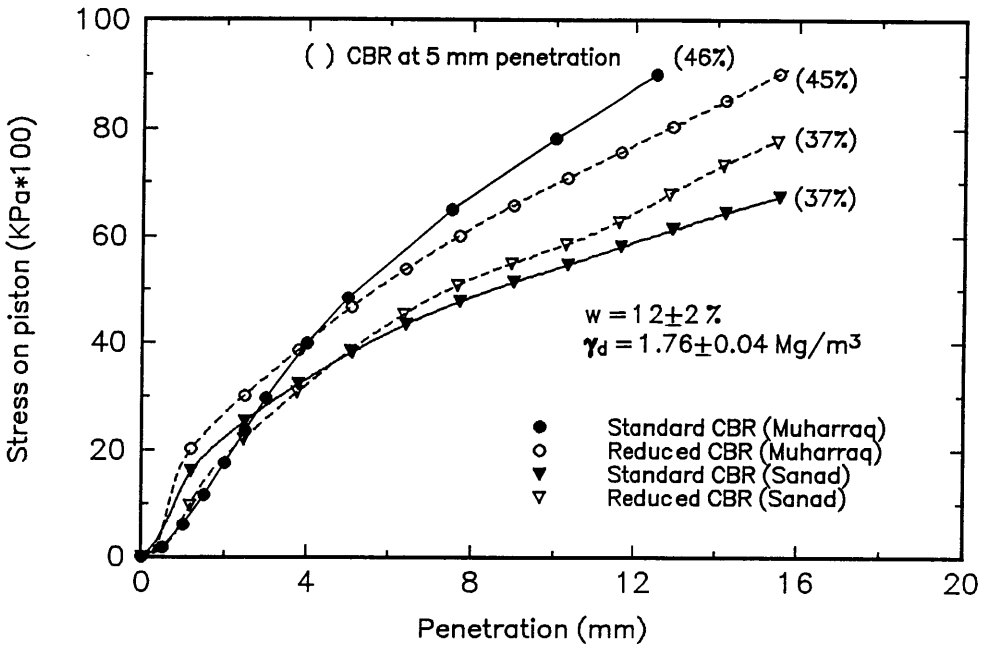


Figure 4.11 - Load-penetration calibration curves for natural unsoaked soil samples.

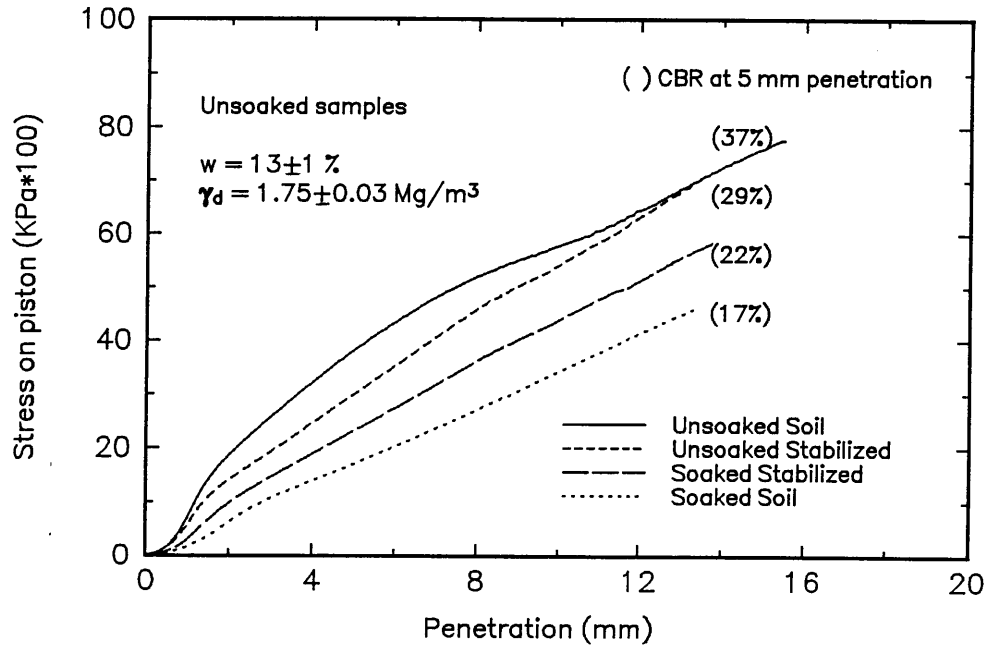


Figure 4.12a - Load-penetration curves for the Sanad soil samples.

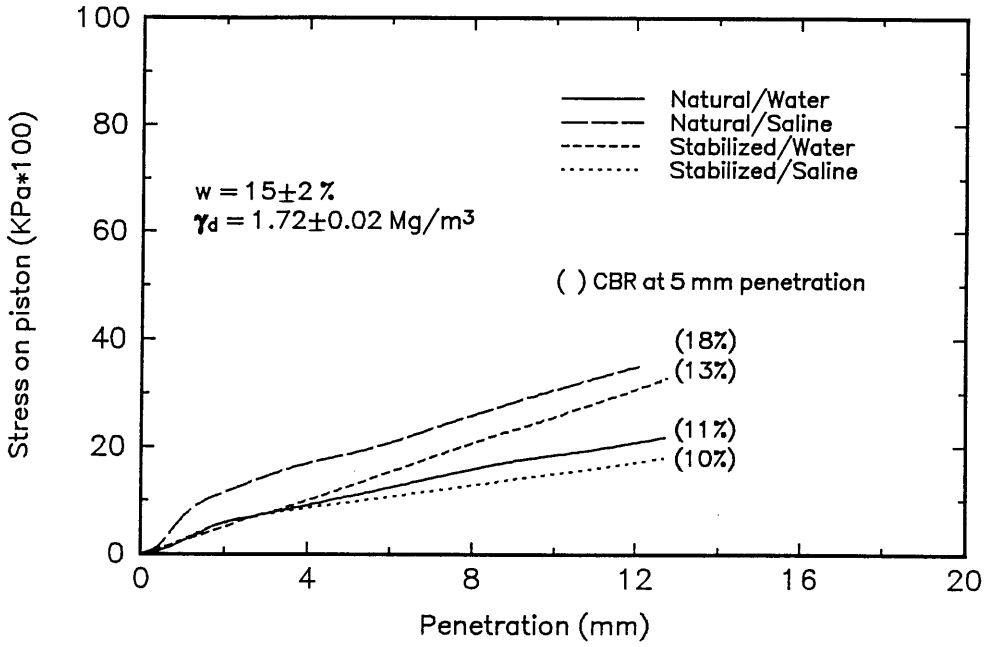


Figure 4.12b - Load-penetration curves for leached samples from the Sanad soil.

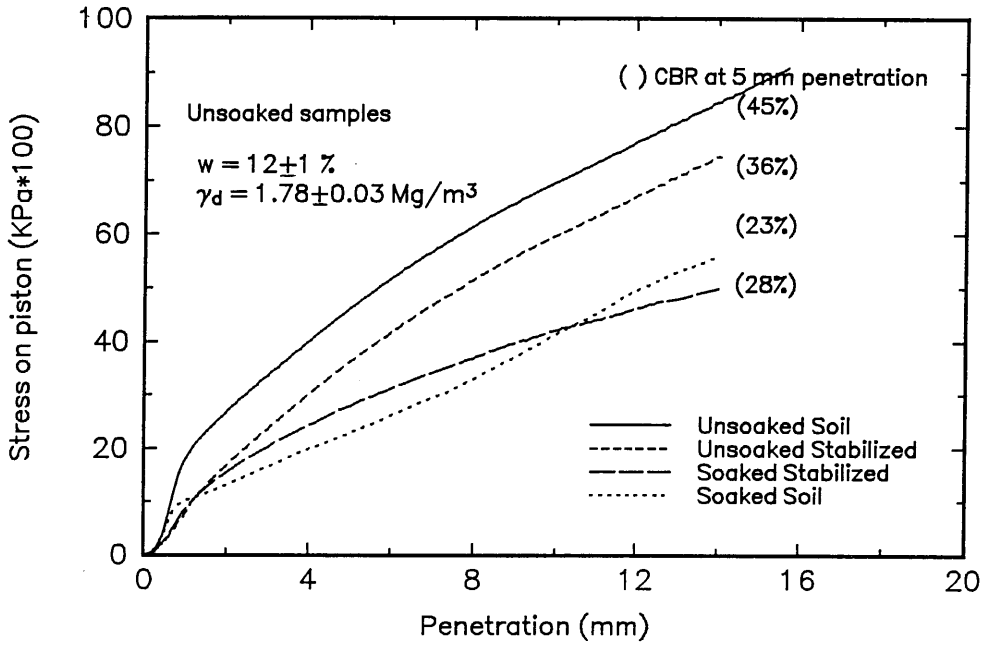


Figure 4.13a - Load-penetration curves for the Muharraq soil samples.

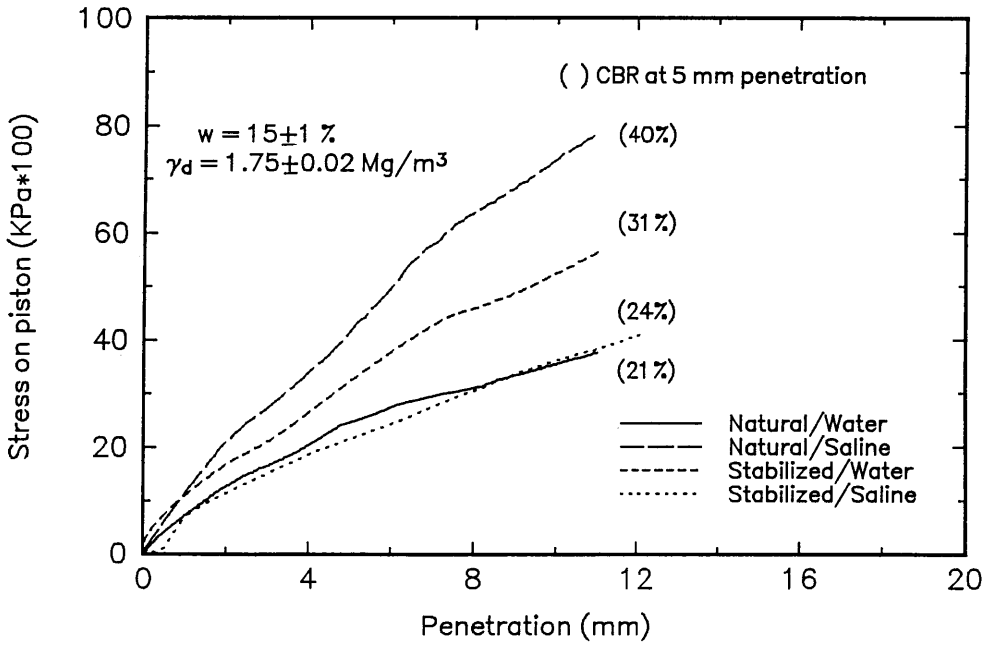


Figure 4.13b - Load-penetration curves for leached samples from the Muharraq soil.

compression test (Section 4.1.1). Therefore, the values of the initial density and initial water content of the samples were maintained constant for each tested sets of soils, as shown in Figures 4.12 and 4.13. The CBR values of the tested samples, measured at 5.08 mm penetration, are given in the figures. The results demonstrate that the overall CBR performances of the tested samples from the two soils share similar trends.

The CBR results reveal that the unsoaked stabilized samples have a lower CBR value than the natural soil samples. A reduction of approximately 20% was observed in the CBR values of the stabilized samples as compared to the natural ones. This can be attributed to the increase in the fluid content of the stabilized samples, by about 4%, in comparison with the natural soil samples. The increase in fluid content of soils is expected to facilitate penetration and hence reduce CBR values.

Both the leaching forces and soaking processes are shown to substantially decrease the CBR values of the tested natural soil samples and stabilized samples. As can be seen from Figures 4.12 and 4.13, there is about 20 to 60% reduction in the CBR values due to soaking or leaching, depending upon soil type and condition. The reduction in the CBR values are found to be more profound in: (a) the leached samples as compared to their identical soaked ones, and (b) the natural soil samples as compared to their corresponding stabilized samples. The increase in the degree of saturation and partial removal of the bonds are likely responsible for the reduction in the CBR values in the above cases. Moreover, these CBR results show a good agreement with the unconfined compression results presented in Section 4.1.1.d.

The CBR values of both the soaked and leached stabilized samples were shown to be slightly higher than the corresponding natural soil samples. The results show an increase of about 20 to 30% in the CBR values of the stabilized samples, i.e. leached or soaked in distilled water, as compared to the leached natural soil samples. This change is likely due to the effect of leaching forces on the internal stability of the soil matrix in each case, as explained in Section 4.1.1.d. However, leaching the samples in saline water showed an opposite effect on the measured CBR values as compared to the same samples leaching with distilled water. A comparison of CBR values of the natural and stabilized samples, both leached with saline water, shows that the natural soil samples have higher CBR values than the stabilized samples.

There is a striking similarity between the CBR and the UC results of the tested samples. The UC results indicate that the presence of 4% oil residue in the tested soils significantly increases the cohesive properties of these soils. Under the same test conditions, an increase in the fluid content of the stabilized soils (containing 4% oil residue) was shown to slightly enhance penetration and hence reduce their CBR values as compared to those of the natural soil samples. The leaching forces reveal substantial reduction in both the unconfined compressive strengths and CBR values of these samples. The strength reduction under various identical testing conditions is found to be consistent in both tests as demonstrated by these situations: (a) the stabilized soils leached with distilled water show higher strength than the natural soils leached with distilled water, (b) the natural soils leached in saline water show higher strength than the same soils leached with distilled water, and (c) the stabilized soils leached with distilled water show higher strength than the same soils leached in saline water.

4.1.4 Effect of Curing Process

Whereas the immediate effects of oil residue on the mechanical properties of the tested soils (i.e. unconfined compressive strength, shear strength, and CBR values) have been determined in the previous sections (Sections 4.1.1 to 4.1.3), the effects of curing on the strength performance of the stabilized soils have not been considered. The curing process is strongly influenced by ambient temperature and humidity, soil moisture, and curing time. A higher temperature, lower humidity and moisture, and longer curing period results in higher strength performance. The process of curing stabilized specimens should simulate actual field situations. Stabilized specimens can be cured in several ways depending on the field conditions. These specimen curing types include: air-cured type (at 22°C), waxed-cured type, vacuum cured type, and oven-cured type (30-40°C). A typical curing period of 7 to 10 days is commonly recommended but it may increase in certain cases (Al-Balbissi, 1989).

The hot climatic conditions in Bahrain is anticipated to accelerate the curing process (Ola, 1978). Previous studies (Dunn and Salem, 1971; Dunn and Salem, 1973) have shown that the curing process under dry conditions significantly enhances the strength performance of the stabilized soils with oil-based constituents. This is attributed

to the fact that, under dry conditions, some of the fluid will evaporate during the curing process. This results in dryer samples with higher strength performance as compared to identical samples tested immediately after preparation, as in this case. Therefore, a substantial gain in the strength of the tested stabilized soils is expected if they are cured under the hot and dry conditions predominant in Bahrain.

4.2 Oil Surface Coverage of Soil

Expression of the oil residue content in terms of *surface coverage* of the oil onto soils can significantly contribute in understanding the overall behavior of the oil-soil-water mixtures. Based on the geotechnical results of Section 4.1, where 4% oil residue content was found to be optimum for the tested soils, an estimate of the potential surface coverage of 4% oil residue onto the soil surfaces is determined herein.

The surface coverage of a given content of oil residue can be computed by knowing the surface areas of both the soil and the oil residue and is based on the assumption that the oil is retained uniformly over the soil surface. Estimation of the molecular surface area of oil residue is assessed by using the benzene molecule as a model, according to the method described by Curtis et al. (1989). The surface area of the oil residue is calculated by multiplying the surface area of a benzene molecule (i.e. 20×10^{-20} m^2) by a ratio of the molecular weight of the oil residue to the molecular weight of benzene (i.e. 900 g/mole divided by 78 g/mole = 11.5). Therefore, the molecular surface area of the oil residue is approximately 230.77×10^{-20} m^2, which corresponds to a molecular size of about 1.7 nm in diameter. This molecular size lies within the range of molecular sizes of complex ring structures reported by Welte (1972), i.e. between 1 and 3 nm. Further, the surface area of the tested soils, previously determined by the Ethylene Glycol Monoethyl Ether (EGME), is 35 m^2/g, 40 m^2/g, and 62 m^2/g for the Muharraq, Sanad, and washed Sanad soils, respectively (Table 3.1).

In order to estimate the oil surface coverage of these soils in the presence of 4% oil residue, the number of oil molecules present in the soils must also be computed. This is determined by multiplying the oil concentration (i.e. 4g/100g in this case) by Avogadro's number (i.e. 6.022×10^{23} molecules/mole). To express this result in terms

of the number of oil molecules per one gram of dry soil (molecules/g), it is divided by the molecular weight of the oil residue (i.e. 900 g/mole). Thus, the presence of 4% oil residue in the soils results in about 0.2676×10^{20} oil molecules per one gram of dry soil. Finally, the oil surface coverage can be determined by multiplying the number of the oil molecules by the molecular surface area of the oil divided by the surface area of the soil.

Based on such calculations, the addition of 4% oil residue to the tested dried soils resulted in a surface coverage of about 1.75 layers of oil molecules (i.e. 3 nm) for the Muharraq soil, 1.5 layers of oil molecules (i.e. 2.5 nm) for the Sanad soil, and 1 layer of oil molecule (i.e. 1.7 nm) for the washed Sanad soil. From these estimates, it was projected that 4% of oil residue was initially sufficient to cover the entire surface of the tested soils, and thus provide the desirable strength improvements. However, an increase in the oil residue content beyond 4% (w/w) will most likely yield an excess in the presence of oil residue in these soils, as explained above and noted previously in the section on strength performance (Section 4.1).

In a similar manner, the soil surface coverage attained by the addition of water to the soils can also be estimated. Based on the assumptions that (a) water has a molecular surface area of 10.8×10^{-20} m^2 (Livingston, 1991), (b) water is sorbed uniformly over the soil surface, and (c) 10% water content is present in the tested soils, it is estimated that the surfaces of the tested soils are covered by approximately 10 layers of water molecules (i.e. 3 nm). The presence of these 10 layers of water molecules prior to oil residue addition will certainly interfere with the direct interaction between the oil residue and soil surfaces, resulting in a significant reduction in the strength performance indicated in Section 4.1.1. The substantial presence of water in these soils, together with the high competition of the water molecules (0.3 nm) to be adsorbed by the soil surfaces as compared to the oil molecules (1.7 nm) are likely responsible for such an interference (Yaron, 1989).

4.3 Rheological Performance (Viscosity)

Since the field temperature in Bahrain (i.e. between 20 and 40°C) is higher than the laboratory temperature (22°C), where most of the samples are tested, it is important to take into account the contribution of temperature. The increase in temperature is expected to alter the strength performance of the stabilized soils, due to its effect in speeding the natural processes and influencing the properties of both oil and soil. The overall effect of temperature is summarized in Section 6.4.1. However, the effect of temperature on one of the major properties of the oil residue, i.e. viscosity, is discussed herein. Viscosity of oil is very sensitive to temperature and is indirectly representative of the influence of temperature on the strength performance of the stabilized soils.

The experimental results of the rheological behavior of oil residue are shown in Figures 4.14a and 4.14b, respectively. As can be seen in Figure 4.14a, all curves exhibit a linear shear stress-shear rate relationship at the tested temperatures. This indicates that the oil residue behaves as a Newtonian fluid at these temperatures, i.e the viscosity is independent of the shear rate. The viscosity of oil residue is determined from the slope of the straight lines.

The variation of dynamic viscosity for the duplicate oil residue samples with temperature is shown in Figure 4.14b. The dynamic viscosity of the oil is observed to exhibit a nonlinear relationship with temperature, and its susceptibility appears to be greater in the lower temperature regions. A substantial decrease in the viscosity of oil residue is noted with an increase in the temperature. The viscosity of oil residue reduces by about 15 times as its temperature increases from 22°C to 50°C. This same trend was recorded from other studies conducted on the effect of temperature on the rheological properties of asphalt (Goodrich, 1991; Garrick, 1992). The molecular chain concept can be used to explain the change in its physical behavior with temperature. Oil residue is composed of a long molecular chain structure. At higher temperatures, the strength of the molecular chain reduces and its structure becomes easily mobilized, resulting in a viscosity reduction (Howeedy and Herrin, 1972). The reduction in oil viscosity has an immediate effect on enhancing the distribution, binding, and curing processes of oil in soils, resulting in an increase in the strength performance of the stabilized soils (Dunn

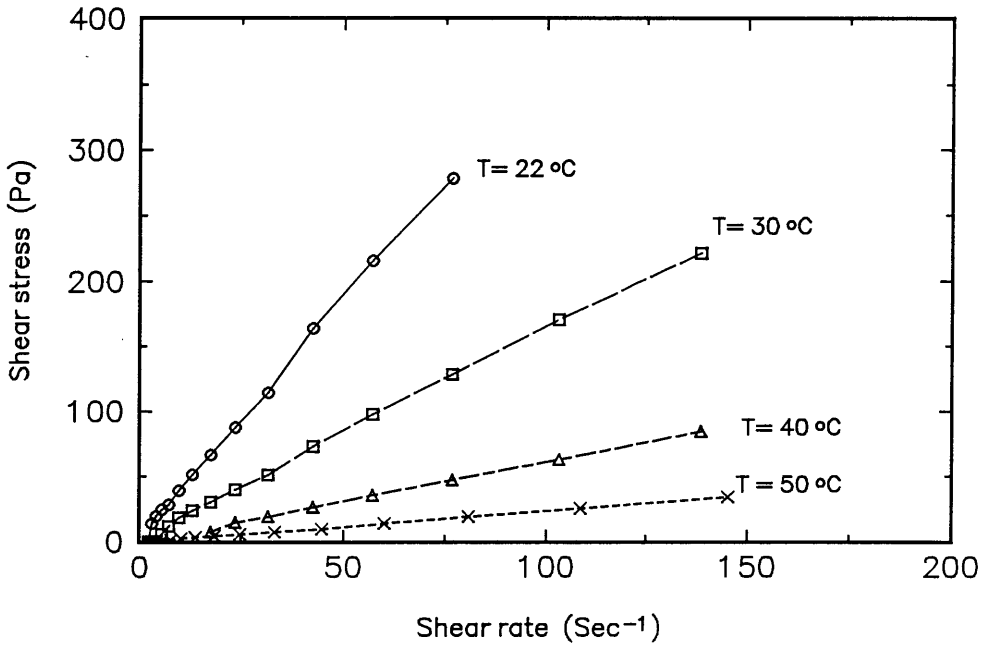


Figure 4.14a - Shear stress-shear rate relation for oil residue at different temperatures.

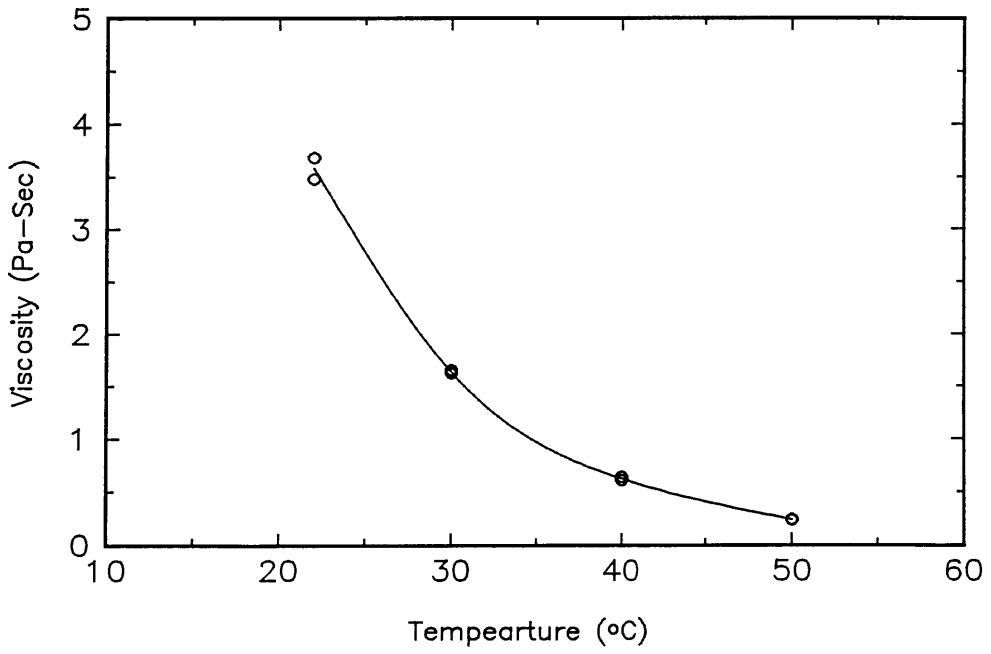


Figure 4.14b - Variation of viscosity of oil residue with temperature.

and Salem, 1973).

In order to complete the rheological study, the rheological performance of the soil-oil mixtures was considered. The results of this study are presented in Figure 4.15, which shows the influence of oil residue content on the overall rheological performance of the soil-oil mixtures in a water suspension system. This figure shows the shear stress versus shear rate curves for the tested suspensions of soil-oil mixtures in distilled water at 10% (w/w) solids concentration. The suspension samples also show Newtonian rheological behaviors. All the suspension samples appear to possess zero yield stress, i.e. the shear stress at zero shear rate. The viscosity of a liquid-solid suspension is commonly expressed at infinite shear rate (η_∞) using Casson's equation described by Solomon and Hawthorne (1983):

$$\tau^{1/2} = \eta_\infty^{1/2} D^{1/2}$$

in which τ is the shear stress and D is the shear rate. The tested suspensions are observed to have insignificant changes in their viscosities with an increase in oil residue content in the soil-oil mixture. For example, the viscosity of the suspension of these mixtures increases from 1.1 to 1.4 centipoises (mPa-Sec) as the oil residue content in the mixture increases from 0% to 12% (w/w). This is mainly attributed to the low presence of oil in the tested suspensions, i.e. the content of oil in the suspensions varies from 0% to 1.2% (w/w). However, if the concentration of oil present in the soil suspension systems are greater than the selected range (i.e. 0-1.2 (w/w)), large variations in their viscosity range are expected. Despite the small variation in the viscosity of the tested suspensions with oil concentration, their trends are relatively consistent. As expected, a slight increase in the viscosity of the suspension is recorded as the oil concentration increases.

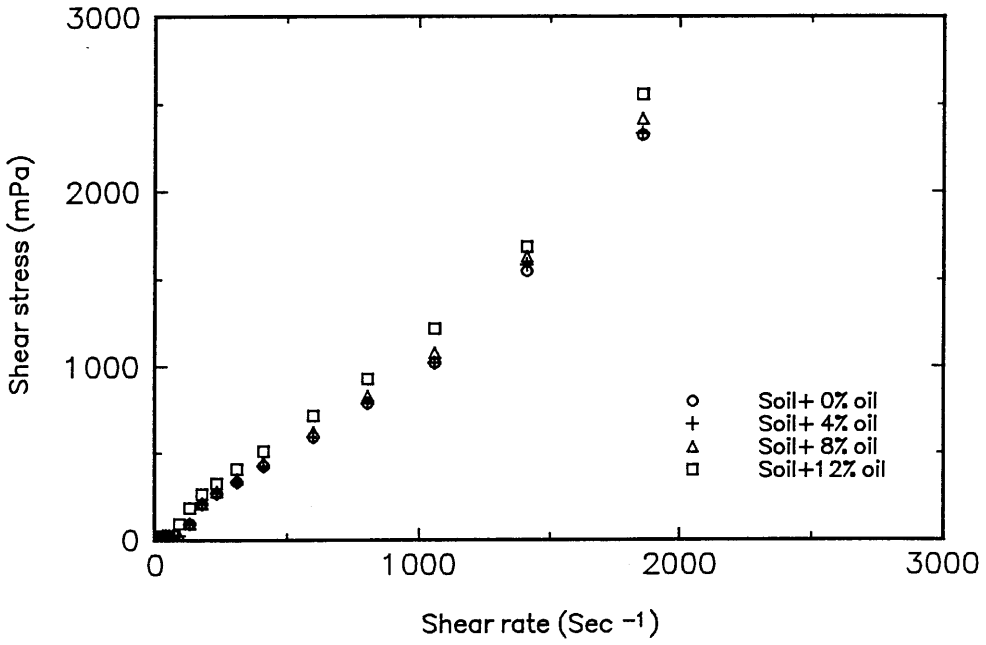


Figure 4.15 - Shear stress versus shear rate relations for suspensions of soil-oil mixtures from the Sanad soil.

4.4 Stabilization Mechanisms

Stabilization of soils with oil residue consists of two major mechanisms. The first one primarily involves bonding processes resulting from adhesion between oil residue and soil surfaces. This mechanism leads to an increase in cohesive strength, especially in cohesionless soils, thereby improving the mechanical properties of soils. The second mechanism is expected to enhance "waterproofing" properties of the stabilized soils.

Stabilization with oil residue appears to strongly affect the shear strength components of the tested soils, primarily the cohesion (physico-chemical component) and to a lesser extent the friction (physical component). The cohesive component significantly increases in the presence of oil residue. This is mainly due to an increase in the overall interparticle bondings of the oil-soil-water systems. In addition, the alteration in the soil structure and variation of the interparticle forces, associated with the presence of oil, can be responsible for such behavior.

Results from the unconfined compression tests suggest that small percentages of oil residue impart cohesion without preventing direct particle to particle contacts. As the proportion of oil residue increases, the area of shearing through oil residue increases and consequently reduces the mobilized frictional resistance. When the content of oil residue exceeds the optimum, the oil residue acts as a lubricant separating soil particles. For a content of oil residue less than the optimum, the increase in cohesive strength is greater than the decrease in the mobilized shearing resistance, resulting in an increase in the shear strength of the soil (Dunn and Salem, 1971). From the unconfined compressive strengths (Figures 4.4 to 4.6), it appears that 4% oil residue content (by dry weight of soil) is the optimum for maximum strength performance.

However, the frictional component of the tested soils is found to be slightly reduced in the presence of oil residue . This is most likely attributed to a reduction in the resistance to sliding and interlocking of soil particles in the presence of oil, as revealed by the results of the direct shear tests (Figure 4.8 and 4.9). Nevertheless, these results have shown that the increase in the cohesion strength is much higher than the reduction in the angle of friction, in the presence of 4% oil residue, resulting in a significant increase in the total shear strength of the stabilized soils.

In the second mechanism, the "waterproofing" property is expected to reduce salt attacks on bases and sub-bases of highways (to be examined later in Section 6.2.1 on leaching). Waterproofing preserves the natural stability of these soils, especially during the rainy season. In soil-oil mixtures, oil residue tends to coat the soil in small aggregates or clods, thereby plugging voids and acting as a "waterproofer" (Ola, 1978).

Whereas the geotechnical aspects of the stabilized soils have been determined in this chapter, the nature of interaction and the bonding between the soil surfaces and oil residue to produce strength improvement is covered in Section 5.1.2. Other characteristics such as fluid retention capability and oil leachability potential, which also influence the geotechnical behavior of the stabilized soils, are addressed in further chapters (5.1.3 and 6.2).

4.5 Construction Methods

Taking into account the results of the compressive strength tests discussed in the previous section, the best results in the field would probably be achieved with the tested soils by the addition of 4% of the oil residue prior to water addition and compacting the mixtures at their maximum dry densities. This would give a mixture having optimum compaction and strength characteristics.

To accomplish in-situ stabilization, the soil should first be prepared by excavating and breaking up the soil particles until a smooth surface is obtained. The oil residue is then applied to the soil, preferably using a mix-in-place method. In this method, oil residue and water (if necessary) are sprayed on the soil surface through spraying bars attached to a mix-in-place equipment. This equipment comprises a rotating shaft carrying mixing blades (Herrin et al., 1968).

Viscosity of oil residue during its application to the soil is an important factor for a proper distribution and binding of the binder. It is recommended that the viscosity of oil should be within the range of 1 to 2 stokes at 50°C in order to achieve an adequate binding condition (Ingles and Metcalf, 1973; Rico Rodriguez et al., 1988). The oil residue used in this study has a viscosity of 2.5 stokes at 50°C, which is sufficient to

meet the above criteria. When the oil is added to the field soil, the soil and oil residue should be mixed thoroughly, aerated if necessary, adequately compacted, and allowed to cure.

Uniform spreading of the oil residue and water on the surface is a critical factor in the success of the stabilization process. For example, in order to ensure a uniform spreading for this particular case, it is preferable to apply oil residue and water in two or three equal distributions totalling about 3.5 L/m^2 and 10 L/m^2, respectively. At this application rate, the applied fluids can penetrate about 50 mm into the soil. The above estimates are based on data obtained from the Sanad soil which includes: (1) maximum dry density of 1.78 Mg/m^3; (2) moisture content of 14%; (3) oil residue of 4% by weight; and (4) oil density 0.97 Mg/m^3. Moreover, to assist in obtaining the highest possible stability in the field, the stabilization process should be performed in layers of approximately 50 to 75 mm thickness. The desired conditions (e.g. maximum dry density and optimum moisture content) must be achieved for each layer (Kezdi, 1979; Hausmann, 1990).

Where time is not a factor, the most effective application time of oil residue to dry saline soil, as in Bahrain, is after the rainy season. Otherwise, in-situ soil washing techniques are sometimes recommended. In-situ washing can be conducted by laying out pits, dug into the ground soil surface, and filling them with water, thus establishing downward water movement through the soil. This can be an effective procedure in removing excess soluble salts from soils and thus enhancing adsorption of oil residue onto soils (Nash and Traver, 1989)

Climatic condition strongly affects the construction performance of the stabilized soil. An ideal condition is hot and dry weather with very low possibility of rain. Therefore, the weather in Bahrain is anticipated to provide a good environmental condition for the application of oil residue (Al-Balbissi, 1989).

CHAPTER 5
RESULTS AND DISCUSSION
- GEOCHEMICAL ASPECTS -

5.1 Soil-oil Interactions

From the preceding chapter, a significant improvement in the mechanical properties of the tested soils, particularly the cohesive component of the shear strength, was observed in the presence of 4% oil residue by weight. In order to assess the nature of interaction between the oil residue and soil surfaces, and type of interparticle bondings and forces to produce such an improvement, various infrared tests and soil suction tests were performed and their results presented herein. The infrared results demonstrate the contribution of the interparticle bondings involved between the interactive surfaces. The soil suction results present the energy status of the stabilized system as a whole.

5.1.1 Surface Charges

The surface charges of interactive compounds can affect the interaction mechanisms, as well as the sorption capacity of their surfaces. The distribution of the surface charges of a compound depends mainly on its ionization potential (expressed in terms of pK value, i.e. the pH value at which functional groups of the compound dissociate), its electron transfer capability (i.e. the potential to accept or donate an electron from the surface), and its iso-electric point (IEP, i.e. the pH value at which surface negative charges equal to positive charges).

Emphasis on the contribution of the IEP concept during interaction will be considered herein. The contribution of the IEP can be simplified as follows: if the pH value of the soil pore fluid media is higher than the IEP of the compound surface, then the surface will possess a net negative charge and thereby will be characterized as an anionic surface. However, the same compound can possess a cationic active surface if the soil pH becomes lower than the IEP of the compound. A summary of some of the conclusions reached in previous studies in relation to the properties of the tested soils and

oil residue are presented below.

The IEP of the soils used in this study is reflected by the IEP values of their constituents, i.e. feldspar and clays (IEP < 4) and carbonate (e.g. calcite and dolomite have an IEP > 8). These constituents are known to possess constant surface charges, i.e. surface charges independent of pH variation, with the exception of carbonate. The presence of high carbonate content in these soils enhance their acid buffering capacities and thus reduce their sensitivity to pH variation (Stumm, 1992). In addition, the presence of small contents of active constituents such as clays and amorphous materials in these soils contributes to their low surface activity potential. Since pH values of most of the natural soils in Bahrain lie in a relatively narrow pH range of 7 and 8.5, the effect of soil pH on the distribution of the surface charges is expected to be insignificant (see Table 3.1). Further, the electron-transfer mechanisms are expected to be limited in these soils due to their low contents of clays. If such mechanisms take place under appropriate conditions, the soil would most likely possess an electron accepter capability (Balogh and Laszlo, 1993).

The IEP of the oil residue is representative of the IEP values of its components, i.e. polycyclic aromatic hydrocarbons (neutral compound), high molecular saturated hydrocarbon (low sensitivity to pH) (Senesi and Chen, 1989), resin (i.e. dominated by positive surface charges with low dependent on pH value), and asphaltene (i.e. dominated by negative surface charges with high dependence on pH value) (Neumann, 1981). The influence of pH on the distribution of surface charges of the oil components are represented within the natural soil pH range (i.e. 5 to 8). Moreover, the iso-electric point of a hydrocarbon oil group measured in terms of its electrokinetic mobility, as reported by Stumm (1992), was found to be relatively low (about 2). The presence of methyl alkanes and activated aromatic rings in the oil residue creates the potential for oil residue to possess an electron donor capability under certain conditions, i.e. pH and temperature (Senesi and Chen, 1989). Due to the presence of a wide range of hydrocarbon groups in the oil residue, its pK value is difficult to estimate. Since oil residue possesses a low water solubility (about 10 ppm), complex molecular structure, and high molecular weight (about 900 g/mole), the potential for such a compound to dissociate in the soil pore fluid is expected to be low. A study by Siffert et al. (1990)

has shown that asphalt and asphaltene particles are slightly charged and possess very low surface charge variation in suspensions at pH of the natural environment. Consequently, soil pH is expected to have little influence on oil dissociation and thus the variation of surface charges of the oil within the natural soil pH is expected to be insignificant.

This reveals that both the tested soils and oil residue are expected to be less sensitive to the variation of soil pH in Bahrain. Therefore, it is expected that their mixtures would possess similar behavior. In addition, the presence of the oil residue in the stabilized soils is expected to satisfy most of the charges on the soil surfaces, as will be explained in Section 5.1.2 on interaction mechanisms. When the soil surface charges are satisfied, they can be relatively stable even during pH changes, but long-term weathering may affect the soil surface stability. In general, the presence of most organic compounds in soils will most likely reduce the IEP of the soils (Robert and Terce, 1989). In turn, one would expect that the presence of oil residue in soils will likely reduces their IEP.

5.1.2 Interaction Mechanisms

The change in the mechanical properties of the tested soils in the presence of oil residue is partially reflected by alterations in the soil surface activity. This change is mainly due to interaction between the oil residue and soil surfaces which results in the formation of interparticle bonds. These bonds are one of the major reasons for the increase in cohesive properties of the tested soils. In addition, the type and strength of these formed bonds will be primarily responsible for the oil retention capability in these soils, which will be discussed in Section 6.1.

The type of active groups present on the surfaces of the tested soils and oil residue, together with the nature of interaction and type of bonding between them, are presented herein.

5.1.2.a *Infrared Spectra*

To obtain a better understanding of the structures of the interacting surfaces and the nature of interaction between them, infrared spectra of the oil, soils and their mixtures were analyzed. The infrared spectra of the oil residue, three tested soils, and

their mixtures with 4% oil residue, by weight, before and after the leaching process are shown in Figures 5.1 and 5.2. Figure 5.1 shows the infrared spectrum for the oil residue, whereas Figure 5.2 portrays the infrared spectra for the tested soils (the Sanad soil, the washed Sanad soil, and the Muharraq soil). Each reported infrared spectrum represents a composite of multiple scans. The corresponding main assignments of various frequency peaks present in the oil residue and soils are summarized in Tables 5.1 and 5.2 (White and Roth, 1986; Yong, et al., 1994).

The major vibrational frequencies present in the oil are associated with the alkyl C-H group, aromatic C-H and C=C groups, and the carbonyl group. The dominant frequencies found in the soils are tentatively assigned to the hydroxyl groups (silicate and water), the carbonate group, and the silanol and siloxane groups. Only the silt and clay fractions, accounting for about 30% to 40% of the total weight of the soil, were analyzed here. The interactive behavior of the remaining fraction of the soils (sand) with oil residue is relatively low and expected to be dominated by surface tension (Yaron, 1989).

5.1.2.b *Bonding Mechanisms*

When soil interacts with oil, the vibrational frequencies of the mixture are expected to differ from that of the oil-free soil. The changes in both the intensity and position of the frequency peaks reflect the general trend of interaction. The extent of the shifts of the frequencies is directly related to the strength of the formed bonds between the interactive surfaces. Higher shifts toward higher frequencies indicate the formation of strong bonds, whereas smaller shifts in the frequencies are interpreted in terms of simple Van der Waal's attractions (Theng, 1974 ; Kiselev and Lygin, 1975).

Since the oil residue consists of large molecules with long chain lengths, it is expected that the primary mode of interaction will be via Van der Waal's attractive forces. In addition, as the number of contact points between the oil residue and soil particle surfaces increase, significant binding interactions of alkyl groups (oil) with surface oxygens or hydroxyls (silicate or adsorbed water) and exchangeable cations also occur (Theng, 1974; Clementz, 1976; Yong, et al., 1992). These interactions are observed in the infrared spectra for the Sanad soil and its mixture with oil, as shown in Figure 5.3. Due to the similarities in the structures of the surfaces of the three tested

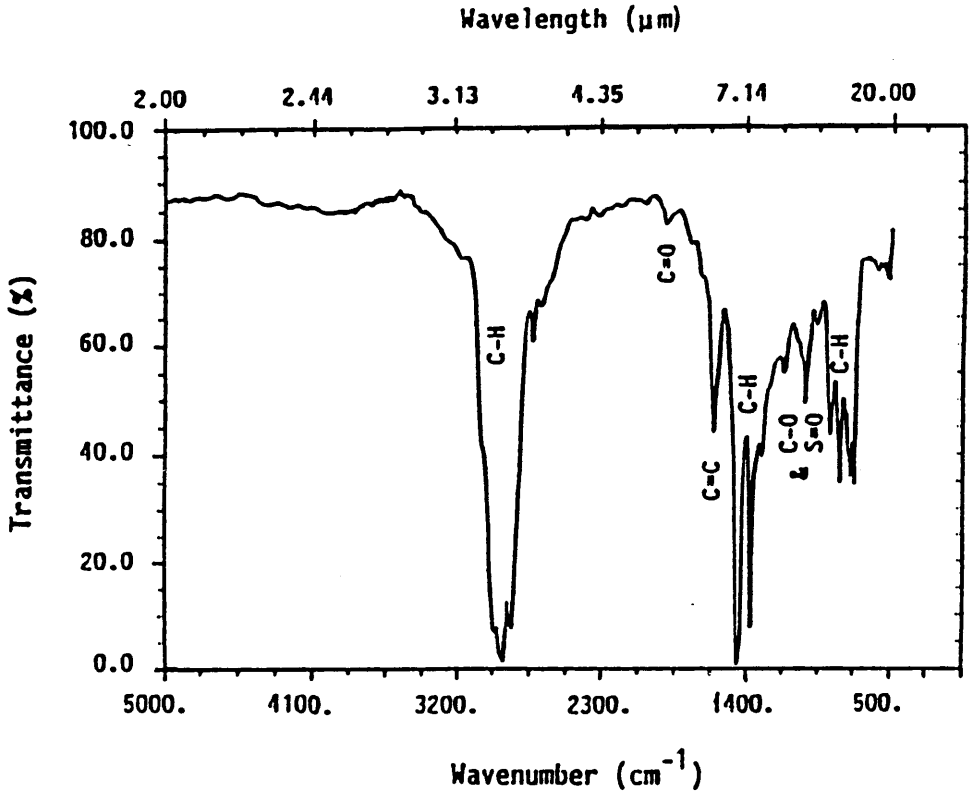


Figure 5.1 - Infrared spectrum of the tested oil residue.

Table 5.1 - Characteristic infrared absorption frequencies present in the tested oil residue.

Wavenumber (cm^{-1})	Intensity	Peak Assignment
2850-2960	Very Strong	C-H stretch
2960		methyl group (CH_3)
2930		methylene group (CH_2)
2860		CH_2 & CH_3
2710	Weak	C-H stretch (aldehyde)
1700	Very Weak	C=O stretch (aldehyde & ketone groups)
1600	Strong	C=C stretch (aromatic) & some C=O stretch
1380-1460	Very Strong	C-H bending
1460		methyl (asymmetric)
1380		methyl (symmetric)
1030	Weak (sharp)	C-O stretch & some S=O stretch
730- 860	Strong	C-H (aromatic)
860,810,740		out of plane bending

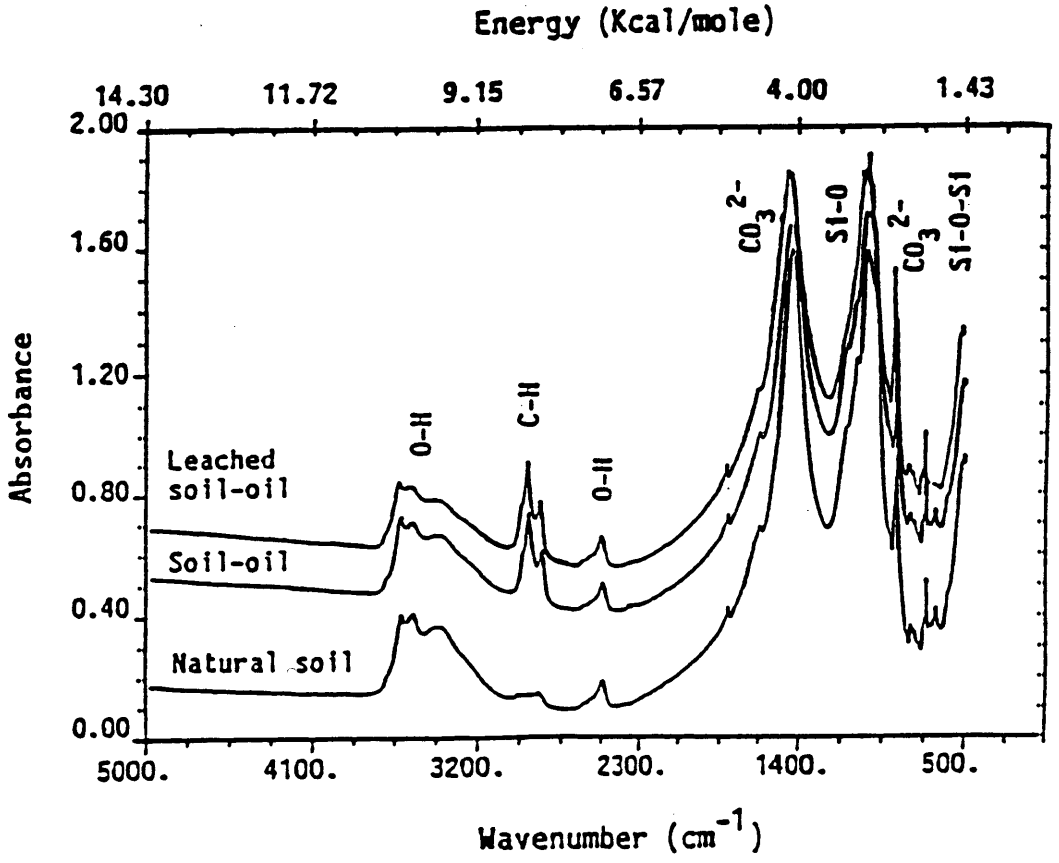


Figure 5.2a - Infrared spectra of silt and clay fractions of the Sanad soil and its mixture with 4% oil residue before and after leaching in distilled water.

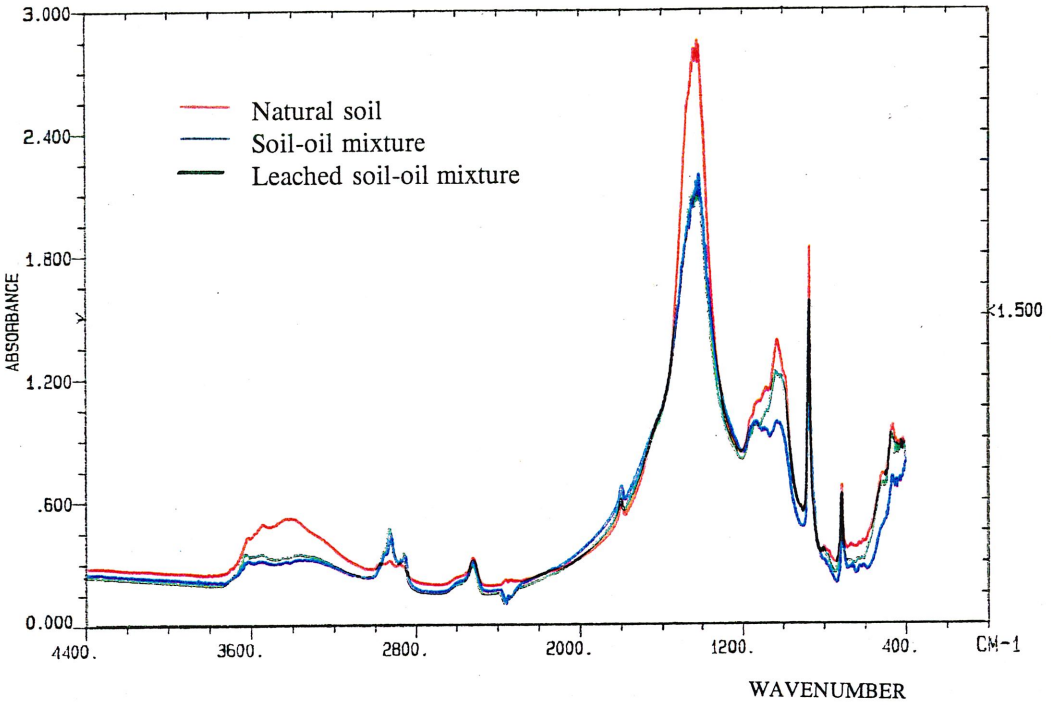


Figure 5.2b - Infrared spectra of silt and clay fractions of the washed Sanad soil and its mixture with 4% oil residue.

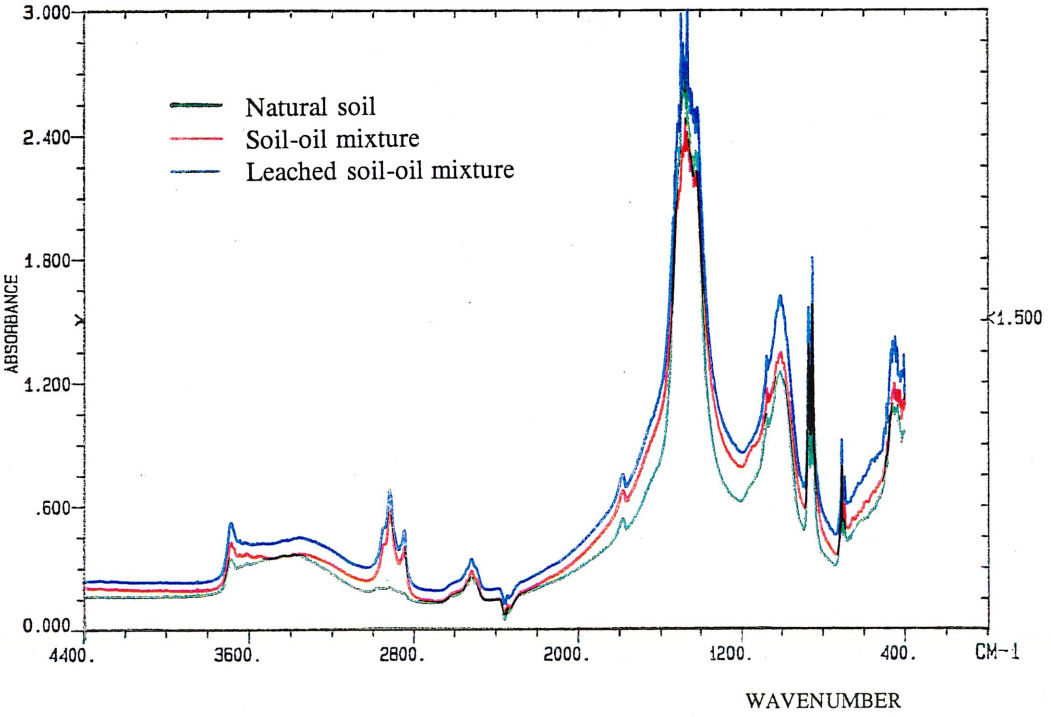


Figure 5.2c - Infrared spectra of silt and clay fractions of the Muharraq soil and its mixture with 4% oil residue.

Table 5.2 - Characteristic infrared absorption frequencies found in silt and clay fractions of the tested soils.

Samples/ Wavenumber (cm^{-1})			Intensity	Peak Assignment	Frequency Range (cm^{-1})[1]
Sanad/ Natural	Sanad/ Washed	Muharraq/ Natural			
3620	3617	3690	Weak	Silicate O-H stretch	3540- 3700
3550	3548	...	Weak	Silicate O-H stretch	3540- 3700
3410	3405	3430	Broad	Water O-H stretch	3350- 3480
2522	2519	2523	Weak	Water O-D stretch	2500- 2700
1443	1442	1477	Strong	CO_3^{2-} stretch	1490- 1410
1027	1030	1024	Strong	Si-O stretch	1100- 900
874	874	875	Sharp	CO_3^{2-} bend	875- 860
803	804	...	Very weak	Si-O-Si stretch	800- 600
713	713	713	Weak (sharp)	CO_3^{2-} bend	750- 680
661	...	...	Very weak	SO_4^{2-} bend	680- 580
469	470	456	Broad	Si-O-Si bend	540- 430

[1] Frequency range based on data obtained from White and Roth (1986).

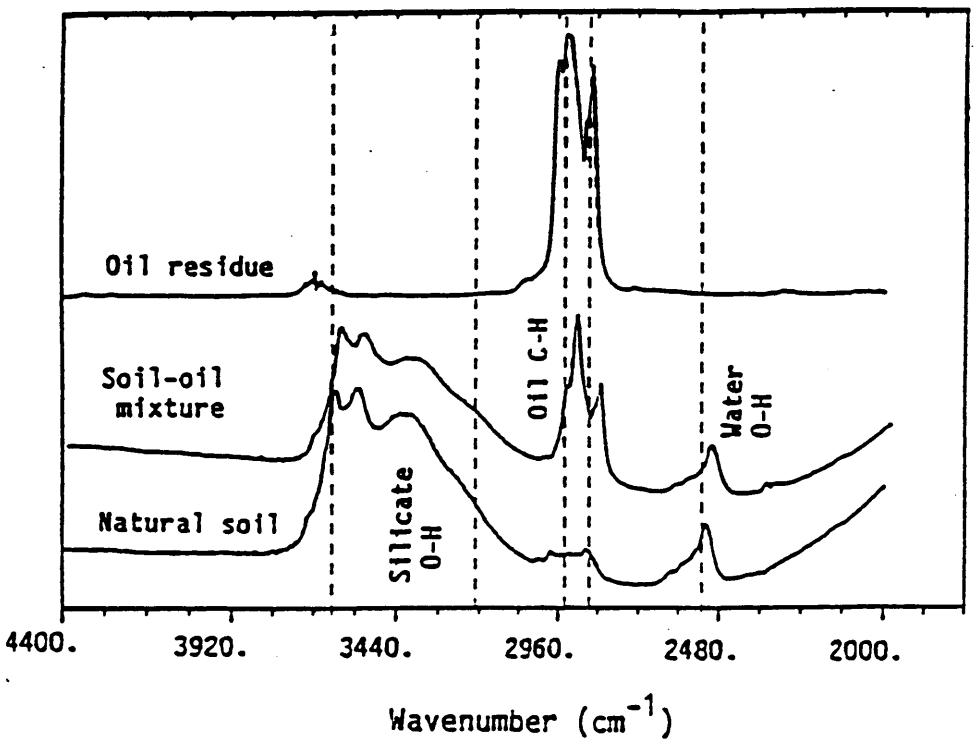


Figure 5.3 - Infrared spectra of oil residue, the Sanad soil and its mixture with 4% oil residue.

soils revealed by the infrared analyses, discussion of the interaction mechanisms will be limited to the Sanad soil.

The adsorbed oil on the soil particle surfaces is characterized by the appearance of C-H stretching (alkyl group) at three different frequencies: 2853, 2924 and 2953 cm^{-1}, in the mixture spectrum (Figure 5.3). This observation suggests the occurrence of an intercalation phenomenon, i.e. penetration of oil into the interlayer spacing of the silica and alumina sheets. The alkyl C-H bands are shifted to lower frequencies (-7 cm^{-1} shift) in the mixture, as compared to their frequencies in the oil, in all likelihood due to the formation of weak hydrogen bonding between the hydrogens of the C-H group and the oxygens or the hydroxyls of the silicate layer. Intercalation of oil leads to reduction in both frequency and energy of the new bond and hence an increase in the interlayer spacing of the tested soils (Vansat and Uytterhoeven, 1973; Gibbons and Soundararajan, 1988; Gibbons and Soundararajan, 1989). This postulate is supported by previous studies conducted on interaction of different hydrocarbon groups with soil surfaces which are summarized by Theng (1974).

A wide absorption band present in the region between 3200 and 3620 cm^{-1} is attributed to the hydroxyl groups. The small frequency peaks or shoulder at 3620 and 3550 cm^{-1} are assigned to O-H stretching (hydroxyls within the silicate structure), and the shift in the hydroxyl group of the mixture to lower frequency (-5 cm^{-1} shift) is due to weak hydrogen bonding between the hydroxyls of the silicate layer and alkyls or carbonyls of the oil. The lower shift in the frequency of the hydroxyl group indicates that the newly formed bonds have lower energy than the original bond.

Soil-oil interactions were examined in a dry state, where the samples are expected to retain very low moisture content ($< 2\%$). The adsorbed water on the soil particle surfaces is identified by the presence of O-H stretching (hydroxyl group) which appears as a broad frequency peak centred at 3410 cm^{-1} of the natural soil. This frequency peak undergoes a slight reduction (-5 cm^{-1}) in the mixture spectrum as compared to the natural soil spectrum. One attributes this to water hydroxyls interacting with either oxygens of the silicate layers or oil carbonyls through hydrogen bonding. Water bridging between the silicate surface and either the oil or calcite surfaces is a likely possibility, as is cation bridging because of the presence of exchangeable cations in the soil system. Surface

tension is another bond that is also produced due to water bridging.

The small frequency peak appears at 2522 cm^{-1} of the natural soil spectrum, which corresponds to heavy water (O-D group), shifted to 2516 cm^{-1} in the mixture spectrum. This indicates that the heavy water (D_2O, deuterium oxide) is involved in bridging the interactive surfaces. The appearance of the O-D group (where D is twice the mass of ordinary hydrogen) is associated with the hydration of some of the hydroxyls present at high frequency peaks (i.e. in the range of 3390-3620 cm^{-1}) due to heating. In this case, samples were heated at 60°C for a few hours prior to the preparation of the pellets. During the heating process, part of the O-H group shifted to lower frequencies, thus resulting in the O-D group. Heating the samples at a low temperature prior to the preparation of the pellets is recommended by a number of researchers (Newman, 1987; Rausell-Colom and Serratosa, 1987). This is because the presence of moisture in the samples during testing has a potential to interfere with the infrared spectra.

The small shift observed in the frequency assigned to the silanol group, from 1027 cm^{-1} in the mixture to 1024 cm^{-1} in the soil, can be due to the fact that oxygens in the silica sheet interact weakly with the hydrogen from the alkyl or hydroxyl groups. The small shifts in most of the frequencies indicate that Van der Waal's attractions are dominant (Clementz, 1976; Gibbons and Soundararajan, 1989). Further, a comparison of the infrared spectra of the soil-oil mixture before and after leaching shows insignificant changes in the frequency peak shifts and absorbances, indicating thereby that most of the adsorbed oil is still bound to the soil surfaces. This is one of the main reasons for the substantial increase in the leached stabilized samples as compared to identical leached natural samples, which is observed in the strength results of Section 4.1.1.d. The contribution of other reasons responsible for such behavior (i.e. soil structure and interparticle forces) will be discussed in the next section (Section 5.1.3).

Since all samples were prepared in thin films containing 3 mg solids per cm^2, the intensity of the observed peaks is applicable for comparison. A comparison of the intensity of the absorbance peaks present in the soil-oil mixture spectrum with the corresponding peaks present in the soil spectrum shows a slight reduction in the intensity of some of the mixture peaks. The absorbance peaks present at 1027 cm^{-1} (silanol), 1443 cm^{-1} (carbonate), and in the range of 3200 - 3620 cm^{-1} (hydroxyls) were slightly

weakened in the mixture spectrum. This is most likely attributed to a direct association between these groups and oil residue.

In summary, the major types of bonding mechanisms between oil and soil surfaces include: Van der Waal's attraction (VW), weak hydrogen bonding (WHB), and water and cation bridging (WB and CB, respectively). A schematic representation of the interactive mechanisms involved in soil-oil mixtures is illustrated in Figure 5.4. Since the extent of the shifts in most of the frequency peaks present in the soil-oil mixtures spectrum are relatively small in comparison with their corresponding individual spectrum, i.e. the soil or the oil residue, the formed bonds are characterized to be relatively weak. Weak bonds are found to be less sensitive to temperature variation (Jury, 1986a).

The infrared spectra of the oil-soil mixtures from the Sanad soil are shown in Figure 5.5a, for natural soil, and Figure 5.5b, for washed soil, as a function of oil content between 0% and 12% by weight. As can be seen from these two figures, a slight increase in the intensity of C-H group peaks was observed as the content of oil increases, indicative of the increase in the presence of oil. Due to lack of shifts in most of the absorption peaks as the oil content increases, insignificant changes in the bonding strength of C-H groups and the oxygens or the hydroxyls of the silicate layers are expected with an increase in oil content. However, there is a slight decrease in the intensity of silanol, carbonate, and hydroxyl groups in the presence of oil, presumably caused by the association of these groups with the oil. This in turn leads to an increase in the interlayer spacing with the increase of the percentage of oil added. The insignificant changes in the strength of the formed bonds together with the increase in the interlayer spacing with the increase in oil content can also be responsible for the reduction in the mechanical properties of these soils at high oil residue content. These results show a close agreement with the unconfined compression results obtained in Section 4.1.1.b.

A comparison of the infrared spectra of the soil-oil mixture for natural and washed soils shows insignificant changes in the frequency peak shifts, indicating similar interaction strength. However, the absorption peaks were observed to be less intense in the soil-oil mixture of the washed samples as compared to the corresponding peaks of the natural samples, probably due to higher adsorption of oil onto the surfaces of the washed

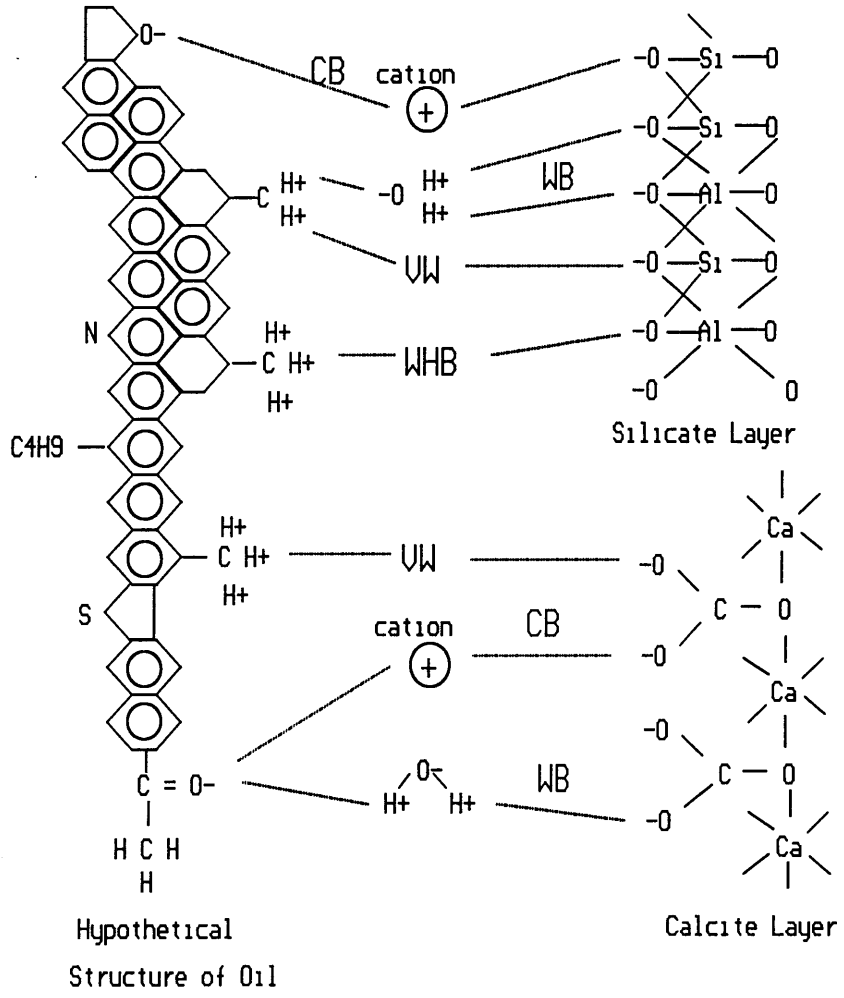


Figure 5.4 - Interaction mechanisms between oil residue and soil surfaces. Oxygens in silicate layer can be replaced with hydroxyls. VW, van der Waal's attraction; WHB, weak hydrogen bonding, WB, water bridging; CB, cation bridging.

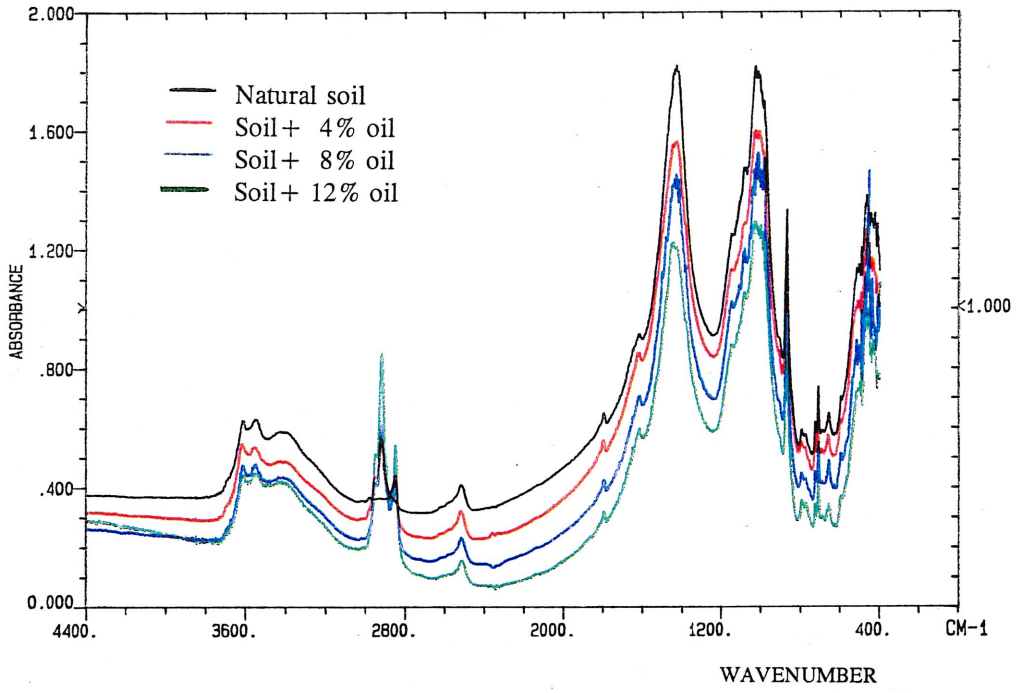


Figure 5.5a - Infrared spectra of silt and clay fractions of the Sanad soil and its mixture with various oil residue contents.

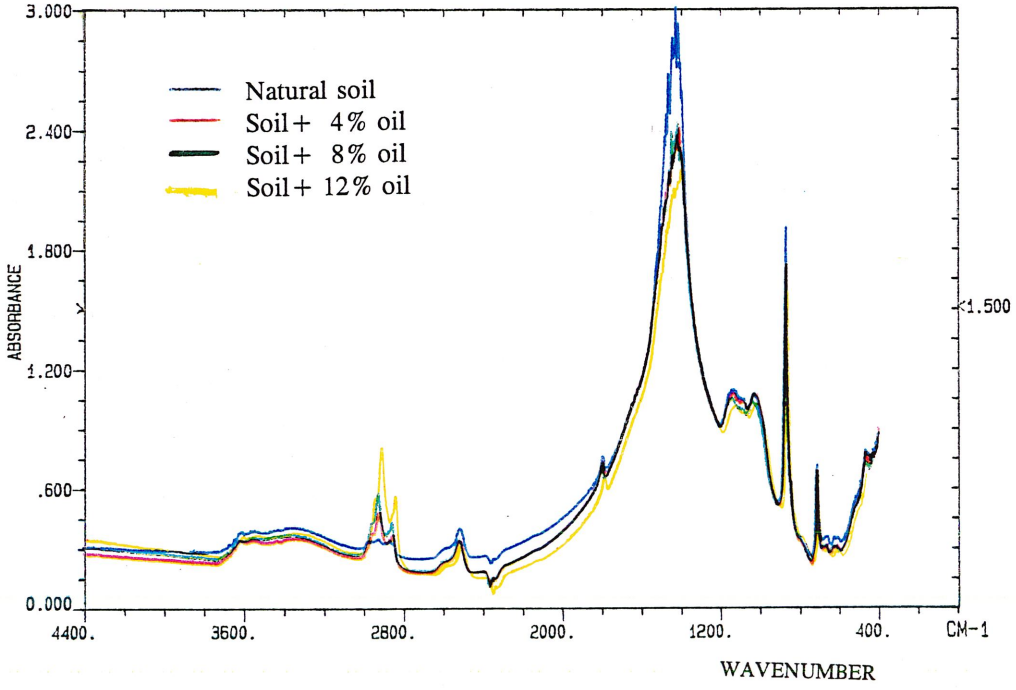


Figure 5.5b - Infrared spectra of silt and clay fractions of the washed Sanad soil and its mixture with various oil residue contents.

samples. This is consistent with the observation that the reduction in ionic strength (electrolytes) of the washed soil increases the surface area by about 50% and thus is expected to increase the absorptive potential of the washed soil (see Table 3.1). The increase in the number of contacts (i.e. bonds) between the interactive surfaces, as in the case of the washed soil, will certainly increase the overall strength performance of the stabilized system (Mitchell, 1993). Therefore, if both washed and unwashed stabilized samples are tested under identical conditions, the washed sample will most likely possess higher strength performance than the unwashed one.

5.1.3 Fluid Retention (Soil Suction)

A soil suction test, measuring fluid retention capability in the soils (soil-fluid characteristic), was conducted to assess the strength of overall bonding between soil surfaces and both water and oil. In contrast with the infrared test, which represents mode of interaction in terms of single bonding between interactive groups, the soil suction test portrays the bonding involved in the stabilized system as a whole. The strength of the overall bonding can be expressed in terms of the internal potential energy of the oil-soil-water system. In these tests, the potential is measured using pF, where pF = log to base 10 of pressure expressed as cms. of water. pF can be expressed in terms of energy units; for example, pF 1, pF 2, and pF 3 are approximately equal to 1 joule/Kg, 10 joules/Kg, and 100 joules/Kg, respectively. The results of the tests illustrate the variation of moisture content with soil suction in two cycles, both in the desorption and absorption processes of the soil suction test.

For purposes of comparison, all the samples tested herein were prepared under the same conditions (i.e. dry density, water content, and oil content) as the set of samples used in the geotechnical testing (Section 4.1). Values of dry density, water content, and oil content, as well as soil condition (e.g. leached, washed, or stabilized) during testing are indicated on the figures. The moisture content of all samples are seen to drop significantly at a suction range from pF 1 to pF 1.5 -- indicative of air-entry into the test samples. Moreover, it is interesting to note that the liquid limit of the tested soils lies at a suction of about pF 1 and the plastic limit between pF 2 and pF 2.5.

Soil fluid characteristics are shown in Figures 5.6, 5.7, and 5.8, for the Sanad

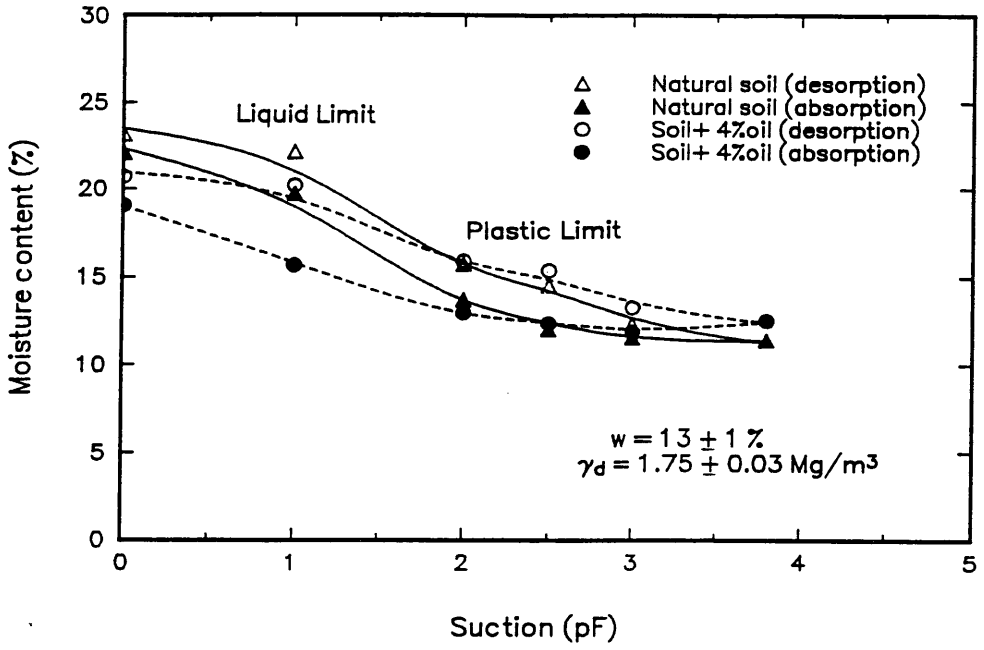


Figure 5.6a - Fluid retention curves for the Sanad soil samples.

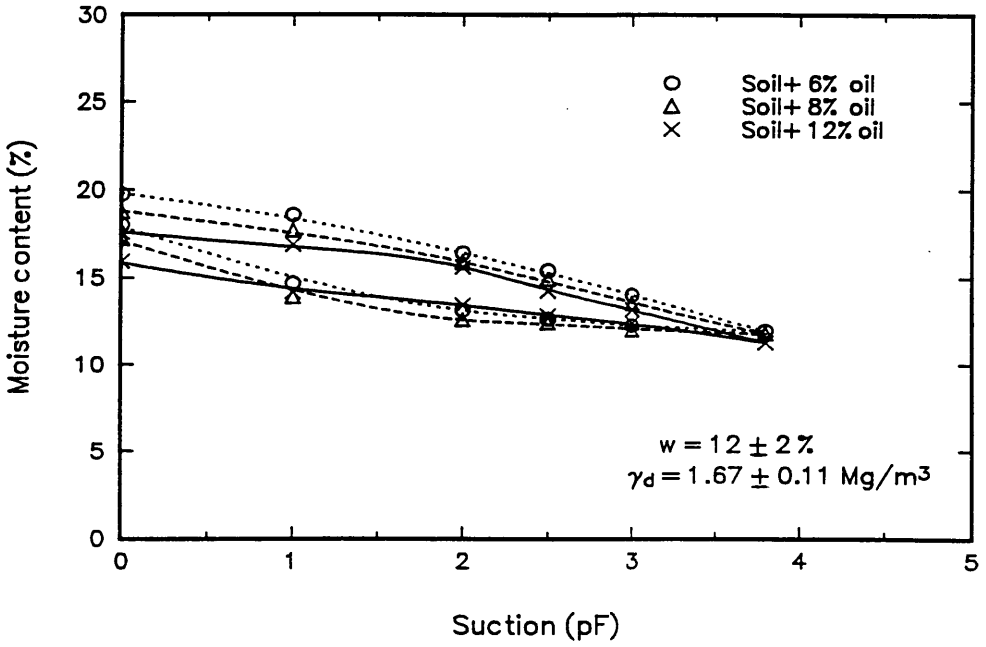


Figure 5.6b - Fluid retention curves for soil-oil mixtures from the Sanad soil.

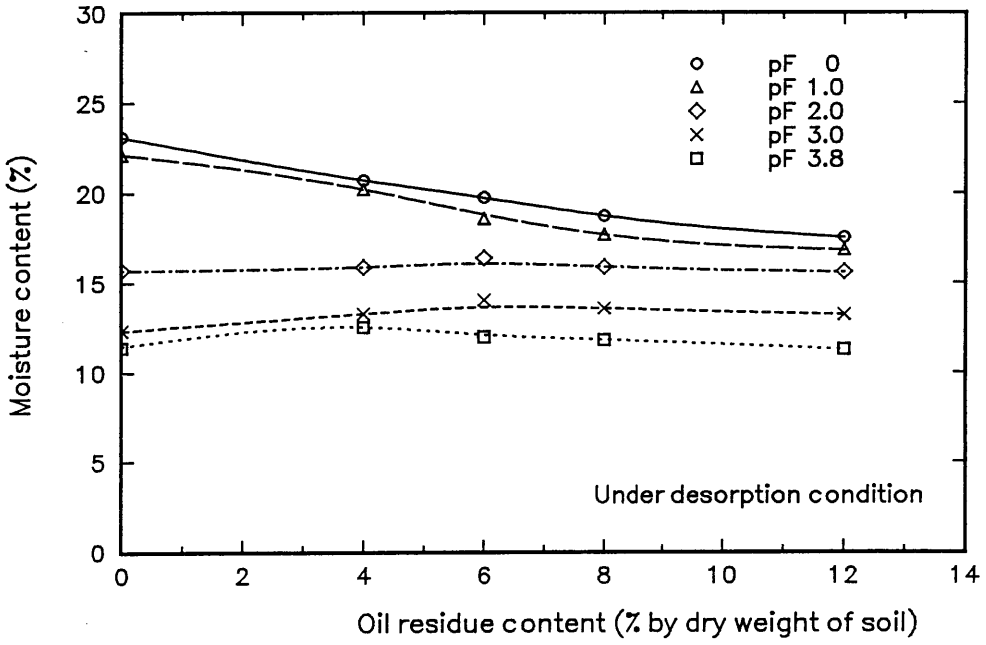


Figure 5.6c - Variation of fluid retention characteristics with oil residue for the Sanad soil samples under different suctions.

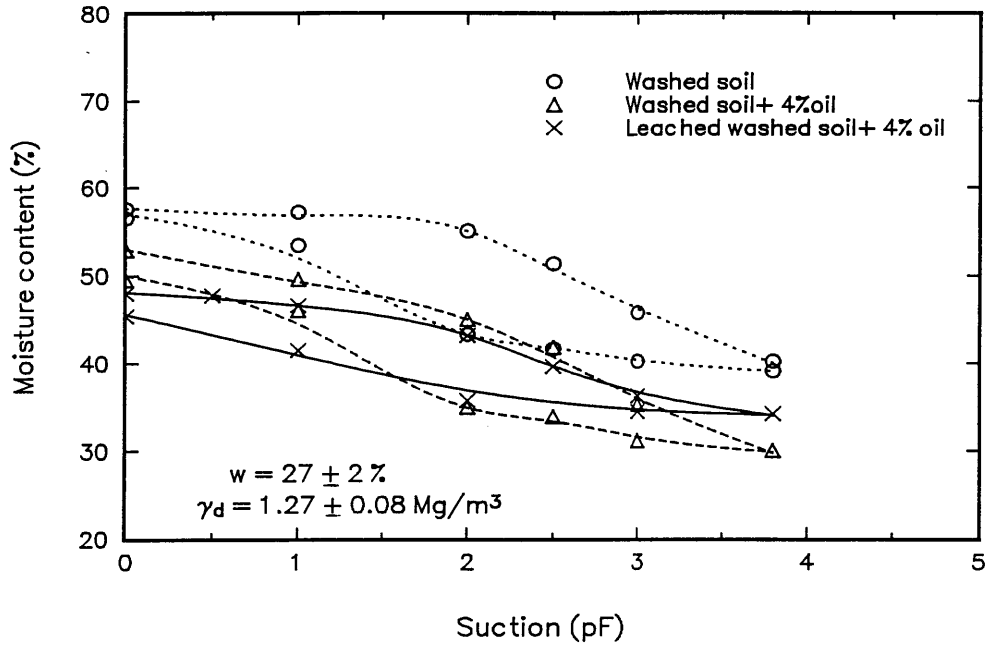


Figure 5.7 - Fluid retention curves for the washed Sanad soil samples.

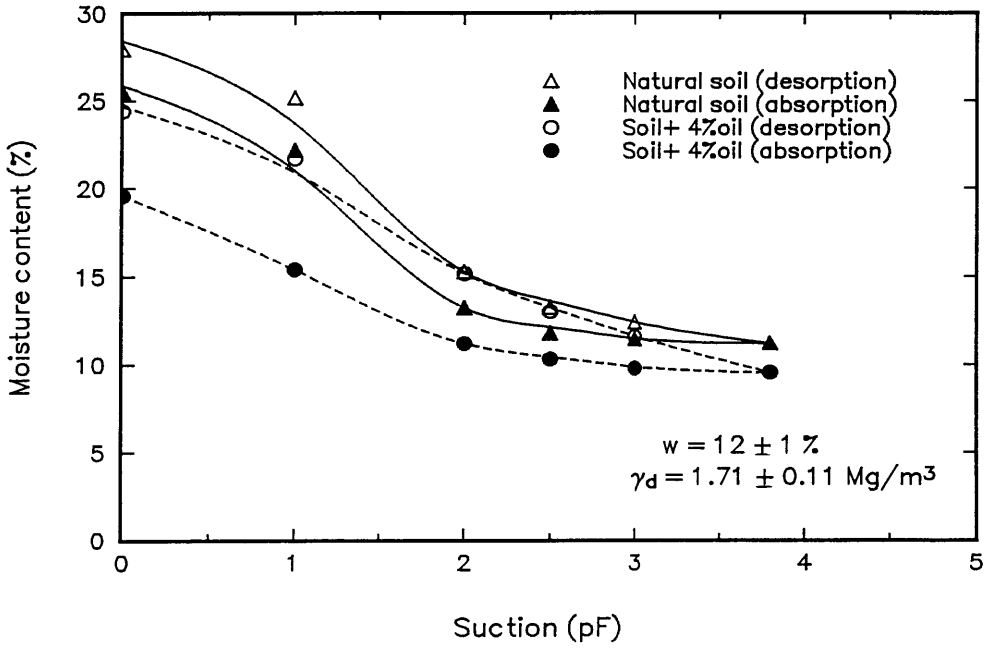


Figure 5.8 - Fluid retention curves for the Muharraq soil samples.

soil, the washed Sanad soil, and the Muharraq soil, respectively. In each of the above figures, two sets of fluid retention curves representing natural soil and stabilized soil are presented, containing 4% oil residue mixed with soil prior to water addition.

The results of Figures 5.6 to 5.8 show that soil fluid characteristic of the natural soils is slightly higher and exhibits a sharper drop in its moisture content as compared to their mixture with oil. The decrease in the fluid retention capability of the soil-oil mixture is likely attributed to a reduction in the thickness of the classical Gouy electrical double layer formed in soil-fluid systems. This in turn results in a tendency towards a flocculated soil fabric and thus lower water potentials (Yong and Warkentin, 1975). This indicates that the oil residue will most likely satisfy the soil surface charges and enhance the water-repellent characteristic of the stabilized soils (Salem, et al. ,1985). The addition of oil to soil appears to enhance its cohesive properties mainly through binding mechanisms at the contact points between particles (as explained in Section 5.1.2 on interaction mechanisms). However, in the natural soils, salt cementation bonds (e.g. carbonate, halite) are found to be dominant. The salt bonds, which are rigid and brittle, are seen to be responsible for the sudden drop in moisture contents at approximately pF 1 (Akili, 1981).

In examining the fluid-retention characteristic of the stabilized soil from Sanad containing various proportions of oil residue (i.e. 4%, 6%, 8%,and 12% of oil, by dry weight of soil), a slight reduction in the retention curve is noted as the oil residue content increases (Figures 5.6 a, b, and c). For instance, the moisture contents of the stabilized samples at a suction value of pF 1 reduce by about 15% as the oil residue content in these samples increases from 4% to 12% (w/w). However, variations in the moisture contents are noted to be less significant at high suction values. This reduction is indicative of the improvement in the "waterproofing" characteristics of the stabilized soils as the oil content increases. Moreover, the presence of 4% oil residue (w/w) was found to be sufficient to entirely cover the surfaces of the tested soils, as explained in Section 4.2. Thus, as the oil residue content increases beyond 4% (w/w), the oil begins to fill the soil pores and may act as a lubricant separating the soil particles. These fluid retention results show good agreement with the unconfined compression results presented in Section 4.1.1.b.

As can be seen from the soil suction results, modest variations were observed between the fluid retention characteristics of the natural and stabilized soils. This indicates that the contribution of the interparticle forces in enhancing the soil strength performance is insignificant. Such behavior is likely due to the fact that the tested samples are well-compacted and contain predominantly silt and sand fractions.

The effect of soil washing on the fluid retention behavior of the Sanad soil is presented in Figure 5.7. The washed soil was prepared by dispersing the natural soil in water in order to remove some of the excess salt initially present in it prior to testing, as explained in Section 3.1.1. A significantly higher fluid retention capability was observed for the washed sample as compared to the natural sample, from the same soil. This in turn leads to a tendency towards a dispersed soil fabric. The change in the fluid retention characteristics of the washed soil is likely a result of the partial removal of the salt present in the soil and alterations in the physico-chemical properties of the soil, due to the washing process. For example, the plasticity and surface area of the washed Sanad soil was increased by about 50% as compared to the natural soil from the same soil (see Table 3.1). The increase in the surface activity is one of the major factors responsible for the higher fluid retention characteristics of the washed soils. In addition, the significant reduction in the compacted density of the washed sample (i.e. 1.35 Mg/m^3) as compared to the natural sample (i.e. 1.78 Mg/m^3) is another contributing factor to the high fluid retention capability of the washed sample (Yong and Warkentin, 1975).

The fluid-retention characteristics of the leached samples are presented in Figures 5.7, 5.9, and 5.10. A comparison of soil fluid curves of each soil and its mixture with 4% oil residue after 40 days of leaching in distilled water shows that the mixture sample has a slightly higher fluid retention capability than the soil sample (Figures 5.7, 5.9a, and 5.10a). This is likely due to the effect of leaching on the interparticle bonds formed in each case. The natural soil sample appears to have lost most of its cementing salt bonds during the leaching process (Ismael, 1993), whereas the mixture sample appears to have retained most of its cohesive bonds. Comparing the soil fluid characteristics of both leached and unleached soil-oil mixtures shows insignificant changes in their retention behavior, which provides a good agreement with the results presented in the interaction section (Section 5.1.2) and the strength section (Section 4.1.1).

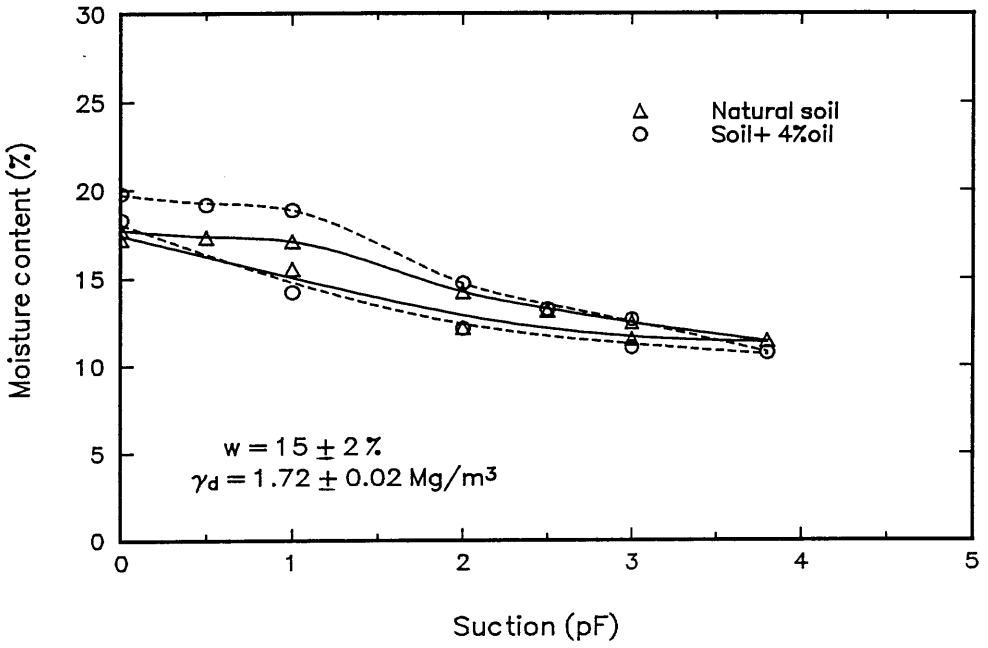


Figure 5.9a - Fluid retention curves for samples leached in distilled water from the Sanad soil.

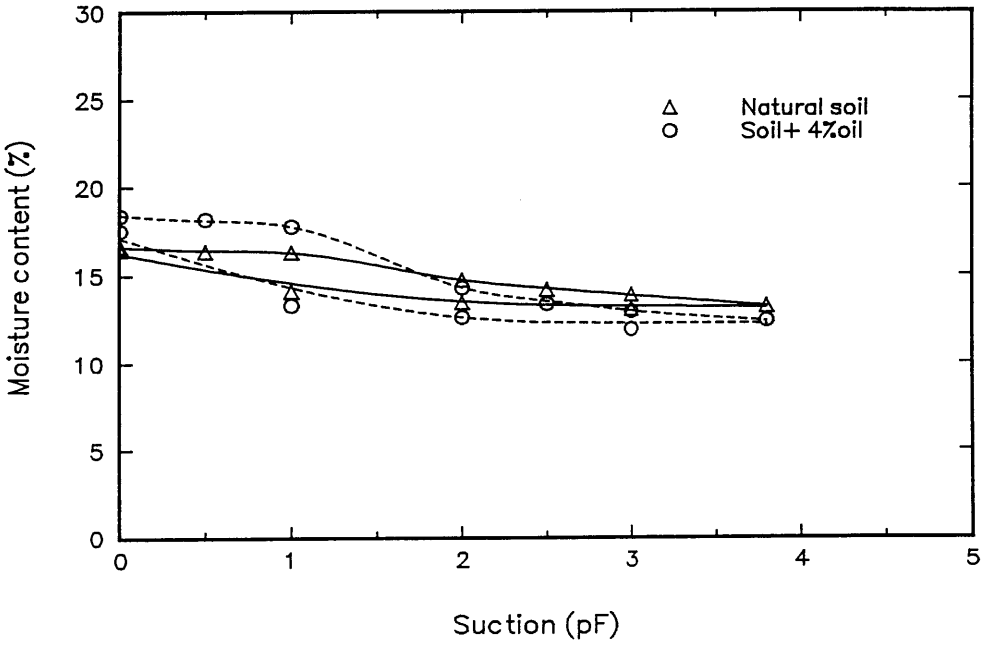


Figure 5.9b - Fluid retention curves for samples leached in saline water from the Sanad soil.

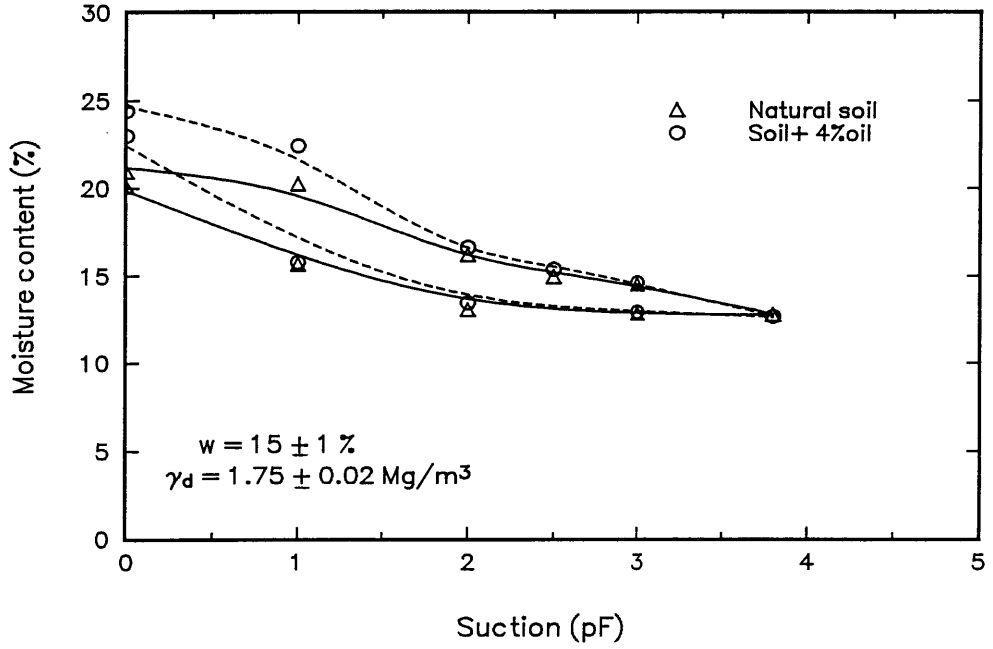


Figure 5.10a - Fluid retention curves for samples leached in distilled water from the Muharraq soil.

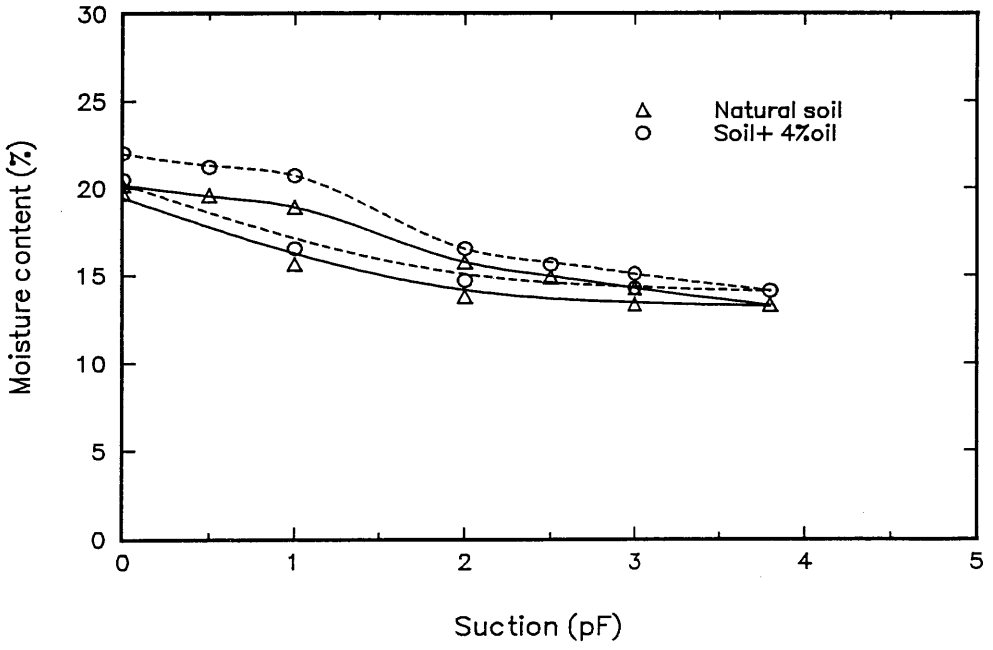


Figure 5.10b - Fluid retention curves for samples leached in saline water from the Muharraq soil.

The slight increase in the fluid retention curves of the samples leached with distilled water compared to the samples leached with saline water (as shown in Figures 5.9 and 5.10) can be explained in terms of an increase in the repulsive forces. This is because leaching with distilled water decreases the electrolyte concentration in the bulk solution and thus enhances the tendency toward a dispersive structure with a higher fluid retention capability (Yong et al., 1985).

Soil fluid retention (soil suction) is mainly due to surface tension acting on the fluid menisci in the soil pores. Studies (Yong and Warkentin, 1975; Mohamed et al., 1992) have shown that soil fluid retention decreases with an increase in salinity and temperature. Therefore, one would expect the fluid retention of in-situ soils in Bahrain, where the mean annual temperature ($27\pm3°C$) is slightly higher than the laboratory temperature ($22\pm2°C$), to be slightly lower than the measured laboratory soils under similar conditions.

5.2 Adsorption-desorption Characteristics

Having established the nature of interaction and the type and strength of the bonding involved between the oil and soil surfaces, it is necessary to determine the oil adsorption potential onto these soils. A batch equilibrium test was used as an indicative measure for oil adsorption potential, as described in Section 3.7, and the results of this test are presented herein.

The adsorption isotherm curves for the soil-oil mixture form the Sanad and Muharraq soils under the effect of distilled water are shown in Figure 5.11. The concentrations of oil retained in soil at different oil contents are plotted as a function of solution equilibrium concentration (supernatant concentration) on a linear scale graph. It is noted that there is a slight increase in the isotherm curves as the concentration of the oil in the soil-oil mixture increases, reflecting the potential of these soils to retain oil at higher oil concentrations, up to 6% (w/w). This is partially attributed to the effect of the cation exchange capacity of the soil on oil retention potential. The cation exchange capacity of the two soils is about 20 cmol/kg, which is higher than the introduced oil

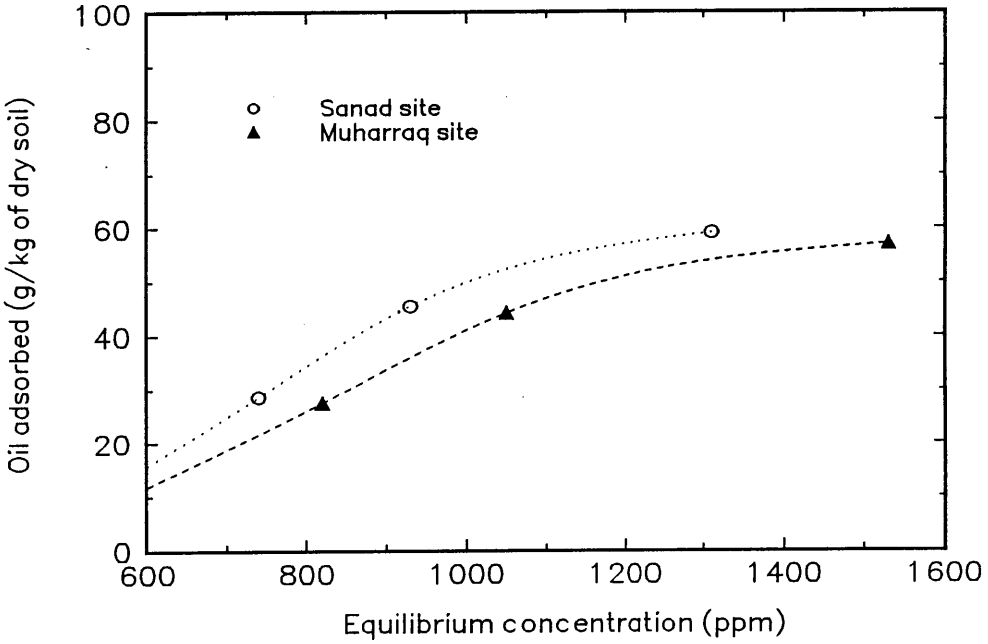


Figure 5.11 - Adsorption isotherm curves for the stabilized soils obtained from the soil suspension test.

concentration of 5, 7, and 9 cmol/Kg, respectively. These results reveal that the tested soils have the potential to adsorb slightly higher oil than the optimum content, i.e. 4%, established from the geotechnical testing. However, the increase in oil adsorption is accompanied neither with an improvement in soil strength nor with increased interaction with oil, as explained in Sections 4.1.1b and 5.1.2.

A comparison of the isotherm curves of the two soils shows that the adsorption of oil in the Sanad soil is slightly higher than in the Muharraq soil, likely due to the influence of cation exchange capacity and surface area of the soil on oil retention potential. The Sanad soil has slightly higher cation exchange capacity and surface area than the Muharraq soil, resulting in higher adsorption of oil and thus higher oil retention in the Sanad soil.

Results on the distribution of oil detected separately in the solid and liquid phases of the tested batches are presented in Figures 5.12a and 5.12b for the Sanad and Muharraq soils, respectively. The relative oil content in each phase is expressed in terms of the ratio (w/w) of the measured oil in that phase to the initial oil input, i.e. 4% oil by dry weight of soil. As can be seen from Figure 5.12, the relative concentration of oil detected in the equilibrated solutions of the Sanad and Muharraq soils in the presence of distilled water are 20% and 22%, respectively.

The desorbed oil detected in the equilibrated solutions of both tested soils is noted to decrease in the presence of saline water as compared to distilled water. This reduction is partially due to the decrease in oil solubility in the presence of salt (Yaron, 1989) and to the increase in the association of oil onto the soil surfaces in a saline water environment (Meyers and Quinn, 1973; Meryers and Oas, 1978).

However, the presence of salt in the soil prior to oil addition shows an opposite effect. The washed Sanad soil is noted to have lower oil desorption than the natural Sanad soil, the latter of which contains high salt content. This is likely attributed to the increase in the oil adsorption onto the surfaces of the washed soil, which has a higher surface area than the natural soil. Moreover, the differences between the initial oil input and the measured oil in the solid and liquid phases, which represent 2 to 4% (w/w), are expected to be due to the effect of other transport processes (e.g. volatilization, degradation, and photolysis) on oil residue.

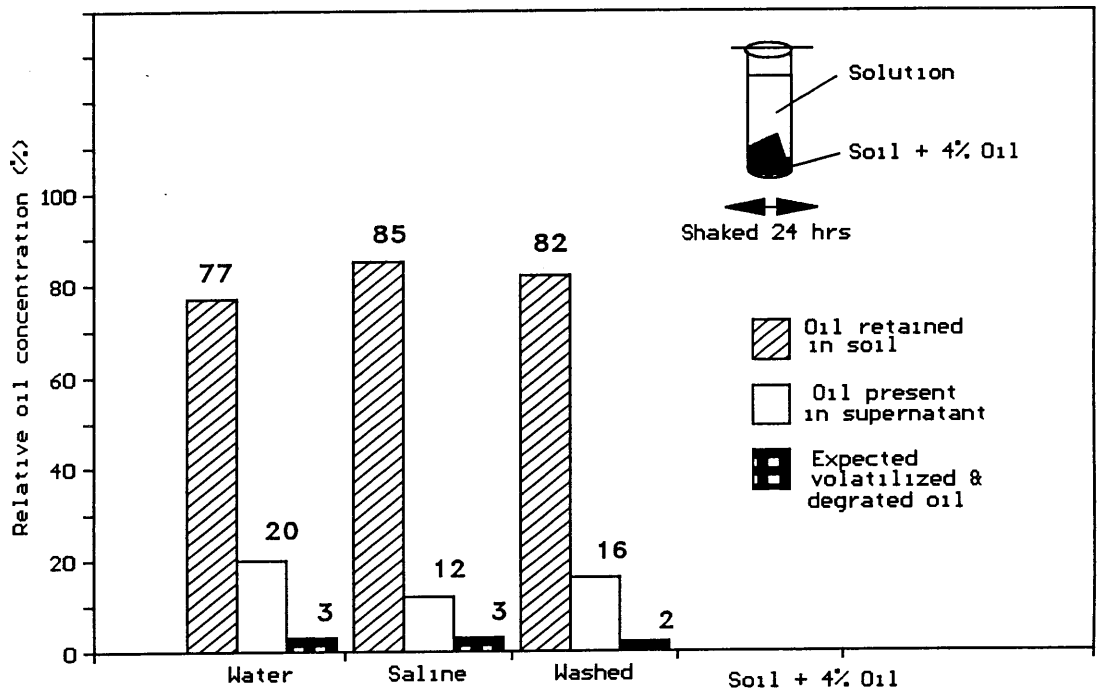


Figure 5.12a - Oil distribution in the Sanad soil obtained from the soil suspension test.

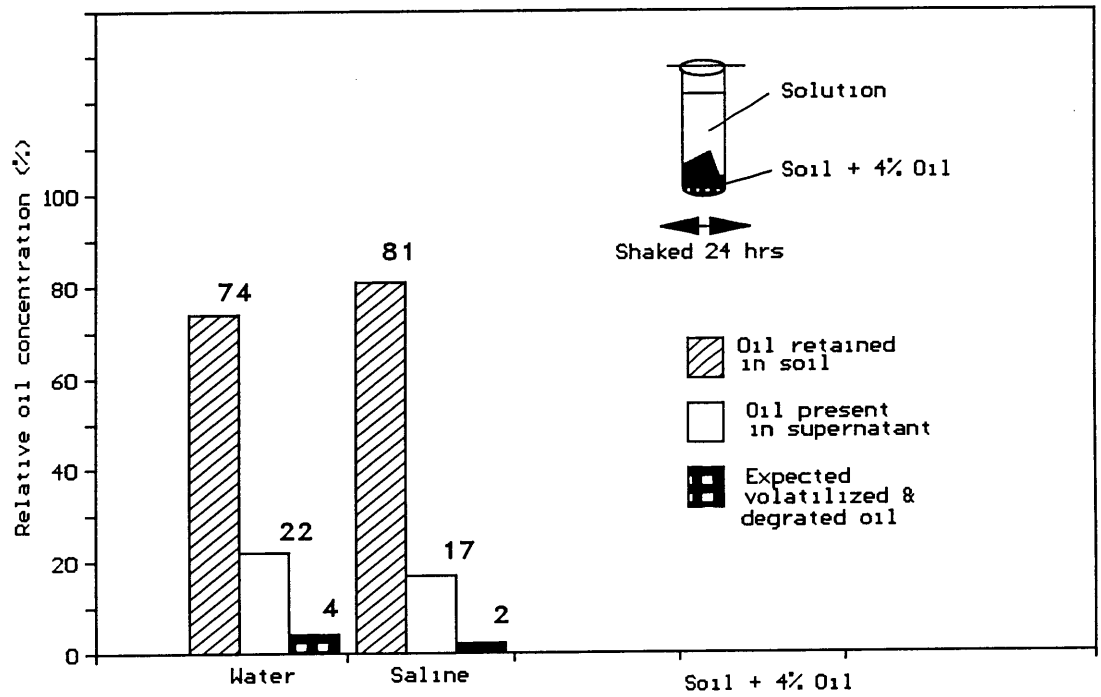


Figure 5.12b - Oil distribution in the Muharraq soil obtained from the soil suspension test.

CHAPTER 6
ENVIRONMENTAL IMPACT ASSESSMENT
- TRANSPORT PROCESSES -

When oil is mixed with soil, one can speculate that at least three different situations can co-exist: (1) oil may adsorb onto the surfaces of the soil constituents, (2) oil may form bonds which link (aggregate) some of the soil particles, and (3) oil may exist separately in the soil pore void. A hypothetical representation of these situations is illustrated in Figure 6.1. In turn, one expects that within the pore void of soil, oil can exist in three separate phases: liquid phase (non-aqueous phase liquid, NAPL); dissolved in soil pore fluid as aqueous phase; and gaseous phase as vapor in soil gas (Hunt et al., 1988). It is expected that the three situations described will co-exist and that the proportions of each (situation) will depend on the interacting constituents and conditions leading to the development of the oil-soil mixture.

Under the effect of climatic forces (e.g. rainfall, temperature), the oil present in the stabilized soils has a potential to contaminate the surrounding environment. Therefore, understanding the environmental fate and transport of oil from the stabilized soils is essential to properly characterize the hazards of oil residue. Under long-term effects, one expects the oil in the stabilized soils to co-exist in different situations: the oil may adsorb onto soil surfaces, be present in an emulsion form trapped in the soil pores due to surface tension, leach from soil pore fluids, volatilize from the soil pore void into the atmosphere, and degrade into another compound. A schematic representation of the major transport processes involved in oil depletion from the stabilized soils is shown in Figure 6.2. The environmental transport processes are dictated largely by the physico-chemical properties of the oil residue, properties of the soil and water that the oil residue comes in contact with, and prevailing climatic conditions (Jernigan et al., 1991). The significance of the main transport processes involved in an oil-soil-water system is shown hereafter.

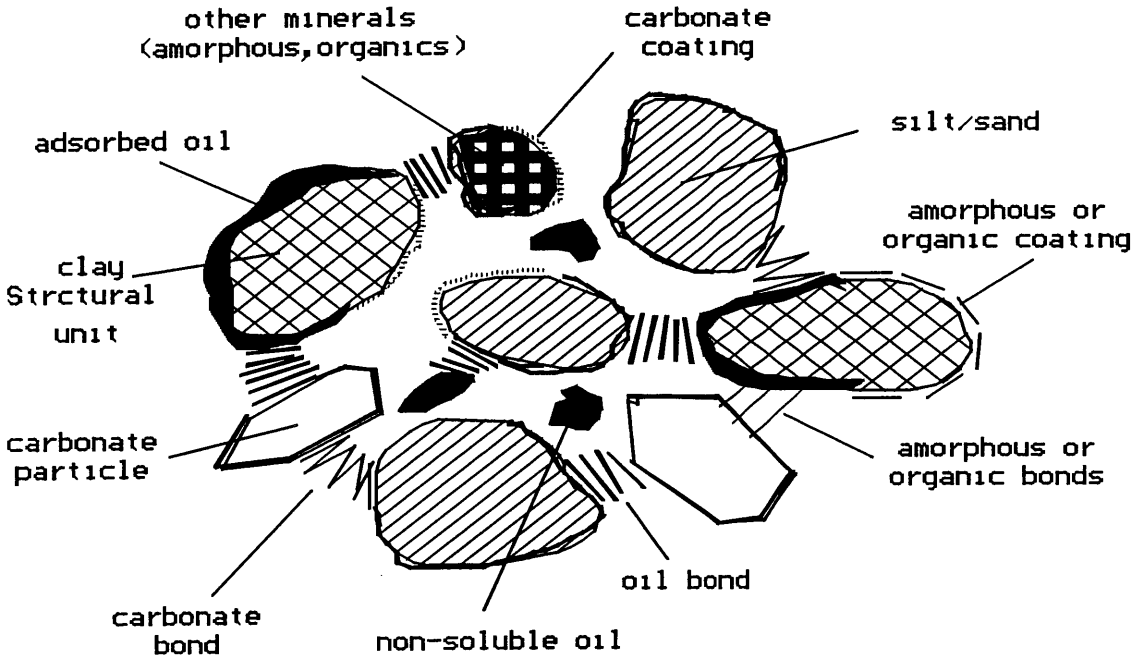


Figure 6.1 - Hypothetical presentation of soil-oil mixture.

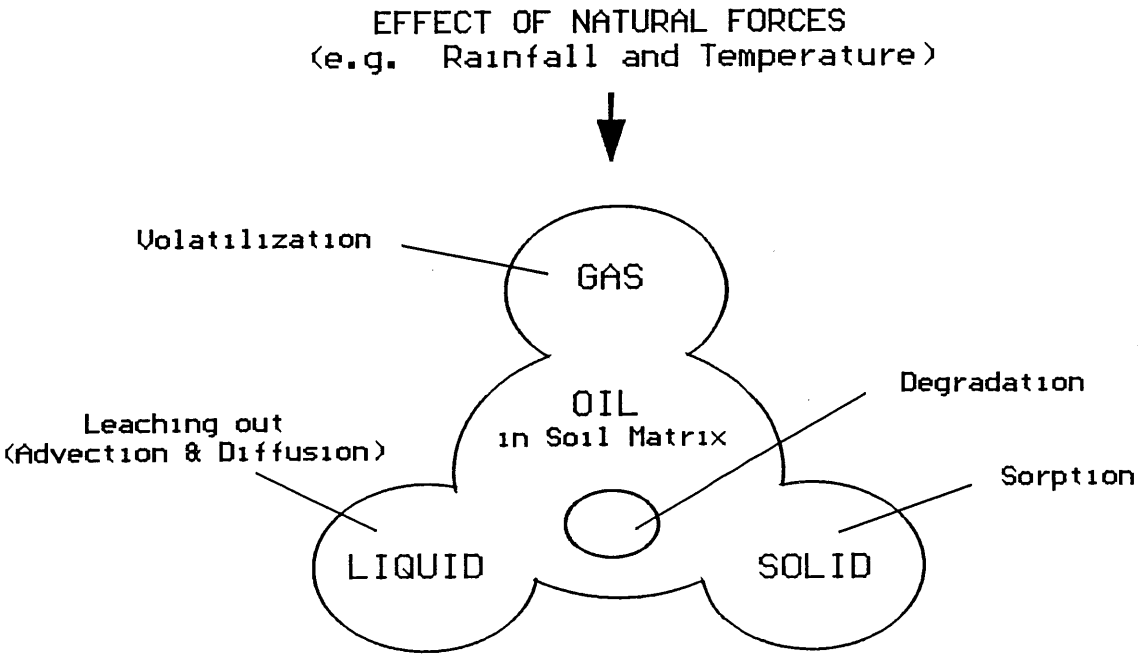


Figure 6.2 - Various forms of oil transport processes from soil-oil mixture.

6.1 Retention of Oil Residue

Most previous studies have dealt with the retention phenomenon and interaction behavior of single hydrocarbon compounds in laboratory manufactured soils. Since simple systems are rarely encountered in nature, this study addresses more complex systems where each soil and oil comprises a wide mixture of different constituents. The contribution of the various constituents involved in the retention process are discussed here.

6.1.1 Retention Forms

The tested soils contain a wide variety of minerals, i.e. quartz, feldspar, carbonate, and clays. The retention of oil residue in quartz surfaces is relatively low and primarily attributed to the action of surface tension forces. Oil retention in carbonate surfaces is representative of its low surface activity. However, oil retention in clay minerals is high due mainly to hydrogen bonds between alkyl groups and surface silicates. The oil residue used in this study consists of various types of hydrocarbons. The lighter molecular weight fractions (saturated hydrocarbons) and slightly polar fractions (heterocyclic compounds) have the potential to adsorb, volatilize or leach out of the soil pore fluid. However, the large hydrophobic portion (polycyclic aromatic hydrocarbons) has a relatively high retention in the soil matrix (Yaron, 1989).

Determination of the contribution of each phase of oil residue to retention capability can be very difficult due to the complexity of the various transport processes involved in the soil-oil system. Both the dissolved and volatilized phases of oil (which represent a small fraction of the oil) are directly involved in the adsorption processes. However, the non-dissolved oil (which represents a large portion of the oil) can adsorb onto soil organics, act as coatings on soil surfaces, or appear as emulsions (bind some of the soil particles) held in the pore spaces by interfacial surface tensions (Bouchard et al., 1989).

6.1.2 Retention Mechanisms

Hydrocarbons retain onto soil surfaces by different types of interactions. These

interactions are expected to include adsorption, hydrophobic, ion exchange, and intercalation. They may take place on both external and internal surfaces of soil, or they may be restricted to the external surfaces (Lagaly, 1985; Shimizu et al., 1992).

The retention of oil residue on the tested soil surfaces, as revealed from infrared analyses (discussed in Section 5.1.2), was mainly attributed to electrostatic and hydrophobic effects. The electrostatic effects are shown to be due to weak hydrogen bonds established between the methyl groups (on oil residue) and oxygen containing functional groups (on soil surfaces). However, the hydrophobic effects are attributed to a high organic carbon partition coefficient and large molecular sizes of oil which enhance the Van der Waal's attraction forces (Bouchard et al., 1989; Senesi and Chen, 1989).

Water and cation bridging effects are also shown to contribute to oil retention in these soils. Water and cations present in the soil-oil system enhance interaction behavior through water and cation bridges. Surface tension forces are another source for oil retention that will be produced due to water bridging. Moreover, the presence of methyl alkanes and activated aromatic rings (electron donor) in the oil residue renders possible interaction based on the formation of electron donor-acceptor between the interacted surfaces under certain conditions (Senesi and Chen, 1989).

6.1.3 Factors Affecting Retention

The retention of oil in soils is primarily affected by parameters such as oil hydrophobicity, which is reflected by the aqueous solubility and organic carbon partition coefficient, soil organic carbon, cation exchange capacity and surface area of the soil. An increase in any of the above parameters can significantly enhance the retention behavior of oil in soils. Additional factors which can affect oil retention in soils include oil concentration, temperature, soil pH, redox condition, magnitude and distribution of surface charges, molecular size and coordination of oil, degree of dispersion, and ionic strength of the medium (Weber and Miller,1989; Bonazountas, 1991).

The cation exchange capacity and content of the organic matter of the tested soils are representative of the amount of oil introduced to the soils (4%, w/w). The cation exchange capacity of the tested soils (about 20 cmol/kg) is found to be higher than the initial oil input of 4% (5 cmol/kg). In turn, one expects most of the soluble fraction of

oil residue to be adsorbed onto soil surfaces. The high organic carbon partition coefficient of oil (3980) and the presence of organic matter (about 1%, w/w) in the soils contribute to the retention of a significant amount of the non-dissolved fraction of oil. The large molecular chain of oil residue (molecular weight of about 900), its substantial surface tension (about 20 dynes/cm at 22°C, (Bowman, 1967; Clark, 1982)) and its high viscosity (3.5 Pascal-Sec at 22°C) also promotes the high retention capability of the non-dissolved phase of oil in soils.

6.1.4 Results of Retention Tests

Oil retention characteristics in the stabilized soils are examined using both soil leaching and batch equilibrium tests. The results of the batch equilibrium test are discussed in Section 5.2, whereas the results of the leaching test are presented herein. Retention of oil residue on the solid phase of the tested soil-oil mixtures, containing 4% oil residue, after ten pore volumes of leaching is shown in Figure 6.3. This figure illustrates the results of the oil retention for the Sanad and Muharraq soils, in which each soil sample is leached separately in distilled and saline water. The results of leaching the stabilized washed soil from Sanad in distilled water is presented also in Figure 6.3. The total bar length represents the initial oil input and the retained oil is expressed in terms of the relative percentage. The detected oil retained onto the surfaces of these soils are noted to be relatively high, above 85% for the Sanad soil and 82% for the Muharraq soil. The high retention of oil in these soils can be attributed to the insignificant changes in the interparticle bonding and the fluid retention capability due to leaching, as shown in Sections 5.1.2 and 5.1.3.

Oil retention is seen to increase for samples leached with saline water as compared to corresponding samples leached with distilled water. The increase in oil retention for the samples leached with saline water is partially due to the effect of salt on the interparticle forces formed in the soil matrix. The presence of salt reduces the electrical double layers formed in the soil-water system, as revealed in the soil suction results (Section 5.1.3). This in turn is expected to increase the attractive forces and enhance cation bridging actions between the interacting surfaces.

However, the presence of high salt content in the natural soils prior to the

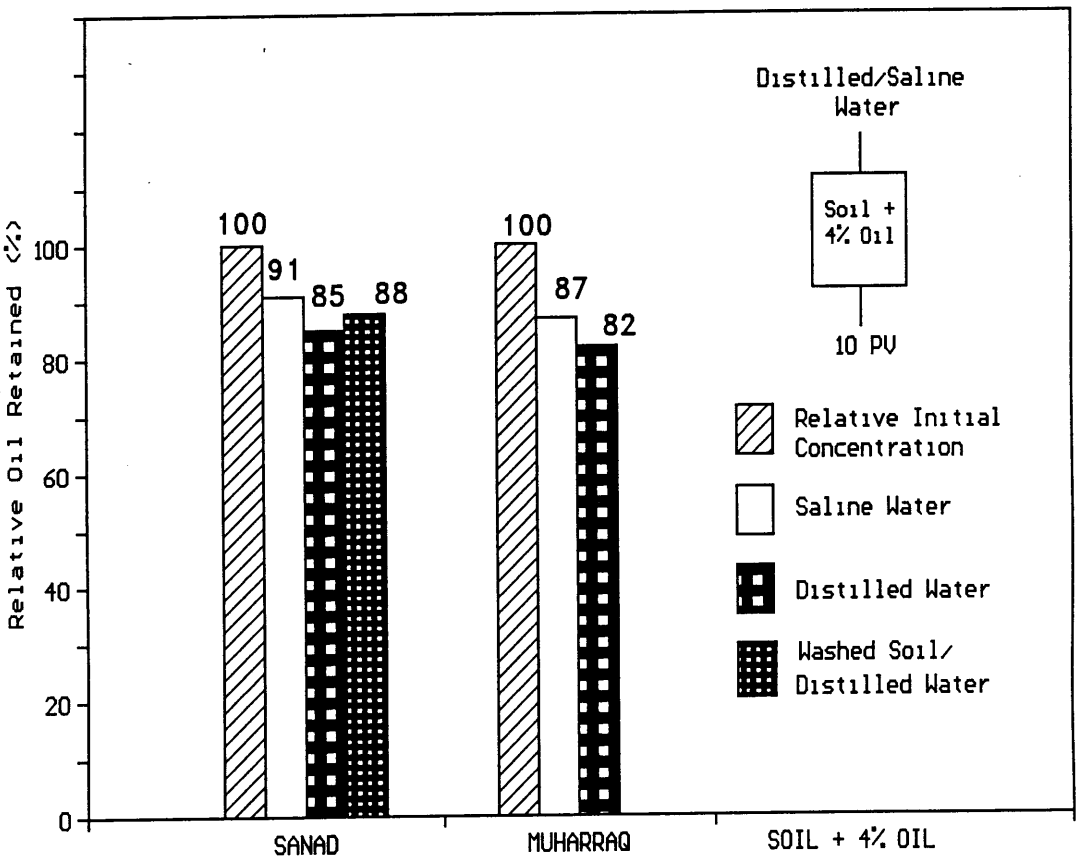


Figure 6.3 - Retention of oil residue in soils after 10 pore volumes of leaching.

addition of oil residue shows an opposite effect. A slight increase is observed in the oil retention of the washed Sanad soil as compared to the natural Sanad soil. This is attributable to changes in the physico-chemical properties of the soil due to the washing process (e.g. surface activity and fluid retention capability). Similar oil retention results were obtained from the batch equilibrium tests discussed previously in Section 5.2.

Besides the environmental aspects of the stabilized soils, which show relatively high oil retention in these soils, the retention of oil in the soils under any condition is critical to their geotechnical properties. The results of the unconfined compression and soil suction tests, Sections 4.1.1 and 5.1.3, demonstrate the persistent contribution of the oil residue in enhancing these properties even under severe leaching conditions as compared to the natural soils. If a soil system cannot retain its binding agents, e.g. salts initially present in the tested natural soils, then the resultant bonds will most likely be removed in the long-term, and hence the soil strength will be reduced.

6.2 Leachability Characteristics

As indicated previously, oil residue has a potential to contaminate the surrounding environment. In order to assess such contamination, its leaching and migration characteristics are examined herein. In addition, the influence of different parameters, e.g. type of permeating solution, soil washing condition, and leaching potential of other contaminants (e.g. heavy metals and soluble ions) on oil leaching behavior is evaluated and presented below.

6.2.1 Leachability of Soluble Salts

The presence of high salt content in the natural soil (chloride, sulfate, sodium and calcium, see Table 3.4), and their high solubilities make it important to assess their potential for leaching -- i.e. leachability potential and effect of oil presence in soil on leachability. In addition, salt leachability was conducted to examine one of the objectives of this research, i.e. feasibility of oil residue to protect sub-structures from salt attacks, especially sulfate.

Figure 6.4 shows the relative salt concentration (C/C_o, ratio of the effluent salt concentration C to the initial salt concentration of the soil C_o) in effluents collected during leaching with distilled water in relation to the cumulative pore volume. The cumulative pore volume represents the accumulated volume of water passing through the specimen in the leaching cell since the beginning of the leaching process. The results are presented for both the natural soil and stabilized soil samples, containing 4% oil residue, from the Sanad and Muharraq sites. The salt concentrations in the collected effluents, measured in terms of concentration of cations (Na, K, Ca, and Mg), are seen to decrease sharply in the early pore volume discharges, followed by a steady and gradual decrease to residual values.

Since sulfate is considered one of the main soluble ions that can cause severe deterioration to the sub-structure, its migration potential is also examined. Figure 6.5 shows the relative sulfate concentration (C/C_o, ratio of the effluent sulfate concentration C to concentration of sulfate in the leaching solution, i.e. saline water, C_o) in effluents collected during leaching the Sanad and Muharraq soils with saline water as a function of pore volume. The sulfate concentrations in the collected effluents are seen to increase in the early pore volume discharges, followed by steady values at 5 pore volumes (breakthrough point for sulfate). It is noted that most of the sulfate initially present in the soils has leached out during the first pore volume of leaching with distilled water prior to leaching with saline water; approximately 75% and 85% of the soil's initial sulfate have leached out from the Sanad and Muharraq soils, respectively.

The results of Figures 6.4 and 6.5 show that the salt leachability from the stabilized samples is slightly higher than from the natural soils. The slight increase in salt leachability in the stabilized samples is expected to be due to complex physico-chemical effects, e.g. possibility of surface exchange potential between the oil molecules and exchangeable ions (Bouchard et al., 1989).

6.2.2 Leachability of Heavy Metals

Although oil residue consists predominantly of hydrocarbons, it contains small quantities of different heavy metals. The nature of these metals and their concentrations can vary depending on the origin and conditions during oil generation and distillation. Vanadium and nickel are commonly the most abundant metals but iron chromium, zinc,

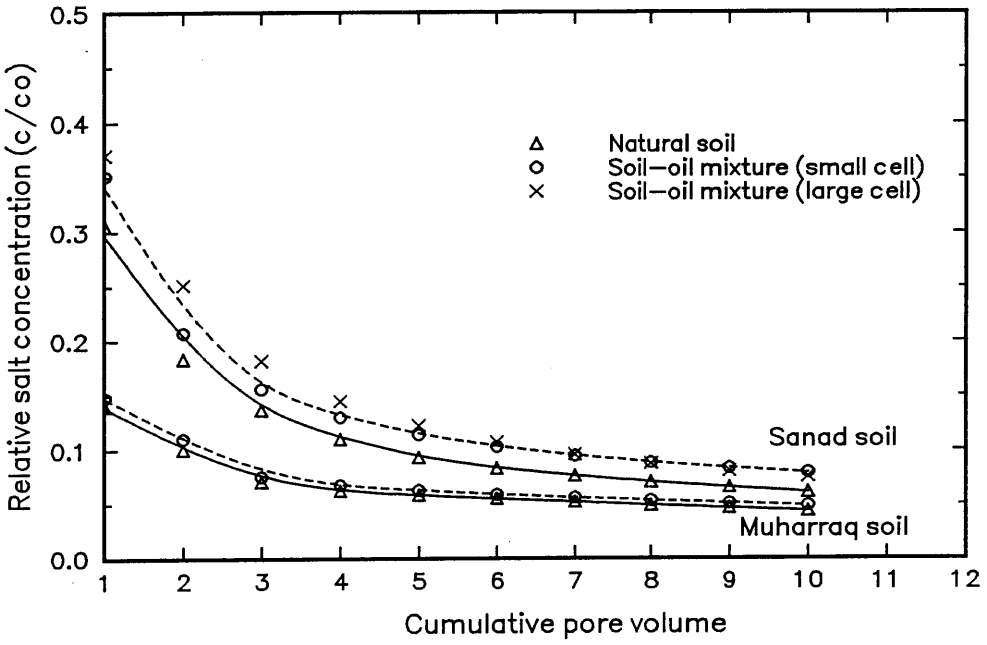


Figure 6.4 - Relative salt concentration in effluents collected during leaching in distilled water.

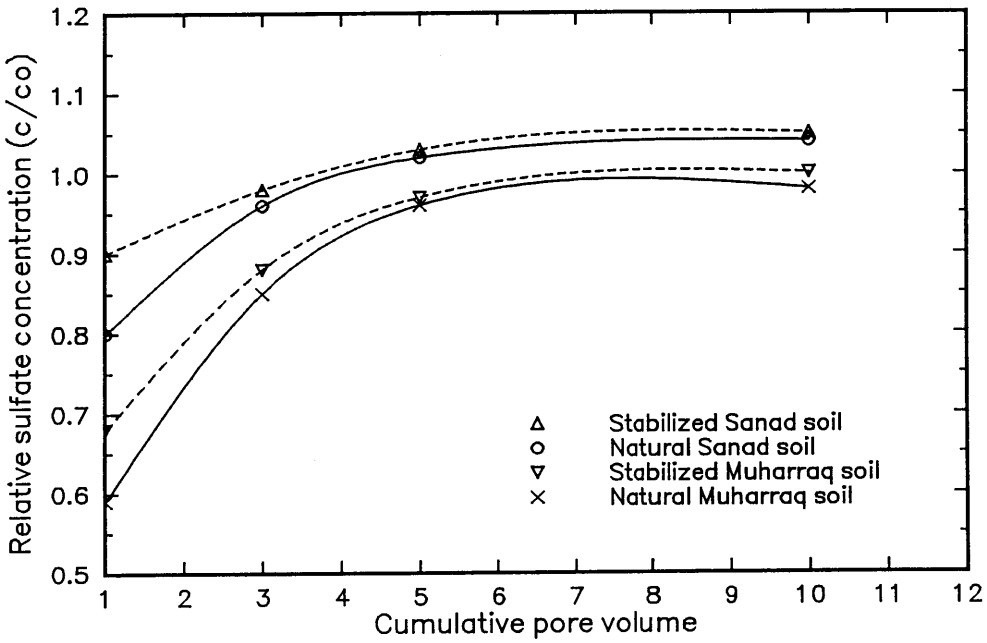


Figure 6.5 - Relative sulfate concentration in effluents collected during leaching in saline water.

barium, lead, and others can also be present (Filby, 1975). Studies have shown that Arabian oil residue (especially the atmospheric type which is used in this study) contains limited types of heavy metals at low concentrations (Dolbear et al., 1987; Kircher, 1989). Moreover, the concentrations of the heavy metals in oil residues are considerably lower than their concentrations in asphalts. The common heavy metals associated with most Arabian oil residue include: vanadium, nickel, iron, and lead (see Table 3.2). The contents of these metals in the Arabian oil residue are very low (Ali and Bukhari, 1989).

The measured concentrations of the heavy metals (e.g. vanadium, nickel, iron, and lead) in the collected effluents were determined to be below the detection level. This is mainly due to their presence at low concentrations in the stabilized soils and the high pH of the soil pore fluids. Based on stabilizing the soils with 4% oil residue, the concentrations of vanadium, nickel, and iron in the stabilized soils were estimated to be 1.64 mg/kg, 0.62 mg/kg, and 0.40 mg/kg, respectively. The concentrations of these metals are below the criteria of the contaminated level in soils set by Environment Quebec (1988), i.e. 50 mg/kg for most of these heavy metals. Similarly, a study conducted by Sciarrotta (1991) has shown that the measured concentrations of various heavy metals in sand contaminated up to 5% with fuel were below the hazardous level.

The mobilities of these heavy metals are expected to be very low in an alkali environment (Yong et al., 1992). This is because the solubilities of such metals are substantially reduced under a saline-alkali environment, as in these soils (pH = 7.8 and 8 for the Sanad and Muharraq soils, respectively). A large portion of these heavy metals are expected to precipitate into insoluble forms under alkali conditions, which poses a low environmental threat (Alloway, 1990; Fergusson, 1990). Moreover, some of these metals may already form chelated complexes with the various components of the oil hydrocarbons or may be adsorbed directly onto the soil surfaces, leading to a further restriction in their mobilities (Filby and Van Berkel, 1987; Frankenberger, 1991).

However, if the presence of heavy metal is detected at a higher level than these, then one would expect that their presence in the soil-oil mixture would cause a hazardous threat and would certainly affect the oil leachability potential. Little emphasis has been given in the literature on the role of heavy metals present in hydrocarbon contaminated soils on the behavior of the hydrocarbons.

6.2.3 Leachability of Oil

Leachability of oil from the soil-oil mixtures under permeating distilled water is found to be relatively low. This can be seen in Figure 6.6, which portrays the relative concentration of oil (C/C_o) for the tested samples in relation to the cumulative pore volume. The relative oil concentration (C/C_o), expressed in terms of percentage, is the ratio of the effluent oil concentration C to the initial oil concentration introduced to the soil C_o. The low aqueous solubility of the oil (10 ppm in distilled water at 22°C, Table 3.2) and its high viscosity (3.5 Pascal-Sec at 22°C, Table 3.2), together with the relative low presence of the oil in these soils (4%) and the low permeability of the soil-oil mixture ($\sim 1x10^{-8}$ m/day), about one order of magnitude less than the permeability of the natural soils, Table 3.1) can be partially responsible for the low leachability of oil.

The results of Figure 6.6 are presented for duplicate samples from Sanad, one washed sample from Sanad, and one sample from Muharraq. The oil ratios are extremely low, but nevertheless follows the same pattern demonstrated by the results in Figure 6.4. One can assume that the rapid reduction in oil concentration in the initial stages of leaching can be attributed to the removal of soluble and lighter fractions of oil present in the soil pore fluid.

The detected oil leached from these samples at the end of the leaching process is noted to be relatively low. Based on determining the oil concentration in each collected pore volume, the percentages of the total leached oil after ten pore volumes of leaching with distilled water were 2.8%, 2.2%, and 1% (w/w) for the Muharraq soil, the Sanad soil, and the washed Sanad soil, respectively. Besides the solubility and viscosity effects, the low leachability of oil can be attributed to: (a) the presence of oil at a concentration just enough to cover the surfaces of these soils (Section 4.2), and (b) the role of bonding mechanisms involved (Section 5.1.2). The results of infrared (Section 5.1.2) and soil suction tests (Section 5.1.3) show the formed bonds between the soil residue and soil surface to be relatively stable and insensitive to leaching forces, which partially explains the reduction in oil leachability.

The reduction in oil leachability for the washed Sanad soil as compared to the natural Sanad soil is attributed to the effect of soil surface area on the leaching potential of oil. The surface area of Sanad's natural soil is increased from 40 m^2/g to 62 m^2/g

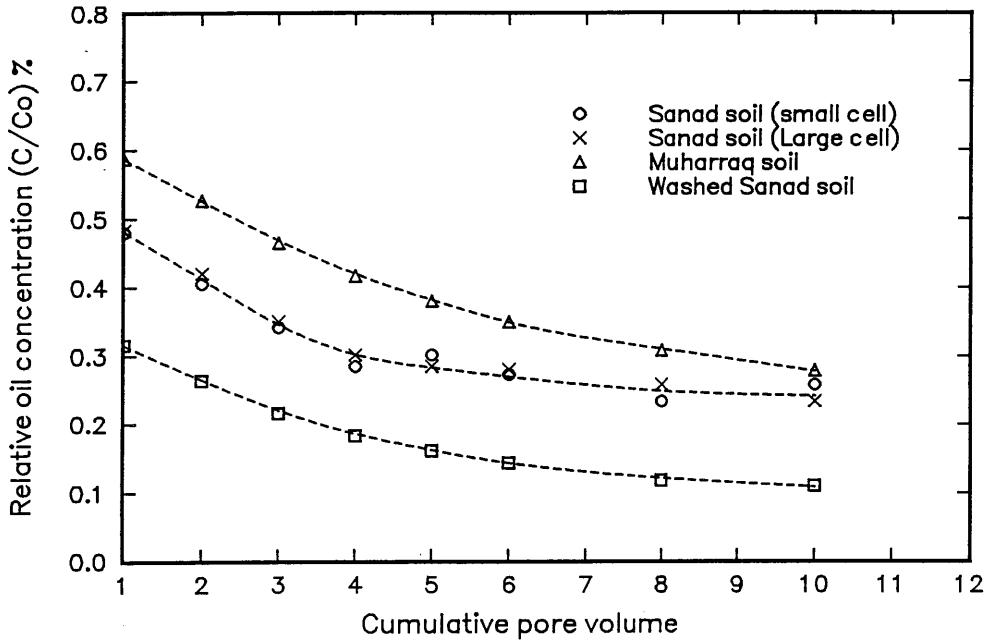


Figure 6.6 - Relative oil concentration in effluents collected from leaching stabilized samples in distilled water.

after the washing process, due to partial removal of soluble ions present in the soil pore fluid. The increase in the surface area of the washed sample is expected to enhance the association of oil onto its surface, resulting in higher oil adsorption and thus lower oil leachability. The infrared results (Section 5.1.2) also revealed the higher association of oil residue onto the surface of the washed soil as compared to the natural one. A similar observation was obtained from the batch equilibrium results (Section 5.2).

The leachability of oil residue is partially attributed to a relatively higher flow rate applied to the samples tested in the laboratory as compared to actual field conditions. The tested samples are subjected to a hydraulic gradient of 14, whereas in the field a much lower gradient is expected, i.e. less than 0.30. A higher flow rate may allow greater momentum to be transferred from the leaching water to the oil in the pore fluid, thereby providing more kinetic energy to reduce the interfacial tensions between the oil, water, and soil. This may enhance the mobility of a large portion of the oil in the soil pore fluid (Mohamed and Yong, 1992). Therefore, a lower oil leachability potential is expected in the field for these samples when subjected to similar laboratory conditions.

6.2.4 Oil Migration

Oil migration profiles, which portray the variation of oil concentration in the soil pore fluid with depth, after one, five, and ten pore volumes of leaching are presented in Figure 6.7. The oil concentration in the soil pore fluid of the three tested samples from the Sanad soil are seen to increase sharply with depth. This significant increase in the oil concentration is noted to increase with pore volumes. The high accumulation of oil at the bottom layers of the soil columns can be expected to be caused by: (i) migration of a portion of the oil from the top layers of the soil-oil mixture, and (ii) reduction in soil permeability due to a partial pore blockage caused by migration of the fine fractions of the soil (Yong, et al., 1991a).

The oil retention isotherm curve for these samples is shown in Figure 6.8, which illustrates the relative percentage of oil retained on the solid phase of the soil in relation to the concentration of oil in the soil pore fluid at equilibrium conditions. It is noted that the isotherm curve increases sharply in the lower oil concentration ranges, followed by a steady value of about 95% oil retention. A similar trend in the oil retention isotherm curve was obtained from the soil suspension test, as discussed previously in Section 5.2.

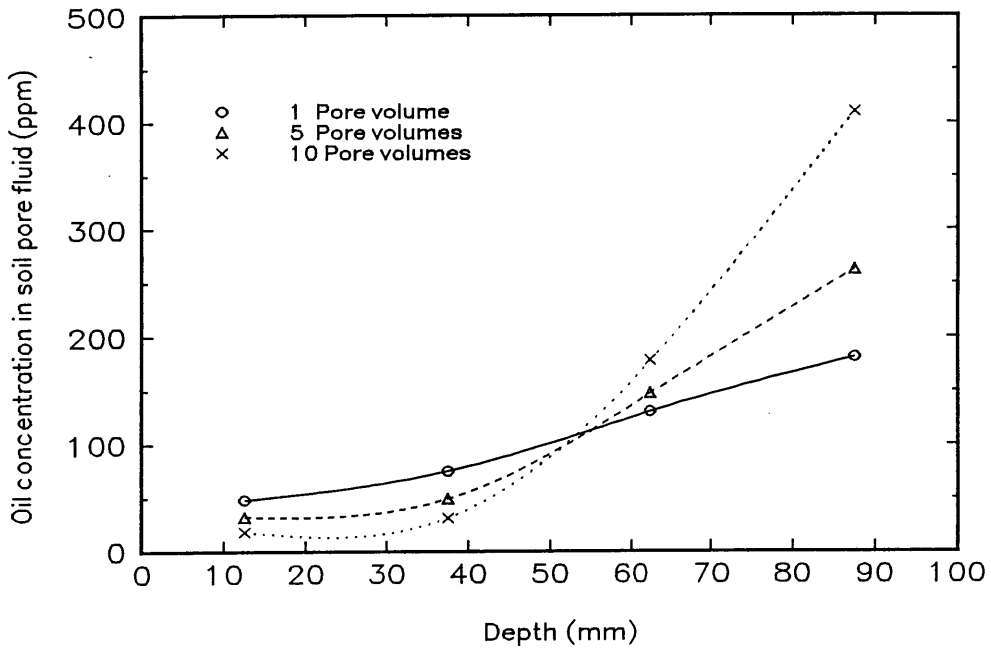


Figure 6.7 - Oil migration profiles in the stabilized Sanad soil as a function of leaching with various pore volumes.

However, the oil desorption isotherm curve for the same samples is presented in Figure 6.9. This figure shows an initial sharp reduction in the oil desorption followed by a steady value of about 5% oil desorption.

6.2.5. Oil Mass Balance

On the basis of oil concentrations detected in different forms, i.e. retained in the soil, present in the soil pore fluid, and leached out, mass balance calculations of the initial oil input is carried out according to a simple algebraic scheme. Results of the oil mass balance in the Sanad soil at the end of one, five, and ten pore volumes of leaching in distilled water (Figure 6.10) indicate that significant amounts of oil are retained in the soil. More than 90% (by weight) of the oil remains in the soil matrix after ten pore volumes of leaching. However, less than 3% of the oil was detected in the collected effluent at the end of the leaching process. A comparison of the initial oil input with the measured oil concentration at the end of one, five, and ten pore volumes of leaching shows respective differences of 2.9%, 3.3%, and 4.3% by weight, for the stabilized Sanad soil. This is likely due to the contribution of volatilization and degradation processes which are not taken into account in the mass balance.

It is useful to estimate the rate of depletion of the oil residue from the soil-oil mixture under the influence of the various transport processes involved, i.e. leaching, volatilization, and degradation. The rate of depletion can be represented in terms of the half-life of the oil residue under the effect of each transport process. If all the transport processes are expressed as a first-order kinetic process, then the half-life of the oil residue can be simply calculated (Mackay and Shiu, 1991). The relative contributions of the major transport processes involved in the depletion of the oil residue can be deduced as shown below. On the basis of 5% volatilization of the oil after 1.5 years of its atmospheric exposure in the laboratory, the half-life of the oil for volatilization is about 20 years. The half-life period of the oil for leaching from the stabilized soil, under a laboratory flow rate of 12 mm/day and based on a relative leached oil of 2.2% over a span of 40 days, is about 3.5 years. The degradation of this oil under the natural soil conditions is expected to exhibit a long half-life period (over one year, (Howard et al., 1991)).

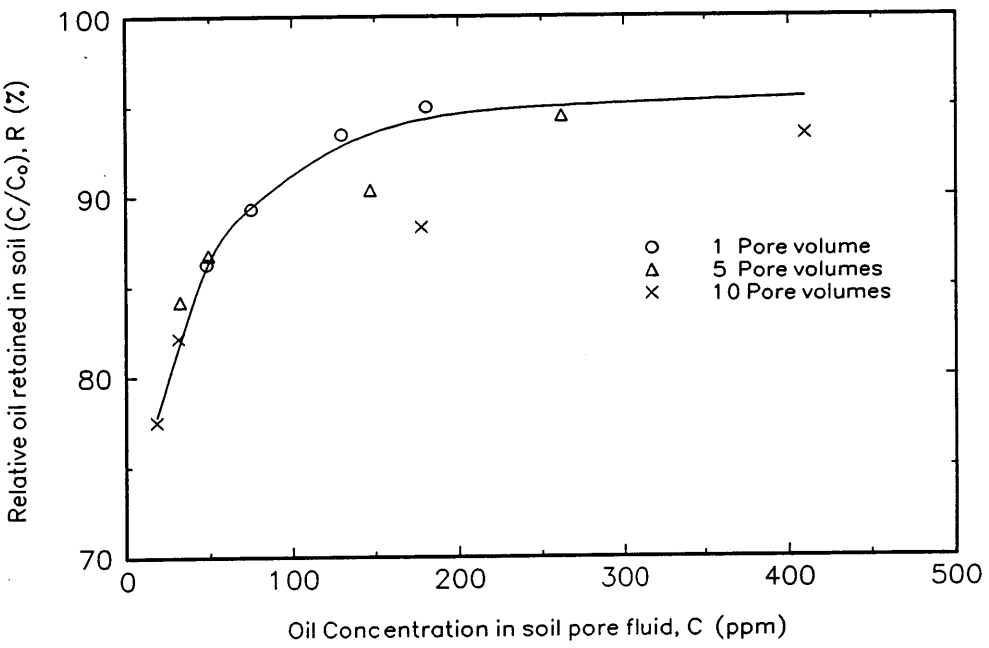


Figure 6.8 - Retention isotherm curve for the stabilized Sanad soil obtained from soil leaching test.

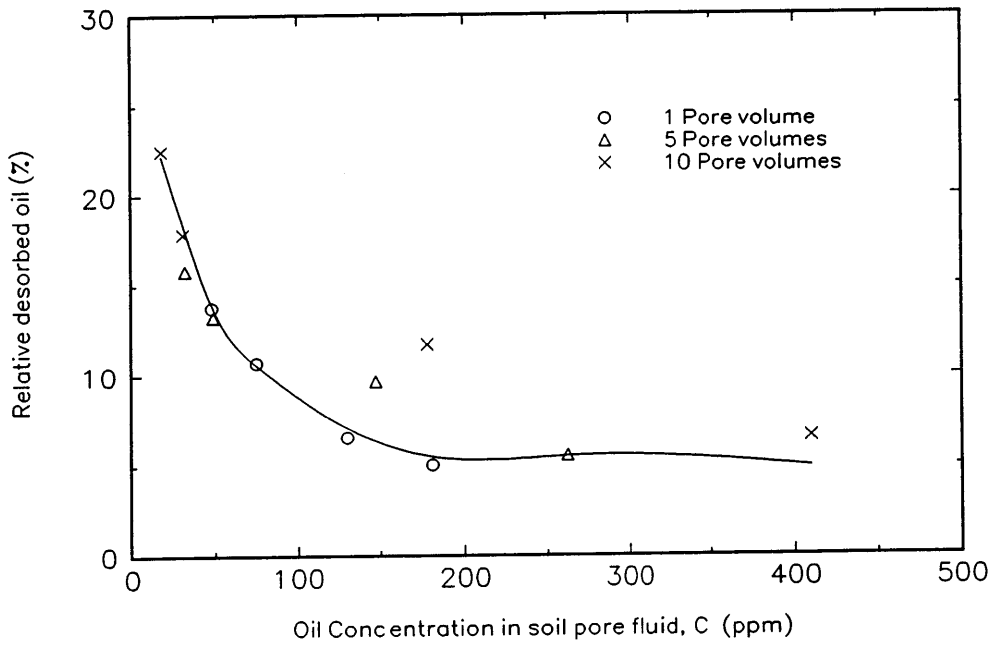


Figure 6.9 - Desorption isotherm curve for the stabilized Sanad soil obtained from soil leaching test.

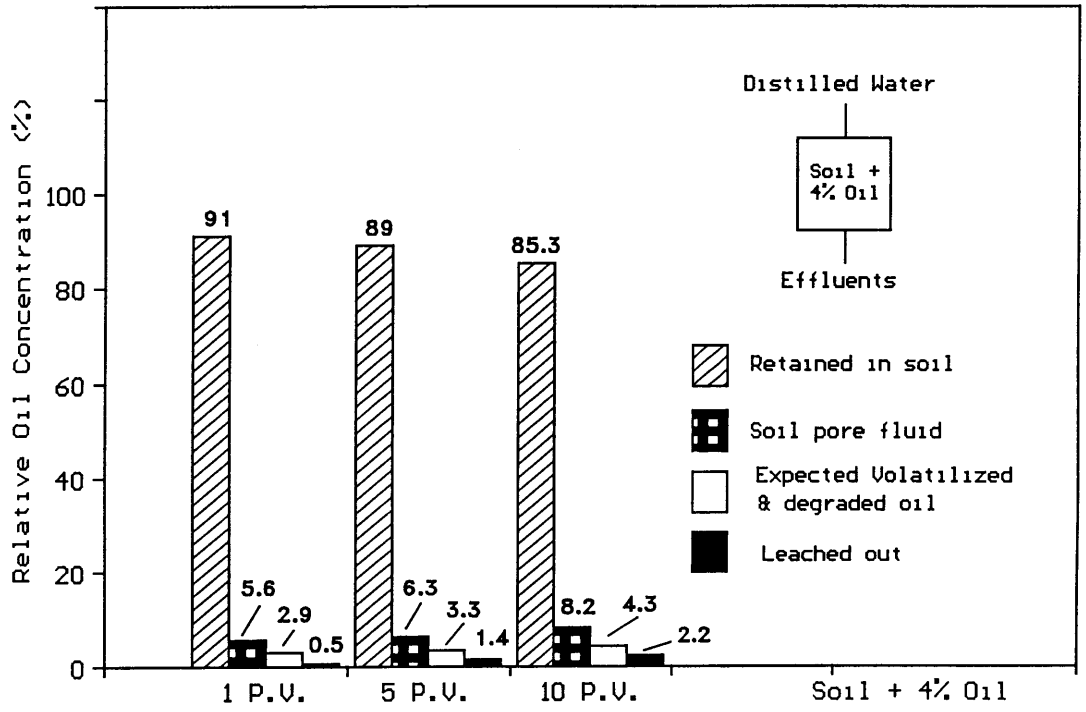


Figure 6.10 - Oil mass balance for the soil-oil mixture from the Sanad soil.

6.2.6 Prediction of Field Oil Leachability

The results obtained from the laboratory leaching tests can be used to predict leachability potential of the oil residue in actual field situations. To estimate the amount of oil penetration into the substrate from the soil-oil mixture due to rainfall infiltration, one can use the average annual precipitation rate in Bahrain (approximately 75 mm/year, (Doornkamp et al., 1980)) and compare this with the laboratory rate. In the case of leaching the stabilized Sanad soil, for example, 2.2 % of the introduced oil by weight was detected in the collected effluents after 40 days (10 P.V.) of leaching in the laboratory at a flow rate of 12 mm/day (4370 mm/year). Extrapolating the laboratory rate to include the low effect of the field rate provides a value of about 2.2% of the oil leaching from the stabilized Sanad soil after approximately 6.5 years of field leaching.

However, since temperature directly affects the physico-chemical properties of oil residue, it is expected to influence the leachability potential of the oil. In Bahrain, where the oil residue is expected to be applied, average temperatures can vary between 18°C in the winter to 35°C in the summer. The rainfall occurs primarily during the winter months, so that the average temperature during the rainfall is very near the tested temperature of 22±2°C. Under the assumption that the oil residue will be applied near the ground surface, it is expected that 2.2% of the oil present in the Sanad soil, for instance, will reach a depth of 100 mm below the ground surface after 6.5 years. Moreover, the clean soil below the stabilized soil is expected to retain most of the leached oil residue before it reaches the aquifers (drinking water source), which are located at more than 40 m below the ground level. The rate of oil movement in the soil matrix is discussed in Chapter 8 on transport modelling.

6.3 Other Transport Processes

The persistence of oil residue in a soil environment is affected by a number of natural processes other than sorption and leaching. These natural processes, which include volatilization, biodegradation, photolysis, oxidation and hydrolysis, tend to occur at very slow rates (or not at all) in subsurface soils. However, hydrolysis, oxidation, and photolysis of most heavy forms of petroleum hydrocarbons, under ambient

environmental conditions are not considered as significant pathways for their transformation in soil environments (Sims and Overcash, 1983; Moore and Ramamoorthy, 1984).

Despite the effect of sorption mechanisms to retard these processes, soil characteristics (e.g. constituents of the solid phase, chemical composition of soil water, biological activity of the soil, etc.) and environmental conditions (e.g. temperature, moisture content, pH, etc.) play a significant role in their contributions. The following sections address in limited details the role of volatilization, biodegradation, and photolysis in the transformation of oil residue in soils.

6.3.1 Volatilization

Oil residue has a potential to volatilize from soil-oil mixtures in a complex manner depending on: (a) oil residue factors such as vapor pressure, melting point, and water solubility, (b) soil factors such as soil temperature, moisture content, and organic matter, and (c) atmospheric factors such as relative humidity, surface wind speed, and solar radiation. Volatilization of the oil residue is significant during its application to the soil and primarily affects the stabilized soil located at the surface zone (Jury, 1986b).

Oil residue contains different classes of petroleum hydrocarbons with a wide volatilization range. The rate of volatilization of the oil residue from soil-oil mixtures depends to a large degree on the type, concentration, and nature of these hydrocarbons. Hydrocarbons with low molecular weights and correspondingly high vapor pressures at ambient temperatures are expected to volatilize highly from the soil. The susceptibility of paraffinic hydrocarbons (Henry's law constant, $K_H < 1$ at 25°C) is higher than aromatic hydrocarbons (Henry's law constant, $K_H < 0.02$ at 25°C, Lyman, 1992).

Volatilization processes involve the removal of the lighter fractions of the oil residue. They include paraffinic with a carbon number less than 18 and aromatics up to 4-ring systems (McGill et al., 1981; Moore and Ramamoorthy, 1984). An increase in oil concentration in the soil system increases the equilibrium vapor density, which in turn increases the volatilization rate. The presence of 4% of oil residue in the stabilized soil is expected to be sufficient to enhance the vapor density of the oil under favourable conditions. Within the various phases of the oil residue, the liquid and dissolved phases

are more susceptible to volatilization than the adsorbed phase (Glotfelty and Schomburg, 1989).

Despite the high melting point and low vapor pressure of the oil residue used in this study, it has a potential to volatilize at a very slow rate. To determine the potential for volatilization of oil residue, triplicate pure oil residue samples were left exposed to the atmosphere (at a temperature of 22±2°C). From the measured changes in their weights (in relation to elapsed time), calculations were made which show that approximately 5% of oil residue by weight will be volatilized over a period of 1.5 years. During the first few months of the oil exposure, a high oil volatilization rate was recorded followed by a steady but insignificant volatilization rate.

Based on the above results and under the assumption that volatilization of oil residue follows the first order kinetic process, the half-life for volatilization of the pure oil residue at 22±2°C is estimated to be 20 years. However, when the oil residue is mixed with soils, under the same environmental conditions, it is expected that the volatilization rate will be lower. This is due in part to adsorption of some of the oil to soil particle surfaces and also to low vapor density of the incorporated oil residue.

To simulate the volatilization potential under actual field conditions, the effect of soil temperature, moisture content, and organic matter should be considered. In arid regions with high temperatures, the volatilization of oil residue from the soil-oil system can be substantial. High summer temperatures (up to an average of 35°C in Bahrain) increase vapor pressure, reduce viscosity, and enhance water solubility of the oil residue. This in turn leads to an increase in the vapor density and thus an increase in the oil volatilization rate. The presence of low organic matter in most arid soils are also expected to enhance volatilization of the oil residue from the stabilized system.

Variations in soil moisture, which is promoted by rainfall or fluctuations in the water table, have a profound effect on volatilization of the oil residue. Stabilized soils with low moisture contents enhance the volatilization rate of the oil residue. Higher moisture contents reduce the air-filled pore space, which reduce vapor density and thereby the volatilization rate of the oil residue from the soil-oil system. However, under dry conditions, the volatilization of oil residue from soil-oil mixtures substantially decreases due to reduction in the vapor density of the oil residue by adsorption on the

dry soil surfaces (Spencer et al., 1982; Frankenberger, 1991; Lyman et al., 1992; Yong et al., 1992).

6.3.2 Biodegradation

Oil residue has the potential to be transformed into a simpler compound (biodegradation) under the action of microorganisms and under appropriate conditions. Biodegradation processes of hydrocarbons in soil systems are dependent upon: the nature of soil micro-organisms, the type and concentration of the hydrocarbon, soil nutrients, moisture content, oxygen status, and soil type. Biodegradation processes can be a significant factor in the breakdown of a portion of the oil residue within soil-oil mixtures, particularly below the surface zone.

Studies (Dineen, et al., 1989; Loehr, 1991; Charbeneau et al., 1992) have shown that the optimum environmental conditions enhancing the biodegradation of petroleum hydrocarbons in soils include: (a) adequate moisture content (15-20 %); (b) the presence of suitable micro-organisms; (c) the presence of soil macro-nutrients (e.g. phosphate, ammonia, and organic carbon); (d) the presence of micro-nutrients (e.g. amino acids and vitamins), (e) warm temperatures (18-30°C); (f) neutral soil pH (6-8), with low salinity (<4 ds/m); (g) aerobic conditions; and (h) sandy soils. Accordingly, the biodegradation of oil residue in the soil-oil mixture in Bahrain is expected to be low due to: (a) low moisture content in the soil leading to dry conditions that drastically decrease biological activities; (b) low amounts of soil macro-nutrients (Bashour et al., 1983); (c) high soil salinity; and (d) a low probability of the existence of suitable microorganisms and micro-nutrients in arid regions.

The rate of biodegradation of oil residue in the stabilized soil is also affected by the type, concentration, and physical state of the hydrocarbons. Hydrocarbons with low molecular weight and simple structure are preferentially degraded. Within the different hydrocarbon classes present in oil residue, their degradation rate in soil systems increase in the order of polycyclic aromatic, aromatic, cycloparaffinic, and paraffinic.

Studies on degradation of petroleum hydrocarbons in soils (Cabridenc, 1985; Hopner et al., 1989; Park et al., 1990; Pitter and Chudoba, 1990) revealed that: (a) branched chains are more resistant to biodegradation than straight chains; (b) alkyl

derivatives are usually degraded more than non-substituted ones; (c) polycyclic with four rings or greater have very low biodegradation rates; (d) the presence of heteroatoms in one cycle and substitution by nitrated radicals, for example, represent obstacles to degradation; (e) the presence of double bonds favours biodegradation; (f) hydrocarbons in a soluble state are more easily degradable than in an adsorbed or immiscible state, whereas a vapor state is not susceptible for biodegradation; and (g) soils with low concentration of hydrocarbon (< 3% by weight) have high biodegradation rates, since high hydrocarbon concentration can severely retard the activities of microorganisms (Ying, et al., 1989).

However, the high molecular weight of the oil residue used in this study and its low solubility in water may further restrict the biodegradation processes. Moreover, a study on the biodegradation of bitumen in tar sands revealed that bitumen is fairly resistant to microbial degradation (Rubinstein at al., 1977).

While the pathways of biodegradation of different constituents of petroleum hydrocarbons may vary, the overall mechanisms involved are similar. The general mechanisms for biodegradation of petroleum hydrocarbons involves the oxidation of the hydrocarbons and the formation of reactive intermediate compounds. The formed compounds can undergo enzymic cleavage followed by further oxidation reactions. The oxidation reactions can proceed to completion (formation of carbon dioxide and water) or terminate at various oxygenated metabolites depending on the media conditions (Connell and Miller, 1984; Moore and Ramamoorthy, 1984).

6.3.3. Photolysis

Photolysis can be significant in arid regions, where a portion of the oil residue in the stabilized system at or near the ground surface can undergo transformation due to absorption of sunlight (solar energy). Photolysis is primarily effective during the application of oil residue to the soil and its occurrence is restricted to the top few centimetres of the soil, since sunlight does not penetrate deeply into the soil. Consideration of the photolysis transformation may be important in order to correctly ascertain the mass balance of the oil residue in the soil-oil system (Valentine, 1986).

Photolysis reactions consist of combined actions of sunlight (energy source) and

oxygen (oxidizing agent) upon transformation of hydrocarbons to another form. Only the sunlight in the near ultraviolet visible range (with wavelength in the range of 290-750 nm) is effective during the photolysis reactions. The energies within the near ultraviolet range (in the order of 100 Kcal/mole) are sufficient to break or restructure some of the chemical bonds in hydrocarbons (e.g. C-H and C-C) (Moore and Ramamoorthy, 1984; Boeve, 1989). Most aromatic and paraffinic hydrocarbons are found to absorb solar radiation and therefore are expected to undergo direct photolysis. Photolysis transformation of petroleum hydrocarbons involves the formation of oxidation products such as oxygenated aromatics, carbonyl compounds, and carboxylic acids, which are more chemically active than the parent compounds (Sims and overcash, 1983).

Photolysis reactions are also influenced by the hydrocarbon characteristics and the environmental conditions. Studies on the photolysis of hydrocarbons in soils are limited. However, there are numerous studies on the photolysis of hydrocarbons in aquatic environments. These studies (Lee et al., 1978; Larson et al., 1979; Eganhouse and Gossett, 1991) have demonstrated that the susceptibility of polycyclic hydrocarbons to photolysis in aqueous media increases for: (a) alkyl types of hydrocarbons; (b) hydrocarbons associated with particulates; and (c) hydrocarbons with a high molecular weight (e.g. chrysene, benzanthracene).

However, in general, the low-molecular weight hydrocarbons can be also susceptible to photolysis. The high volatility and solubility of most low-molecular weight hydrocarbons are expected to increase the extent and rate of photolysis, if the interference of the other transport processes is insignificant. Moreover, in a soil-hydrocarbon system, the vapor and soluble phases of the hydrocarbon are expected to be more susceptible to photolysis than the adsorbed phase. A study by Yokley et al. (1986) has shown that some polycyclic aromatics hydrocarbons (e.g. pyrene and benzo[a]pyrene) are more resistant to photolysis when adsorbed on stack ashes.

Previous studies (Valentine, 1986; Miller et al., 1989) have reported that the optimum environmental conditions for photolysis of hydrocarbons in soils increase with: (a) application of hydrocarbons at the ground surface; (b) intense solar radiation, as in Bahrain (Al-Sadah and Ragab, 1991); (c) a good aeration site and a high oxygen concentration; (d) high concentrations of hydrocarbon (e) high temperatures; (f) the

presence of photosensitizing agents (e.g. organic matter, ferric salts), which are expected to enhance the indirect photolysis of compounds with less ability to absorb sunlight; and (g) low moisture content, since excess moisture content limits oxygen availability and hence reduces the photolysis rate. Accordingly, it is expected that the photolysis of oil residue mixed with the upper portion of the soil in Bahrain would contribute in the transport of the oil residue.

6.4 Environmental Considerations

The performance of the tested stabilized soils from Bahrain under certain conditions was experimentally evaluated in the previous chapters. However, to accommodate for the field situations, some of the environmental considerations which are not directly taken into account in this study are discussed herein. These environmental considerations, which are expected to affect the behavior of oil residue in these soils and are critical to its application in Bahrain, include temperature and toxicity effects.

6.4.1 Temperature Effects

All the laboratory experiments were performed in this study at a room temperature of 22 ± 2°C. However, field conditions in Bahrain, where the oil residue is expected to be applied, differ slightly. The average temperature can vary from about 18°C in winter to more than 35°C during the summer (Doornkamp, et al., 1980). Because of such differences in temperature, particularly during the summer season, it is necessary to examine the effect of temperature on soil behavior. Whereas the behavior of the stabilized soils during the rainy season (winter) has been tested in the laboratory, their behaviors during the hot season (summer) are approximated below. A number of studies (Jury, 1986a; Lyman, et al., 1992; Yong et al., 1992) have been reported on the influence of temperature on the properties and characteristics of soils. Some of the conclusions reached in these studies are summarized herein.

Soil temperature is known to affect the properties of both oil residue and soil as well as the transformation rates associated with the natural processes involved in the soil

media. The response of soils to temperature effects varies depending on soil depth, soil type, and moisture content. Temperature primarily affects the soil at the surface zone (within the top 0.5 m). Sandy soils are strongly influenced by temperature variation due to their high ability to transmit heat as compared to clayey soils. The presence of water in the soil-oil mixture ameliorates temperature extremes because of the high heat of vaporization of water (Kemp, 1992; Lyman, et al., 1992).

Due to the complexity of the temperature dependence on the overall performance of the natural processes in soil-oil mixtures, the effect of temperature on the individual process is considered separately. The major natural processes involved in unsaturated soil-oil mixtures include adsorption, leaching, and volatilization. Increasing temperature causes an increase in the vapor pressure and water solubility of the oil residue, especially the non-aqueous phase liquid, which directly affects the oil concentration in the soil voids. This in turn is expected to enhance the interaction mechanisms and may increase the adsorption capacity of oil onto soil surfaces. Moreover, temperature variations have four distinct effects on the adsorption process: vapor-surface interaction effects, solute-surface interaction effects, vapor-atmosphere interaction effects, and solute-water interaction effects. The difference between the first two effects and the last two effects will determine the direction of dependence of the temperature. The first two effects usually contribute to the increase in oil adsorption onto soil surfaces (Jury, 1986a).

High temperatures, within a natural range, are expected to favour the intercalation phenomena of the oil residue, due to their disruptive effect on the oil structure, and may initially enhance the surface-interaction forces (Raussell-Colom and Serratosa, 1987). The acceleration in the chemical reactions between the soil surfaces and oil solution or vapour with temperature can also be another contributing factor in enhancing interaction and adsorption phenomena. This is mainly due to alteration in the soil structural arrangement and increase in the solubility and volatilization of oil with temperature. For instance, Yaron (1989) has studied the effect of temperature (up to 34°C) on the adsorption of selected petroleum hydrocarbons (e.g. m-xylene, n-decane, and n-butyl-benzene) on different soils (sandy and clayey soils). The study showed that the adsorption of both aliphatic and aromatic components of the tested hydrocarbons increases with an increase in soil temperature. The increase of oil adsorption onto soil

surfaces is attributed to the reasons explained above.

However, an increase in temperature decreases the physical forces held under the capillary action (i.e. surface tension forces) and oil density and viscosity, as explained previously in Section 4.3 on the rheological performance. This corresponds to a slight decrease in the long-term liquid-surface interaction forces (Lyman, et al., 1992). In general, the effect of temperature on adsorption is a direct indication of the strength of the adsorption; therefore, the weaker the bond the less is the influence of temperature (Jury, 1986a).

The partitioning coefficients of oil residue in unsaturated soil-oil mixtures are also sensitive to temperature changes. Emphasis on two types of partitioning coefficients, i.e. adsorption coefficient and Henry's law constant, are considered here. Since adsorption is an exothermic process (heat-producing), adsorption coefficients (K_p) of most compounds, involving partitioning between dissolved and/or vapor and adsorbed phases, are expected to decrease with an increase in temperature (Yong et al., 1992). However, a number of studies have found that changes in adsorption coefficients of neutral organics onto soil surfaces are insignificant for ambient temperature variations beyond a factor of two (Lyman et al., 1992).

Henry's law constant (K_H), involving partitioning between dissolved and vapor phases, increases with an increase in temperature due to the increase in vapor density of the oil residue with temperature. This in turn enhances the potential for oil volatilization from the soil-oil mixtures. Most organics will partition proportionately more of their total mass into the vapor phase than the liquid phase at higher temperatures. Thus, the vapor diffusion is much more strongly enhanced by increases in temperature than the liquid diffusion. In general, the transport of oil residue by both mechanisms will increase with temperature for the reasons explained above (Jury, 1986b; Jury, 1986c, Yong et al., 1992). Under dry soil conditions, typically during the summer season in Bahrain, vapor diffusion and adsorption of the vapor phase of the oil residue onto soil surfaces are expected to be the most significant processes in soil-oil mixtures. However, the liquid diffusion phenomenon is anticipated to be dominant during the winter rainy season.

Besides the physico-chemical effects, temperature can also influence the

mechanical properties of the stabilized soils, e.g. soil-fluid potential, permeability, and strength. The increase in temperature is expected to reduce the fluid retention capability (Mohamed et al., 1992) and slightly increase the oil leachability potential. A rise in temperature reduces the dielectric constants of the fluids, thereby resulting in a reduction in the Gouy electrical double layers formed in the oil-soil-water system. This can lead to an increase in the attractive forces of the system and a tendency towards a flocculated structure with a high soil permeability potential (Mohamed et al., 1992; Yong et al., 1992). The substantial reduction in the viscosity of the oil and capillary forces with temperature, mainly above 50°C, can also contribute in increasing the oil leachability, particularly the non-aqueous phase liquid (Lyman et al., 1992).

The variation of the mechanical properties of soils with temperature depends strongly on the conditions in which the soils are subjected to (e.g. saturation and aging conditions). For instance, under wet conditions, an increase in temperature causes a decrease in the initial shearing strength of most soils, due to a reduction in the effective stress and cohesive and frictional properties of the soil with temperature (Dunn and Salem, 1973). As a consequence, a partial collapse of the soil structure and a change in the void ratio occurs, until a sufficient number of additional bonds are formed to enable the soil to carry the stresses at the higher temperature (Dunn and Salem, 1973; Mitchell, 1993). However, the increase in temperature under dry conditions has been found to enhance the long-term strength performance of the soil-oil mixtures (Dunn and Salem, 1971).

6.4.2 Toxicity of Oil Residue

In this section, the toxicity potential of the oil residue based on literature reviews is summarized. It is important to consider the toxicity of oil residue in the stabilized soil because of its potential to cause acute or chronic effects, depending on its concentration. The toxicity of oil residue in the environment is hard to follow as a result of detection and separation difficulties during its various phases. Oil residue has been found to possess weakly semi-volatile, highly hydrophobic, low soluble, and slightly degradable properties. Consequently, one expects the oil residue to have high retention capability in soils at the concentrations used in this study (i.e. 4%, w/w), and thus lower toxicity

potential (McGinnis et al., 1992). However, further studies toward such conclusions need to be performed.

In this study, stabilization of soil with oil residue is expected to be used in arid regions such as Bahrain, where rainfall is low even during the relatively wet winter season. During the dry seasons (spring, summer,and fall), the stabilized soils are expected to retain most of the oil residue. However, during the winter season, it is expected that the effect of rainfall would provide the opportunity for the migration of oil residue from the stabilized soils. In addition, fluctuations in the water table can have a profound effect on oil migration. These situations can pose a threat to the surrounding environment in the form of groundwater and surface water contamination. Since oil residue contains toxic substances (hydrocarbons and heavy metals), its leachability from the stabilized soils can cause a significant threat to human health and other living creatures.

Oil residue is a complex mixture of several chemical classes that are potential health hazards. To assess the toxicity of the oil residue, consideration is made of the toxicity of the individual classes, as reported in the literature. The toxicity of these classes is highly variable, depending on the chemical type and concentration, the level of human exposure, and the environmental conditions. Various chemical classes of oil residue have different levels of toxicity, which increase in the following sequence: paraffins, cycloparaffins, heterocylics, heavy metals, and aromatics (especially polycyclic aromatics). In general, the higher is the mobility of a certain contaminant in soil media, the higher is considered its toxicity potential in the environment. For instance, within each hydrocarbon series, the larger molecules with high carbon numbers are considered less toxic than both the smaller molecules and the halogenated types. In addition, in paraffinic hydrocarbons, the straight chain structures are more toxic than the branched chain structures. However, the angular structures of polycyclic aromatic hydrocarbons possess higher toxicity than the linear structures (Moore and Ramamoorthy, 1984).

Aside from short-term toxicity, the greatest concern about the chemical classes present in oil residue is their carcinogenic potential. Long-term exposure to high concentrations of oil residue can cause a significant carcinogenic risk. Previous studies (Bingham et al., 1980; Gilbert and Calabrese, 1989) have reported that heavy forms of

aliphatic hydrocarbons (paraffinic and cycloparaffinic) are not carcinogenic when acting alone. However, some of these aliphatics (e.g. n-hexadecane, octadecane) are found to enhance the carcinogenic activities in the presence of polycyclic impurities.

Several studies (Gilbert and Calabrese, 1989; Onuska, 1989) have reported that a number of polycyclic aromatics present in oil residue (e.g. naphthalene, phenanthrene) have non-carcinogenic activity. These studies have also found that the polycyclic aromatics with four to six rings (e.g. dibenzathracene, pyrene, chrysene) are usually responsible for their carcinogenic behavior. Most of these aromatics, with four rings or greater, are not found to be toxic within the limit of their solubility. However, since even some of these chemical classes are either known or suspected carcinogens, their concentration in groundwater, as recommended by CCREM (1992) for maximum protection of human health, should be zero.

Another constituent of the oil residue includes aromatic heterocyclic compounds and heavy metals. The heterocyclic compounds have not been classified as carcinogenic because of the insufficient studies in this field. However, studies on the toxicity of quinoline (nitrogen heterocycle) and thiophene (oxygen heterocycle) to mammals revealed their potential for significant toxic risks (Gilbert and Calabrese, 1989; Sims and Overcash, 1983).

The toxicity of the heavy metals can vary widely depending on their type and concentration, and the pH and redox condition of the soil. The low content of heavy metals present in this oil residue (vanadium, nickel, iron, and lead) reduces their toxic potential. The toxicity of these metals to mammals is found to increase in the order of vanadium, iron, nickel, and lead (Connell and Miller, 1984). Moreover, since a portion of the oil residue in the stabilized soils can undergo degradation (photo or microbial), there is a potential for the formation of new intermediate compounds. The formed compounds usually possess different physico-chemical properties and can be more toxic than the parent compound (oil residue).

A large portion of the oil residue consists of neutral organic chemicals (such as aliphatic and aromatic hydrocarbons), which exhibit neutral behavior at the natural soil pH in Bahrain of 7-8.5. Neutral organics are known to be less toxic than organics with more specific modes. In addition, the large molecular weight of the oil residue and its

high octanol/water ratio have the potential to reduce its toxic effects. Studies (Nabholz et al. 1993) have reported that compounds with a molecular weight greater than 1000 and an octanol/water ratio greater than 5 possess very low toxic effects. As the octanol/water ratio increases (or as the compound becomes more insoluble in water), the amount of excess toxicity decreases.

The presence of a saline environment, such as in Bahrain, reduces the solubility of the oil residue and hence lower its toxicity potential. Further, the low content of the leached oil in the tested soils, together with the depth of the aquifers (at least 40 meters below ground level (Doornkamp et al., 1980)) in Bahrain, suggests that the potential for contamination of the aquifers is low.

CHAPTER 7
ASSESSMENT OF THE EXPERIMENTAL RESULTS

Detailed experimental studies on the performance of oil residue in two sandy loam soils from Bahrain have been presented in the previous chapters. Emphasis was placed on assessing the geotechnical, geochemical, and environmental aspects of the oil residue in these soils. A summary of the experimental results obtained in this study in relation to different influencing conditions are discussed herein. These conditions take into account the effects of oil residue, leaching forces, soil salinity, and soil washing on the overall performance of the stabilized soils.

7.1 Oil Residue Effects

The presence of oil residue in the tested soils has two main effects on the soil properties. Physical properties (e.g., strength performance and fluid-holding capacity) are shown to substantially change, likely due to a potential alteration in the soil fabric and the development of additional adhesive bondings. Soil surfaces will also vary due to the presence of oil coating and bonding, thus inducing changes in the soil chemical properties.

A summary of the experimental results in relation to the effect of oil on the soil performance is presented in Tables 7.1 and 7.2, for the Sanad and Muharraq soils, respectively. As can be seen from these two tables, the unconfined compressive strength and total shear strength of these soils were significantly increased, with 4% oil residue (w/w). The cohesive component of the soil strength was shown to increase by more than 150% from the strength of the non-stabilized soil, when mixed with 4% oil residue. This is mainly attributed to the addition of oil cementation bonds (Section 5.1.2) and improvement in the soil packing condition (Sections 4.1.1.a and 5.1.3). However, the presence of 4% oil residue was shown to slightly reduce the frictional resistance and CBR value of these soils; less than 20% reduction was observed in these properties. The increase in the fluid content of the stabilized soils, due to the presence of "lubricating"

Table 7.1 Comparison of soil performance from the Sanad site before and after stabilization with oil residue.

Test type	Soil sample, oil content (%)		
	Natural, 0%	Stabilized, soil + 4%	Stabilized with 6%, 8%, 12%
Compaction γ_d (Mg/m^3) w (%)	1.78 14.00	1.71 13.50	1.62±0.05 12.50±0.50
Permeability (m/sec)	$20x10^{-8}$	$1x10^{-8}$	....
UC test q_u (KPa) σ-ϵ curve Direct shear C (KPa) ϕ (°) CBR CBR (%), at 5mm penetration	118 flat slope (less packed) 10 32 37	357 steep slope (well packed) 25 29 29	278, 246, 117 reduction in curve slope ....
Infrared	Presence of O-H, Si-O, and CO_3^{2-} groups.	Introduction of C-H group and slight shifts (~-5 cm^{-1}) in the frequencies of the interactive groups of the natural soil.	Increase in intensity of C-H group and insignificant change in the frequencies shifts and intensities of interactive groups.
Soil suction	Stabilized soil with 4% oil retains slightly more fluids (~8%) at higher suction but less (~6%) at low suction.		Slight reduction in the overall fluid-holding capacity.
Soil leaching Leached salt	Stabilized soil with 4% oil leached slightly higher salt (~15%) than natural soil.		....

- All the stabilized soils were prepared by first mixing the oil residue with the soil then water.
- Soil stabilized with 4% oil residue was compared to the natural soil, whereas soil mixed with more

Table 7.2 Comparison of soil performance from the Muharraq site before and after stabilization with 4% oil residue.

Test type	Soil sample, oil content (%)	
	Natural, 0%	Stabilized, 4%
Compaction γ_d (Mg/m^3) w (%)	1.82 12.50	1.75 12.00
Permeability (m/sec)	$85x10^{-8}$	$6x10^{-8}$
Unconfined compression q_u (KPa) Stress-strain curve Direct shear C (KPa) ϕ (°) CBR value (%), at 5 mm penetration	 64.00 flat slope 8.50 33.00 45.00	 297.00 steep slope 32.00 27.00 36.00
Infrared	Presence of O-H, Si-O, and CO_3^{2-} groups.	Introduction of C-H group and slight shifts in the frequencies of the natural soil interactive groups.
Suction	Reduction of about 10% in the overall fluid-holding capacity of the stabilized soil, indicative of an increase in its water-repellent characteristics.	
Soil leaching Leached salt	Stabilized soil leached slightly higher salt (~6%) than the natural soil.	

fluid (oil residue), is considered responsible for such reductions.

The presence of 4% oil residue in these soils was shown to slightly reduce their fluid-holding capacities (Section 5.1.3). This in turn enhances the water-repellent characteristics of the stabilized soils and improves the potential for satisfying the soil surface charges. The reduction in the fluid-holding capacity of the stabilized soils is likely attributed to a decrease in the double layer thickness formed in the oil-soil-water system, as explained in Section 5.1.3 on soil fluid retention characteristics. Since both natural and stabilized soils were tested at a well-compacted condition and consist predominantly of sand, the variation of their fluid retention characteristics was found to be relatively small.

Nevertheless, the increase in the oil residue content beyond 4% was shown to reduce the strength properties of these soils and the fluid-holding capacities. The presence of 4% oil residue in the soils was found to sufficiently cover the entire surface, satisfy their charges, and provide the necessary bonding between the oil residue and soil (Sections 4.2 and 5.1.2). However, as the content of oil residue increases, insignificant bondings were observed from the infrared results (Section 5.1.2). In addition, at high oil contents, the oil starts to fill in the soil pores and acts as a "lubricant", separating the soil particles. At this stage, the consistency of the soil-oil mixtures becomes too plastic and loses strength.

The results of the soil suspension and soil leaching tests revealed substantial oil retention in the tested soils (Sections 5.2 and 6.1.4). The soil suspension results showed that about 75% of the introduced oil (by weight) was retained in the stabilized soils, containing 4% oil residue, after 24 hours of shaking in distilled water. This can be attributed to the nature of bonding formed between the oil and soil surfaces. Also, the retention of oil in these soils was found to be slightly enhanced in the presence of saline medium for the washed soil. From the soil leaching results, the concentration of salt leached from the soil systems was shown to be slightly higher in the stabilized soils (with 4 % oil residue) than in the natural soils (Section 6.2.1).

Results of the infrared test (Section 5.1.2) indicated that the formed bondings, which are primarily responsible for strength improvement, include: Van der Waal's attraction, weak hydrogen bonding, and water and cation bridging. These bonds are

found to be relatively weak but stable and insensitive to leaching forces. Moreover, despite the potential of soil to adsorb oil at a slightly higher content then 4% (Section 5.2), insignificant changes in the bonding mechanisms are associated with strength improvements.

7.2 Leaching Effects

Leaching forces have significant effects on the behavior of the soils and their mixtures with oil residue. To assess these effects, various sets of soil leaching tests, together with other experimental tests (e.g., unconfined compression, California bearing ratio, soil suction, and infrared) were performed. In these experiments, the unleached samples were tested under unsaturated conditions immediately after preparation, while the leached samples were tested under saturated conditions at the end of the leaching period. A comparison between the performance of the leached natural soils and leached stabilized soils are presented in Table 7.3 for the Sanad and Muharraq soils, and in Table 7.4 for the washed Sanad soil.

The geotechnical tests revealed that leaching forces resulted in substantial reductions in the strength performance (unconfined compressive strengths (q_u) and CBR values, Tables 7.1 and 7.3) and fluid retention characteristics (Section 5.1.3) of the tested natural and stabilized soils. This is mainly due to alterations in the internal stability of the soil mass during leaching. Consequently, the interparticle forces and bonds and soil density and fabric are expected to be affected.

As noted previously, the increase of the cohesive component of the soil strength due to the addition of oil residue can be attributed mainly to cementation effects and interparticle forces effects. Due to the presence of high initial salt content and low content of active constituents (i.e., clays) in these soils, the contribution of salt and oil residue (which act as cementing agents) in enhancing the soil strength is expected to be more significant than the effects of the interparticle forces. Moreover, Mitchell (1993) reported that cementation bonds exhibit much higher strength (i.e., cohesive strength) than the interparticle forces. Leaching forces are also expected to weaken the soil fabric and reduce the sliding forces between the particles, resulting in lower frictional

Table 7.3 Comparison of performance of leached soil samples before and after stabilization with 4% oil residue.

Parameters	Sanad soil		Muharraq soil	
	Natural	Soil + 4% oil	Natural	Soil+ 4%oil
Saturated condition				
γ_d (Mg/m^3)	1.74	1.70	1.77	1.73
w (%)	17.00	14.00	16.00	13.00
q_u (KPa)				
Distilled water	90.00	180.00	52.00	152.00
Saline water	110.00	140.00	70.00	132.00
CBR values (%)				
Distilled water	11.00	13.00	24.00	31.00
Saline water	18.00	10.00	40.00	21.00
Soil leaching				
Oil retained onto surface (%)	...	91.00	...	87.00
Leached oil (%)	...	2.20	...	2.80
Leached salt (%)	56.00	65.00	42.00	45.00
Infrared	Similar interactive groups. Slight reduction in intensities of these groups for stabilized leached soils as compared to natural leached soils and appearance of C-H group in the stabilized samples.			
Fluid-holding capacity	Stabilized leached samples showed an increase of ~ 10% in their fluid-holding capacities as compared to natural leached samples. Fluid-holding capacities of samples leached with saline water was slightly reduced as compared to same samples leached with distilled water.			

- All leached samples were tested after 10 pore volumes of leaching (at end of ~ 40 days of leaching).

Table 7.4 Comparison of washed soil performance from the Sanad site before and after leaching in distilled water.

Parameters	Before leaching		After leaching	
	Washed soil	Washed soil + 4% oil	Washed soil	Washed soil + 4% oil
γ_d (Mg/m^3) w (%)	1.35 29.00	1.30 27.50	1.20 42.00	1.16 38.00
q_u (KPa)	104.00	233.00	76.00	112.00
Fluid-holding capacity	Slight reduction (~ 6%) in the fluid-holding capacity of leached stabilized soils as compared to same unleached soils, indicating that stabilized samples retain most of adhesive bonds.			
Infrared	Leaching stabilized samples showed insignificant changes in the frequencies and intensities of interactive groups as compared to same unleached samples, indicative of insignificant changes in the formed bonds due to leaching forces.			

resistance. However, since the tested samples are well compacted and consist predominantly of sandy soils, the effect of leaching on soil density and fabric is found to less significant (Yong and Warkentin, 1975).

In all the tested samples, the leached stabilized samples showed significantly higher unconfined compressive strength and fluid-holding capacity than the leached natural soils. This is mainly as a result of the contribution of the cementation bonds introduced in the presence of oil residue, which have been found to enhance the soil performance under saturated conditions. The results of both soil suction and infrared tests indicated that the tested soils retained most of these cementation bonds after the leaching process (Sections 5.1.2 and 5.1.3). Moreover, the stabilized samples were shown to possess lower values of water content (about 15%) compared to their natural water content after the leaching process, indicative of their potential toward water-repellent characteristics.

Results of the leaching tests revealed that the tested soils retained most of their oil residue; more than 90% of the introduced oil (by weight) was retained in the soil matrix at the end of the leaching period. Moreover, the oil retention capability was found to be enhanced in the case of the washed soil and the soil leached in a saline water. Consequently, oil leachability potential was significantly reduced in the preceding two cases. In addition, the amount of leached oil detected in the effluents after 40 days of leaching with distilled water was relatively low; less than 3% of the oil (by weight) was detected. These observations provide a good agreement with the soil suspension results presented in Section 5.2.

The characteristics of the leached samples are strongly influenced by the chemical composition of the permeating solutions. In this study, two types of permeating solutions were employed: distilled water and saline water. Leaching with distilled water was shown to considerably reduce the strength characteristics and fluid retention capabilities of the tested soils. This is mainly attributed to dissolution of some of the salt present in these soils, resulting therefore in partial removal of the cementing associated with it. However, the modest reduction (about 10%) in the soil density of the washed soil due to leaching forces (Table 7.4) suggests the potential contribution of the interparticle forces in the soil strength performance. This is because the washed soil was shown to

possess higher surface activity and lower initial dry density than the corresponding unwashed soil from the same site (Table 3.1).

However, leaching the natural soils in a saline water was shown to cause insignificant changes to their strength characteristics. Despite the potential for precipitation of additional salts present in the permeating solution onto soil surfaces and in soil pores (which can enhance cementation), the initial salt content seems to be sufficient to maintain acceptable strength performance, provided the salt can be retained in the soil matrix. In contrast with the natural soils, the stabilized soils have shown a substantial reduction in their strength performance when leached in saline water. Such a reduction is partially due to the interference of salt, present in the leaching solution, with the physico-chemical processes involved between the soil surfaces and the oil residue. In addition, modest reductions in the fluid retention capabilities of all tested samples were observed. The contribution of salt in reducing the double layer thickness formed in the soil-fluid system is likely responsible for such a reduction.

7.3 Salinity Effects

The presence of high salt content in the tested soils was shown to affect the behavior of oil residue in the oil-soil-water mixtures. This may result from an interference of salt with the natural processes involved in the soil media, e.g., adsorption, interaction, leaching, volatilization, and biodegradation. Thus far, natural disturbed soils have been used in this study, which already contain high salt contents. Here, the influence of salt on the behavior of the oil-soil-water system is considered. Two different aspects of salt effects are examined herein; the effect of initial salinity of the soil and the effect of salinity of the soil pore fluid on the behavior of the stabilized soils.

A reduction in the initial salinity of the soil, due to the washing process, has been shown to strongly affect the properties and characteristics of the tested soil from the Sanad site. Among the affected properties recorded in this study are: (a) a significant increase in the plasticity of the soil (Table 3.1); (b) a substantial reduction in the maximum dry density of the soil and a significant increase in the soil optimum moisture

content (Table 3.1); (c) a significant increase in the surface area of the soil (Table 3.1); (d) a substantial increase in the fluid retention capability and a potential change in the soil fabric (Section 5.1.3).

As a result of these changes in the soil properties due to the washing process, the following is noted: (a) the unconfined compressive strength (q_u) of the stabilized washed soil was found to be lower than the stabilized unwashed soil (Section 4.1.1.c), (b) the oil absorptive potential and oil retention capacity of the washed soil were slightly enhanced in comparison with the unwashed soil (Sections 5.2 and 6.1.4), and (c) the oil leaching potential from the stabilized washed soil was found to be significantly reduced as compared to the stabilized unwashed soil (Section 6.2.3).

The effect of the salinity of the soil pore fluid on the performance of the natural and stabilized soils from the Sanad site is summarized in Table 7.5. These tabulated results compare the performance of the leached soils in saline water with the performance of the same soils leached with distilled water at the end of the leaching period. The influence of the soil pore fluid salinity on the soil strength, fluid retention, oil desorption, oil retention, and oil leaching characteristics have been presented in Table 7.5.

As can be seen from Table 7.5, an increase in the strength performance (i.e., q_u and CBR values) of the natural (unwashed) soil is noted at high salinity of the soil pore fluid. An increase of approximately 20% was observed in the q_u value of the natural leached soil in saline water as compared to the same soil leached with distilled water. This is likely attributed to the addition of salt cementing bonds precipitated in the soil pore fluid during leaching in saline water. Nevertheless, the presence of excess salt in the pore fluid seems to reduce the strength performance of the stabilized soils. A reduction of about 20% was noted in the q_u value of the stabilized soil leached in a saline water as compared to distilled water. This can be as a result of a potential interference of the salt with the adhesive bonds formed in the presence of oil. In addition, the slight reduction in the fluid-holding capacity of the stabilized samples observed in the presence of high pore fluid salinity (Table 7.5) suggests the potential reduction in the double layer thickness formed in the oil-soil-water system at higher salt concentrations. This can lead to a tendency towards a flocculated structure possessing a lower strength performance (Yong and Warkentin, 1975; Yong et al., 1985).

Table 7.5 Effect of soil pore fluid salinity on performance of natural and stabilized soils from the Sanad site.

Parameters	Leached in distilled water		Leached in saline water	
	Natural	Soil + 4% oil	Natural	Soil + 4% oil
γ_d (Mg/m^3)	1.74	1.70	1.75	1.70
w (%)	17.00	14.00	16.00	13.50
q_u (KPa)	90.00	180.00	110.00	140.00
CBR values (%)	11.00	13.00	18.00	10.00
Soil suspension				
Oil retained in soil matrix (%)	...	77.00	...	85.00
Desorbed oil (%)	...	20.00	...	12.00
Soil leaching				
Oil retained onto surface (%)	...	85.00	...	91.00
Leached oil (%)	...	2.20	...	< 1.00
Fluid-holding capacity	Insignificant changes in fluid-holding capacity were observed for the natural soil samples leached in distilled water as compared to the same soil samples leached in saline water. Slight reduction (~ 7%) in the fluid-holding capacity of stabilized samples leached in saline water as compared to the same samples leached in distilled water.			

Despite the decrease in the strength of the stabilized soils in the presence of excess salts, the oil absorptive and retention capacities of the tested soils are shown to be slightly enhanced in a saline environment (Table 7.5). An increase of approximately 7% was observed in the oil retention capacity of the stabilized soil leached in saline water as compared to the same sample leached with distilled water. The increase of hydrocarbon adsorption on soil surfaces in a saline medium has been reported previously in a number of studies (Yong and Rao, 1991; Yong, et al., 1992). Karickhoff et al. (1979) found that the adsorption of pyrene on a silty soil in a saline solution, containing 20 mg/ml of NaCl, increases by 15% over the non-saline solution; studies by Meyers and Quinn (1973) and Meyers and Oas (1978) on the association of different hydrocarbons with soils in a saline solution confirmed these findings. The increase in the hydrocarbon adsorption is explained in these studies as a result of the reduction in the electrostatic repulsions between the soil surfaces and hydrocarbons in the presence of salt (Lagaly, 1985). The effects of surface charge variation, ion condensation, ion exchange, and ion bridging reactions also have significant roles in enhancing the adsorption phenomenon (Chauveteau, 1991; Fox, 1991).

The presence of salt in the oil-soil-water system is found to slightly reduce the fluid-holding capacity of the tested soils (Table 7.5). The reduction in the fluid-holding capacity of the stabilized soil is noted to be slightly higher than in natural soil. This is because the presence of salt has a potential to suppress the electrical double layer formed in the soil-fluid system, leading to a lower fluid retention capability. In addition, salt enhances the osmotic potential of the soil-fluid system, which also contributes in a further reduction in the soil-fluid potential (Yong and Warkentin, 1975; Yong et al, 1985). The presence of oil residue in the stabilized soils also enhances such reduction in fluid retention characteristics (Section 5.1.3; Hillel, 1971).

The oil desorption potential from the stabilized soil is shown to slightly reduce under saline conditions (Table 7.5). A reduction of approximately 40% was observed in the concentration of the desorbed oil in a saline solution as compared to distilled water. This reduction is partially attributed to a decrease in the oil solubility in the presence of salt (Yaron, 1989) and to an increase in the potential association of oil onto the soil surfaces in such environments (Meyers and Quinn, 1973; Meyers and Oas,

1978).

The presence of salt in a hydrocarbon-soil-water system generally reduces the solubility of most hydrocarbons (Yaron, 1989). This is due to the effect of salt in decreasing the dispersive forces which are considered to be primarily responsible for the solubility of hydrocarbons in solutions (Luck, 1984). Therefore, one would expect that the octanol/water ratio (K_{ow}) of hydrocarbons would increase with increasing salinity of the soil media. The higher the value of K_{ow}, the higher the oil retention, the lower the soil permeability and thus the smaller the expected leaching potential of hydrocarbons from soil systems (Yong, et al., 1992). In addition, Henry's law constant for most hydrocarbons, which represents the volatilization potential, is expected to increase slightly with increasing salinity of the soil media (Lyman, et al., 1992). However, the presence of high content of salt in soil significantly retards the biodegradation of hydrocarbons (Frankenberger, 1991).

7.4 Soil Washing Effects

The soil washing process, in this case involving dispersion of the soil in distilled water to reduce its salinity, affects the properties and behavior of the soil. A comparison of the performance of the Sanad soil before and after washing in distilled water is summarized in Table 7.6. Among the tested soil properties affected by the washing process are: particle size distribution, plasticity, surface area, strength, and fluid-holding capacity.

As can be seen from Table 7.6, the washing process has significantly increased the soil plasticity, its surface area, and its fluid-holding capacity. The substantial increase in the fluid-holding capacity of the washed soil leads to the tendency towards a dispersed structure. Increasing the surface area is expected to increase the number of interparticle contacts in the washed soil. Consequently, the interparticle bonds formed and repulsive forces of the washed soil are expected to be higher in comparison with the natural soil (Yong and Warkentin, 1975; Mitchell, 1993).

Despite the potential increase in the repulsive forces of the washed soil, the unconfined compressive strength (q_u) of the washed soil is higher than the natural soil.

Table 7.6 Comparison of soil performance from the Sanad site before and after washing with distilled water.

Test type	Soil sample	
	Natural soil	Washed soil
Soil condition Conductivity (ds/m)	Disturbed saline soil 1.50	Dispersed in distilled water 0.47
Soil gradation < 0.075 mm (%)	20.00	30.00
Liquid limit (%) Plastic limit (%)	21.00 16.00	41.00 28.00
Surface area (m^2/kg)	$40x10^{-3}$	$62x10^{-3}$
Compaction γ_d (Mg/m^3) w (%)	1.78 14.00	1.35 29.00
Permeability (m/s)	$20x10^{-6}$	$5x10^{-6}$
UC test q_u (KPa) Failure strain (%)	118.00 3.00	104.00 8.00
Infrared	Presence of O-H, Si-O, and CO_3^{2-} groups in both soils. However, slight increase in the intensities of these groups were observed for the washed soil.	
Soil suction	Significant increase in the fluid holding capability of the washed soil (> 100%).	

A reduction of about 12% was observed in the value of q_u of the washed soil as compared to the natural soil. The lower initial density of the tested washed soil from the Sanad site (i.e., about 24% reduction in density, Table 7.6) is mainly responsible for the strength reduction. Despite the removal of about 68% of the initial soluble salt present in the soil due to the washing process, the remaining salt cementing bonds were found to be sufficient to provide substantial strength. A similar strength effect was recorded for the same soils when subjected to leaching forces. The leaching forces were found to reduce the q_u value of the washed soil by about 25% (Table 7.4). The reduction in soil strength is likely as a result of the substantial decrease in the soil density and the change in the soil fabric of the washed soil as compared to the natural soil.

The performance of the stabilized natural soil in comparison with the stabilized washed soil from the Sanad site is summarized in Table 7.7. The unconfined compressive results reveal that the presence of the oil residue in the soils significantly enhances their strength performance. However, the stabilized washed soil from the Sanad site shows lower strength performance than the stabilized natural soil. The decrease in the initial density of the washed soil as compared to the unwashed soil, together with the substantial alteration in the soil fabric can be primarily responsible for such a strength reduction.

The geochemical results indicate that the oil adsorption and retention capabilities of the stabilized washed soil from the Sanad site as well as its overall strength of bonding to the soil surfaces are slightly enhanced as compared to the stabilized unwashed soil from the Sanad site. However, the mode of soil-oil interaction and the type of bonds formed between the oil and soil surfaces have shown insignificant changes in their interaction changes as compared to their corresponding bonds formed in the stabilized natural soil. Further, the oil leachability potential of the stabilized soil is substantially reduced in the case of the washed soil as compared to the unwashed one. A reduction of approximately 50% was observed in the concentration of the oil leached from the washed soil as compared to the unwashed soil. The substantial increase in the surface area of the washed soil as compared to the natural soil is likely attributed to the increase in oil retention and thus the reduction in oil leachability.

Table 7.7 Comparison of performance of the stabilized natural soil and stabilized washed soil from the Sanad site.

Test type	Soil sample	
	Natural soil + 4% oil	Washed soil + 4% oil
Compaction γ_d (Mg/m^3) w (%)	1.71 13.50	1.30 27.50
UC test q_u (KPa)	357.00	233.00
Soil suspension Oil retained in soil matrix (%) Desorbed oil (%)	 77.00 20.00	 82.00 16.00
Soil leaching Oil retained onto soil surface (%) Leached oil (%)	 85.00 2.20	 88.00 1.00
Soil suction	Significant increase (~ double) in the overall fluid-holding capability of the stabilized washed soil.	
Infrared	Similar interaction mechanisms. However, interactive groups were observed to be less intense in washed soil as compared to natural soil, indicative of higher oil adsorption for the stabilized washed soil.	

CHAPTER 8
ENVIRONMENTAL IMPACT ASSESSMENT
- TRANSPORT MODELLING AND PREDICTION -

The presence of oil residue in the stabilized soils can pose a threat to the surrounding environment in the form of surface water and groundwater contamination and air pollution. Oil residue is strongly hydrophobic, barely soluble in water, weakly semi-volatile, and can possess toxic behavior. In order to describe its potential for long-term contamination, a transport model that can predict the movement of oil residue in the environment must be developed and tested. In this study, emphasis is placed on examining the migration behavior of oil residue present in the pore fluid of the stabilized soil.

As discussed previously, the transport of oil residue from the stabilized soils is controlled by several processes: desorption from the solid phase, distribution in the water phase, volatilization into the air phase, and degradation. When all these processes are combined to simulate the transport of multi-components of oil residue in time and space in porous media, a quantitative description becomes quite complex. Few comprehensive transport models for non-aqueous phase liquids (NAPL) have been developed. Among these is one developed by Yong et al. (1992); this model has been utilized in this study, with the incorporation of a few modifications.

The transport model applies the concept of irreversible thermodynamics, Fick's laws, Darcy's law, and equilibrium mass transfer principles. One-dimensional flow in a saturated condition is considered in this study. The non-linear partial differential governing equations resulting from the model are numerically solved using an explicit finite difference method. All the unknown material coefficients (7 unknowns in this case) in the governing equations are optimized using Powell's optimization method and experimental data obtained from the oil migration profile discussed previously in Section 6.2.4. A computer program that combines the model with previous soil leaching test results (Section 6.2.4) is developed to solve and predict oil migration under a given set of imposed circumstances.

8.1 Model Development

In a saturated soil-oil system permeated with water, a non-equilibrium state between the different phases of oil (i.e. adsorbed, dissolved, undissolved, and vapor) is expected. In order to consider establishment of equilibrium, irreversible thermodynamic concepts are applied, i.e. $J_i = L_{ij}X_j$, where J_i = rates of flow (fluxes); X_j = thermodynamic forces responsible for the fluxes; and L_{ij} = phenomenological coefficients (Onsager, 1931).

Using the second postulate of irreversible thermodynamics for pore water pressure flux (J_w) and oil concentration flux (J_c) in one dimension gives:

$$J_w = L_{ww}\frac{\partial \psi_w}{\partial z} + L_{wc}\frac{\partial \psi_c}{\partial z} + L_{wv}\frac{\partial \psi_v}{\partial z} \tag{1}$$

$$J_c = L_{cw}\frac{\partial \psi_w}{\partial z} + L_{cc}\frac{\partial \psi_c}{\partial z} + L_{cv}\frac{\partial \psi_v}{\partial z} \tag{2}$$

where L_{ij} represents the phenomenological coefficients (i = j = w, c, and v); $\partial\psi_w/\partial z$, $\partial\psi_c/\partial z$, $\partial\psi_v/\partial z$ are thermodynamic forces due to pore water pressure, oil concentration gradient, and vapor density gradient of oil, respectively; and z is the distance in the vertical direction (soil depth). These thermodynamic forces can be described as follows:

$$\frac{\partial \psi_w}{\partial z} = V_w \frac{\partial(-u_w)}{\partial z} \tag{3}$$

$$\frac{\partial \psi_c}{\partial z} = \frac{RT}{C}\frac{\partial(-C)}{\partial z} \tag{4}$$

$$\frac{\partial \psi_v}{\partial z} = \frac{RT}{\rho} \frac{\partial(-\rho)}{\partial z} \tag{5}$$

where V_w = water molar volume; R = universal gas constant; T = absolute temperature; u_w = pore water pressure; C = total oil concentration in soil pore fluid (that includes both dissolved and non-dissolved phases), and ρ = vapor density of oil. The negative sign in the above equations accounts for the fact that flow occurs in the direction of decreasing gradient.

Diffusivity of oil residue in soil air is neglected here due to the low vapor density of the oil residue (0.15 X 10^{-6} Mg/m^3, see Table 3.2). However, the influence of volatilization processes is indirectly incorporated in the water and oil concentration fluxes described above. The contribution of biological processes on oil transformation under the prevailing environmental conditions in Bahrain is expected to be minimal and thus, their effect is neglected in this model.

Substituting Equations (3), (4), and (5) in Equation (1) and applying Darcy's law for the cases where $\partial(-C)/\partial z = 0$ and $\partial(-\rho)/\partial z = 0$ produces:

$$L_{ww} = \frac{K_w}{\gamma_w V_w^2 n} \tag{6}$$

where K_w = soil permeability; γ_w = specific weight of water, n = effective porosity of soil.

Similarly, substituting Equations (3), (4), and (5) in Equation (2) and applying Fick's first law for the cases where $\partial(-u_w)/\partial z = 0$ and $\partial(-\rho)/\partial z = 0$ gives:

$$L_{cc} = \frac{C}{RT} D_{mw} \tag{7}$$

where D_{mw} represents the diffusion parameter of oil component in the soil pore water. The remaining phenomenological parameters (i.e. L_{wc}, L_{wv}, L_{cw}, and L_{cv}) are defined in

terms of their corresponding coupling coefficients (i.e. K_{wc}, K_{wv}, K_{cw}, and K_{cv}) as described by Yong et al. (1992).

$$L_{wc} = \frac{C}{V_w RT} K_{wc} \quad ; \quad L_{wv} = \frac{\rho}{V_w RT} K_{wv} \tag{8}$$

$$L_{cw} = \frac{C}{nV_w} K_{cw} \quad ; \quad L_{cv} = \frac{C\rho}{nRT} K_{cv} \tag{9}$$

Substituting Equations (3), (4), (5), (6), and (8) into Equation (1), and using the relationship $u = \gamma_w h$, gives:

$$J_w = \frac{K_w}{V_w n}\frac{\partial(-h)}{\partial z} + \frac{K_{wc}}{V_w}\frac{\partial(-C)}{\partial z} + \frac{K_{wv}}{V_w}\frac{\partial(-\rho)}{\partial z} \tag{10}$$

Equation (10) represents the water flux under hydraulic, oil concentration and vapor density. The deviations from Darcy's law are due to the chemico-osmotic effect (the second term in Equation (10)) and the volatilization effect (the third term in Equation (10)).

Similarly, substituting Equations (3), (4), (5), (7), and (9) into Equation (2), and using the relationship $u = \gamma_w h$, gives:

$$J_c = \frac{C\gamma_w K_{cw}}{n}\frac{\partial(-h)}{\partial z} + D_{mw}\frac{\partial(-C)}{\partial z} + \frac{CK_{cv}}{n}\frac{\partial(-\rho)}{\partial z} \tag{11}$$

The deviations from Fick's first law in the water phase of Equation (11) are attributed to the interference of soil surfaces with both oil movement (the first term in Equation (11)) and oil volatilization (the third term in Equation (11)).

Substituting Equation (10) in the relationship for the flow seepage velocity (advection velocity): $V_z = J_w V_w$, gives:

$$V_z = \frac{K_w}{n}\frac{\partial(-h)}{\partial z} + K_{wc}\frac{\partial(-C)}{\partial z} + K_{wv}\frac{\partial(-\rho)}{\partial z} \tag{12}$$

The oil concentration flux relative to a fixed coordinate system can be expressed as:

$$J_c' = J_c + CV_z \tag{13}$$

The mass conservation equation for the diffusion of oil present in the pore fluid of the stabilized soil which involves the effect of desorption reactions can be written as:

$$\frac{\partial C}{\partial t} = -\frac{\partial J_c'}{\partial z} + \frac{\rho_s}{n}\frac{\partial S_c}{\partial t} \tag{14}$$

where ρ_s is the dry density of soil, t is the time, and S_c represents the desorbed concentration of oil in the soil pore fluid, which is directly proportional to C. The positive sign in the desorption term accounts for the desorption phenomenon which is responsible for releasing oil from the solid phase into the soil pore fluid (i.e. acts as an internal source for oil).

Substituting for J_c from Equation (11) into Equation (13) and for J'_c from Equation (13) into Equation (14) gives the final governing differential equation:

$$\frac{\partial C}{\partial t} + \left(\frac{\gamma_w K_{cw}}{K_w} + 1\right)V_z\frac{\partial C}{\partial z} + \frac{\gamma_w K_{cw} K_{wc}}{2K_w}\frac{\partial^2 C^2}{\partial z^2} + \left(\frac{\gamma_w K_{cw} K_{wv}}{K_w} - \frac{K_{cv}}{n}\right)\frac{\partial c}{\partial z}\frac{\partial \rho}{\partial z} = \frac{\partial}{\partial z}\left(D_{mw}\frac{\partial c}{\partial z}\right) + \frac{\rho_s}{n}\frac{\partial S_c}{\partial t} \tag{15}$$

8.2 Model Parameters

The parameters required in this model (Equation (15)) can be classified into three groups: (1) parameters related to initial and boundary conditions, i.e. ρ_s, n, K_w, V_z,and

γ_w, (2) parameters related to physico-chemical processes, i.e. D_{mw}, S_c, K_{cw}, and K_{wc}, and (3) parameters related to volatilization process, i.e. ρ, K_{wv}, and K_{cv}. The first group can be determined very easily; however, the second and third groups need experimental data and application of a numerical technique to obtain these parameters.

8.2.1 Initial and Boundary Conditions

Laboratory leaching columns were used to obtained the required experimental data. The migration of oil residue from a compacted soil-oil mixture, containing 4% oil by weight, and permeated with distilled water at a constant flow rate of 12 mm/day, was experimentally investigated (see Section 6.2.4). The initial and boundary conditions for this particular case, that will be used to solve Equation (15) can be specified as follows:
(a) Total oil concentration in soil pore fluid (C)

$$\begin{aligned} C &= C_o && \text{for } 0 \le z \le L, && t = 0 \\ C &= C(z,t) && \text{for } 0 < z < L, && t > 0 \\ C(z,t) &= 38.615 + 0.183\, C^{1.490} && \text{for } 0 < z < L, && t = 4 \text{ days} \\ C(z,t) &= 23.236 + 0.013\, C^{2.198} && \text{for } 0 < z < L, && t = 20 \text{ days} \end{aligned} \qquad (16)$$

Equation (16) was determined from fitting the experimental oil migration profiles, presented in Figure 6.7, at the end of 1 pore volume (4 days) and 5 pore volumes (20 days) of leaching in distilled water, using the commercial curve-fitting program TABLECURVE.

(b) Water head (h) along the sample

$h(z,t) = 1400 - 14\, z$ for $0 \le z \le L$, $t > 0$

where C_o = initial oil concentration in soil pore fluid, $C(z,t)$ = concentration profile at a specified time step (obtained from leaching column experiments) and L = length of the soil sample (100 mm in this case) or depth of the stabilized soil. The applied air pressure at the top of the leaching column samples is 13.8 KPa (2 psi or equivalent to a head of 1.4 m). However, the head at the bottom of the leaching samples is zero because their outlets are exposed directly to the atmosphere.

8.2.2 Physico-chemical Parameters

The diffusion-dispersion parameter is expressed here in terms of the total concentration of oil present in the soil pore fluid (C), which includes both dissolved and non-dissolved phases of oil. Due to the difficulties involved in extracting the dissolved and non-dissolved phases of oil in an oil-water system, the extracted oil in this case includes both phases. Since only the dissolved phase of oil theoretically contributes to the diffusion process, experimentally estimated oil diffusion in the soil pore fluid is expected to be higher than the theoretical one. Therefore, such a simplification likely leads to over-estimated results. Previous studies on the migration of organic chemicals in a soil medium has also considered the contribution of the total chemical concentration presents in the soil pore fluid (Jury et al., 1983). Simplification of some of the model parameters was needed to facilitate the task of assessing oil diffusion parameters in such a complex system.

To establish a proper trend for the diffusion function for a specified contaminant under a particular condition, Yong, et al. (1992) have suggested the function can be described from the migration profile of the contaminant. Accordingly, based on the leaching column test data in Figure 6.7, the diffusion function of oil (D_{mw}) in the liquid phase can be described as:

$$D_{mw} = a\, e^{bC} \tag{17}$$

where a and b are diffusion coefficients experimentally estimated. Substituting Equation (17) into the diffusion term of Equation (15) gives:

$$\begin{aligned}\frac{\partial}{\partial z}\left(D_{mw}\frac{\partial C}{\partial z}\right) &= D_{mw}\frac{\partial^2 C}{\partial z^2} + \frac{\partial D_{mw}}{\partial z}\frac{\partial C}{\partial z} \\ &= D_{mw}\frac{\partial^2 C}{\partial z^2} + \frac{\partial D_{mw}}{\partial C}\left(\frac{\partial C}{\partial z}\right)^2 \\ &= ae^{bC}\frac{\partial^2 C}{\partial z^2} + abe^{bC}\left(\frac{\partial C}{\partial z}\right)^2\end{aligned} \tag{18}$$

Desorption of oil refers to the removal of a portion of the oil from the solid phase to the pore fluid solution due to the washing process. The desorption isotherm/characteristic of oil in the oil-soil-water system (S_c), obtained from leaching column experimental data presented in Figure 6.9 (Section 6.2.4), is described as follows:

$$S_c = E + A\, e^{-BC} \tag{19}$$

where E, A, and B are desorption coefficients experimentally determined and C is the total concentration of oil present in the soil pore fluid. A graphical presentation of Equation (19) is shown in Figure 8.1. It is noted that the desorption of oil decreases rapidly as the concentration of oil in the soil pore fluid increases. Substituting Equation (19) into the desorption term of Equation (15) gives:

$$\frac{\partial S_c}{\partial t} = \frac{\partial S_c}{\partial C}\frac{\partial C}{\partial t} = -ABe^{-BC}\frac{\partial C}{\partial t} \tag{20}$$

Assuming homogenous, isothermal, and isotropic soil-oil mixture conditions, the chemico-osmotic parameters (L_{wc} and L_{cw}) are expected to be equal. Therefore, the oil restriction coefficient (K_{cw}) can be expressed in terms of the osmotic coefficient (K_{wc}) as follows (Yong, et al., 1992):

$$K_{cw} = \frac{n}{RT}K_{wc} \tag{21}$$

where n = effective porosity of soil; R = universal gas constant; and T = absolute temperature.

8.2.3 Vapor Parameters

Due to complexities in experimentally measuring the variation of vapor density of the oil residue present in the stabilized soil during testing, its vapor density (ρ) is

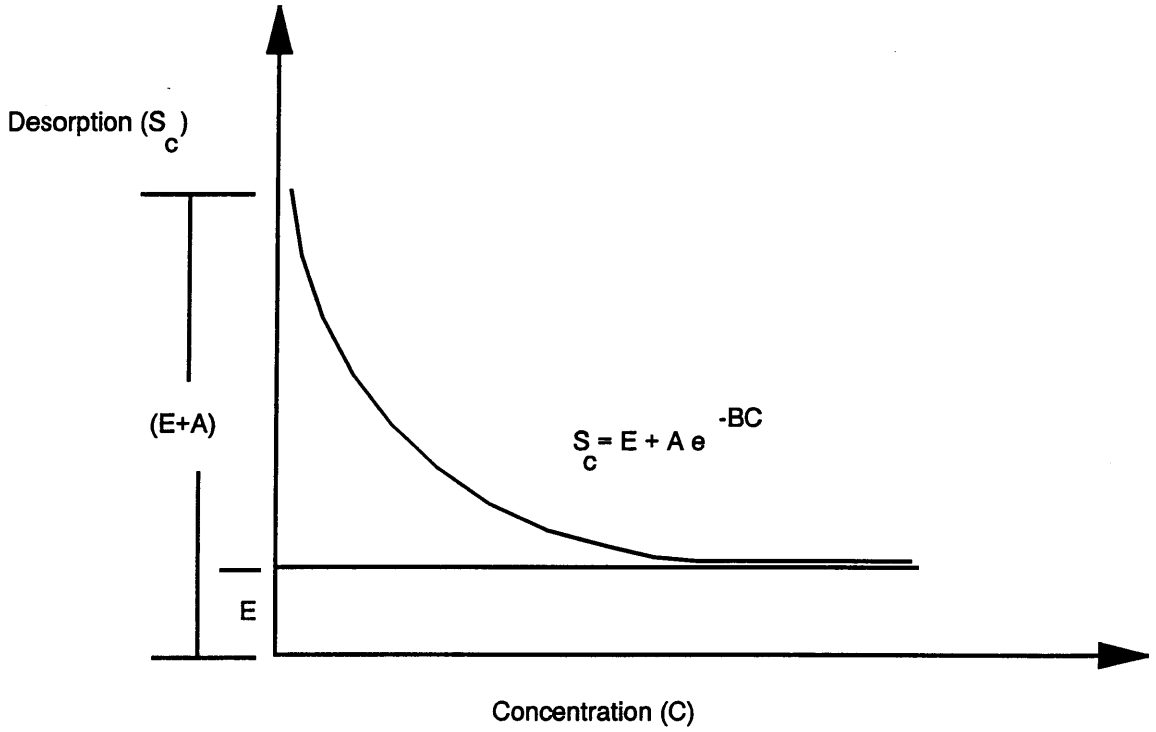


Figure 8.1 - Oil desorption isotherm/characteristic obtained from soil leaching test.

estimated here in terms of the total oil concentration in the soil pore fluid (C) as follows:

$$\rho = h_c C \tag{22}$$

where h_c represents a vapor-liquid partition coefficient, i.e. ratio between the vapor density of oil and C at equilibrium. The value of h_c is expected to be in the range between Henry's law constant value (K_h) and maximum volatilization ratio measured in the laboratory based on atmospheric exposure of bulk oil (i.e. 5% w/w or 0.05, see Table 3.2). The dimensionless Henry's law constant value (K_h/RT) is estimated to be 0.015 for this oil residue (see Table 3.2). Equation (22) is analogous to the usual Henry's law equation ($\rho = K_h C_s$) suggested by Yong et al. (1992) in describing the vapor density of a chemical in relation to its solute concentration (C_s) at a saturated condition. Substituting Equation (22) into the vapor term of Equation (15) gives:

$$\frac{\partial C}{\partial z}\frac{\partial \rho}{\partial z} = \frac{\partial C}{\partial z}\frac{\partial (h_c C)}{\partial z} = h_c\left(\frac{\partial C}{\partial z}\right)^2 \tag{23}$$

The vapor coefficients (K_{wv} and K_{cv}) represent two unknown parameters that need to be generated from the model. K_{wv} is the vapor coefficient which involves the volatilization of oil from the water phase. K_{cv} is the vapor restriction coefficient which is attributed to an interference of the soil surfaces with the oil volatilization process.

8.3 Model Solution

Substituting Expressions (18), (20), and (23) into Equation (15) and manipulating the final differential equation to be used in modelling the transport of oil in the oil-soil-water system (discussed in Section 6.2.4), we obtain:

$$\{1+\frac{\rho_s}{n}(ABe^{-BC})\}\frac{\partial C}{\partial t}+(\frac{\gamma_w K_{cw}}{K_w}+1)V_z\frac{\partial C}{\partial z}+(\frac{\gamma_w K_{cw}K_{wc}}{2K_w})\frac{\partial^2 C^2}{\partial z^2}$$
$$\{\frac{\gamma_w K_{cw}K_{wv}}{K_w}-\frac{K_{cv}}{n}\}h_c\left(\frac{\partial C}{\partial z}\right)^2 = ae^{bC}\frac{\partial^2 C}{\partial z^2}+abe^{bC}\left(\frac{\partial c}{\partial z}\right)^2 \quad (24)$$

For simplicity in representing Equation (24), it can be rewritten as:

$$(DES)\frac{\partial C}{\partial t}+(CRP)V_z\frac{\partial C}{\partial z}+(OSM)\frac{\partial^2 C^2}{\partial z^2}+(VDP)\left(\frac{\partial C}{\partial Z}\right)^2$$
$$=ae^{bC}\frac{\partial^2 C}{\partial z^2}+abe^{bC}\left(\frac{\partial C}{\partial z}\right)^2 \quad (25)$$

where:

$$DES = 1+\frac{\rho_s}{n}(ABe^{-BC}) = \textit{Desorption Factor}$$

$$CRP = \frac{\gamma_w K_{cw}}{K_w}+1 = \textit{Oil Restriction Parameter}$$

$$OSM = \frac{\gamma_w K_{cw}K_{wc}}{2K_w} = \textit{Osmotic Parameter}$$

$$VDP = (\frac{\gamma_w K_{cw}K_{wv}}{K_w}-\frac{K_{cv}}{n})h_c = \textit{Vapor Density Parameter}$$

The unknown material coefficients resulting from the model can be summarized as follows:

(1) Diffusion/dispersion coefficients (a and b)

(2) Desorption coefficients (A and B)

(3) Coupling effect coefficients (K_{wc}, K_{wv}, and K_{cv})

In the present study, the governing differential equations (Equations (12) and (25)) are numerically solved using the finite difference technique. Dividing the time, t, and the vertical distance, z, into j and n intervals respectively, as shown in Figure 8.2 yields:

$z = n\,\Delta z$, for $n = 1, N$

$t = j\,\Delta t$, for $j = 1, J$

Equations (12) and (25) can be expressed in terms of the explicit central finite difference form as:

$$V_z = -\frac{K_w}{n}\left[\frac{h^j_{i+1} - h^j_{i-1}}{2\Delta z}\right] - (K_{wc} + K_{wv}h_c)\left[\frac{C^j_{i+1} - C^j_{i-1}}{2\Delta z}\right] \tag{26}$$

Concentrations at time level j+1 (C^{j+1}_i) can be obtained explicitly from concentrations at time level j as given:

$$DES\left[\frac{C^{j+1}_i - C^j_i}{\Delta t}\right] + CRP\left[\frac{C^j_{i+1} - C^j_{i-1}}{2\Delta z}\right]V_z + OSM\left[\frac{(C^j_{i+1})^2 - 2(C^j_i)^2 + (C^j_{i-1})^2}{(\Delta z)^2}\right]$$
$$+ VDP\left[\frac{C^j_{i+1} - C^j_{i-1}}{2\Delta z}\right]^2 = ae^{bC^j_i}\left[\frac{C^j_{i+1} - 2C^j_i + C^j_{i-1}}{(\Delta z)^2}\right] + abe^{bC^j_i}\left[\frac{C^j_{i+1} - C^j_{i-1}}{2\Delta z}\right]^2 \tag{27}$$

$$C^{j+1}_i = C^j_i + \frac{\Delta t}{(DES)}[AA_4 - AA_3 - AA_2 - AA_1] \tag{28}$$

where:

$$AA_1 = CRP\left[\frac{C^j_{i+1} - C^j_{i-1}}{2\Delta z}\right]V_z$$

$$AA_2 = OSM\left[\frac{(C^j_{i+1})^2 - 2(C^j_i)^2 + (C^j_{i-1})^2}{(\Delta z)^2}\right]$$

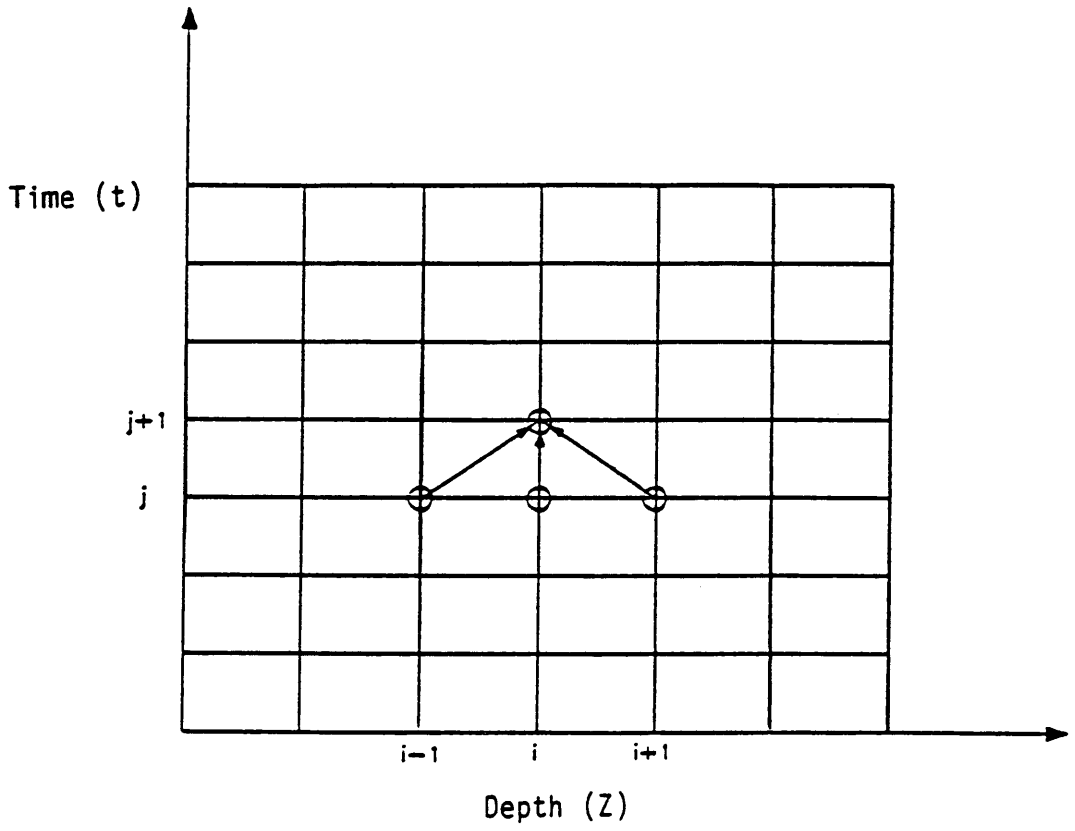


Figure 8.2 - Explicit finite difference mesh.

$$AA_3 = VDP\left[\frac{C^j_{i+1}-C^j_{i-1}}{2\Delta z}\right]^2$$

$$AA_4 = ae^{bC^j_i}\left[\frac{C^j_{i+1}-2C^j_i+C^j_{i-1}}{(\Delta z)^2}\right] + abe^{bC^j_i}\left[\frac{C^j_{i+1}-C^j_{i-1}}{2\Delta z}\right]^2$$

Equations (26) and (27) are the final differential equations in a finite difference form. These equations will used with an optimization technique to obtain the unknown material coefficients described above.

8.4 Determination of Unknown Material Coefficients

From the experimentally measured oil concentration profiles (Equation (16)) and assumed material coefficients, the oil concentration profiles can be numerically calculated (Equation (28)). If the measured and calculated concentrations are designated as $C_{exp.}(z,t)$ and $C_{calc.}(z,t)$ respectively, then the best choice for these coefficients (i.e. a, b, A, B, K_{wc}, K_{wv}, and K_{cv}) are those which minimize the following function:

$$\sigma = \sum_{i=1}^{m} \left| C_{exp.}(z,t) - C_{calc.}(z,t) \right| \qquad (29)$$

where m represents number of measured concentrations in experiments and σ is a function of the unknown material coefficients.

The value of σ is minimized using Powell's conjugate direction method of non-linear optimization (Powell, 1964). For the problem under consideration, the derivatives

of σ, with respect to a specific unknown coefficient, cannot be determined in a simple way. This makes Powell's method more useful because it does not require derivatives of the objective function.

A computer program that combines the finite difference solution, Powell's optimization method, and the experimental data, i.e. results obtained from soil leaching test (Section 6.2.4), was developed to solve and calibrate the model under the specified conditions (see Appendix A). A flow chart of the computer program is presented in Figure 8.3. All the input and output data are well explained at the beginning of the program. With the exception of the Powell optimization subroutine (Shooshpasha, 1993), the algorithms in the modelling program were all developed by the author. In order to calibrate the model, experimentally measured concentrations (Equation (16)) were correlated with the corresponding calculated concentrations through the following equation:

$$r = \sqrt{1 - \frac{\sum_{i=1}^{m} [\, C_{exp.}(z,t) - C_{calc.}(z,t)]^2}{\sum_{i=1}^{m} [\, C_{exp.}(z,t) - C_{av.}(z,t)]^2}} \qquad (30)$$

where r represents a coefficient of correlation and $C_{av.}$ is the average experimental concentration.

Using the aforementioned computer program, the unknown coefficients (a, b, A, B, K_{wc}, K_{wv}, and K_{cv}) were determined as shown in Table 8.1. The calibrated oil profile curve together with its experimentally measured one are presented in Figure 8.4. In addition, the variation of oil diffusivity in the water phase, as a function of soil depth (length of soil sample) after 20 days of leaching with distilled water is shown in Figure 8.5.

As expected, the calculated values of the oil diffusion parameter are relatively high. This is because the oil concentration in the soil pore fluid is represented in terms of both the dissolved and undissolved fractions of the oil. However, only the dissolved phase of the oil which represents a very small portion (10 ppm) is expected to contribute

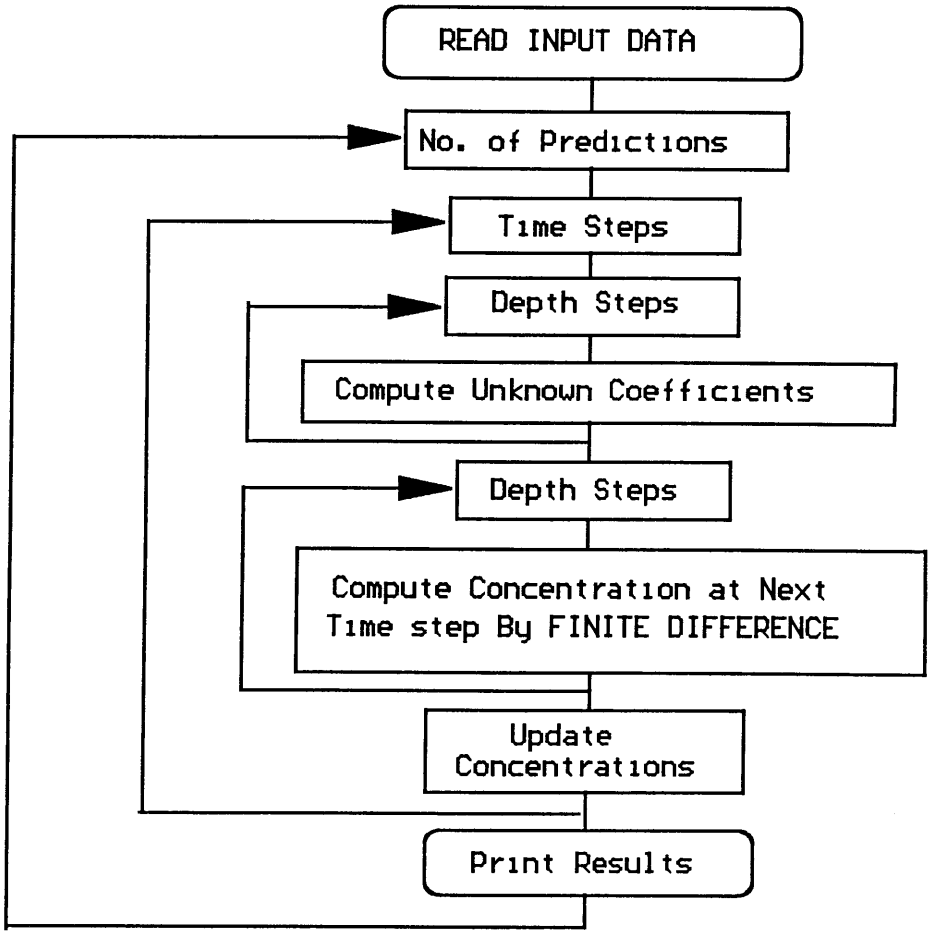


Figure 8.3 - Calibration program flowchart.

Table 8.1 - Coefficients determined from the calibration model.

Unknown Coefficients	Value
Diffusion/Dispersion	
a	2057.459 mm^2/day
b	1800.191 ml/g
Desorption	
A	9881.518 mg/kg
B	15.616 ml/g
Coupling Effect	
K_{wc}	13627.518 $mm^5/g/s$
K_{wv}	1188111.635 $mm^5/g/s$
K_{cv}	- 7010.380 $mm^5/g/s$

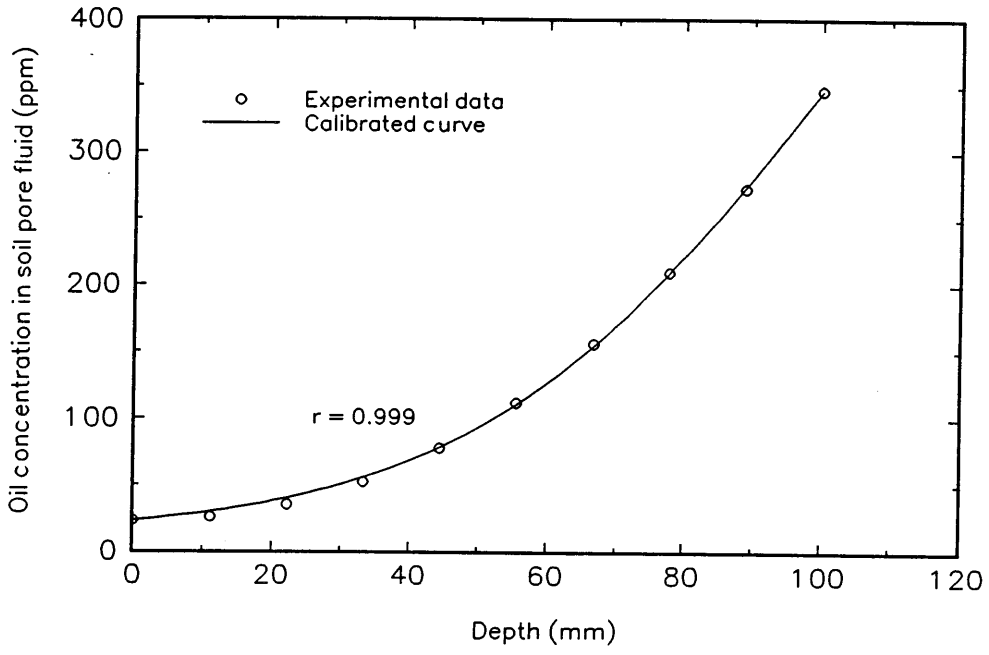


Figure 8.4 - Model calibration curve for oil concentration profile after 5 pore volumes (20 days) of leaching in distilled water.

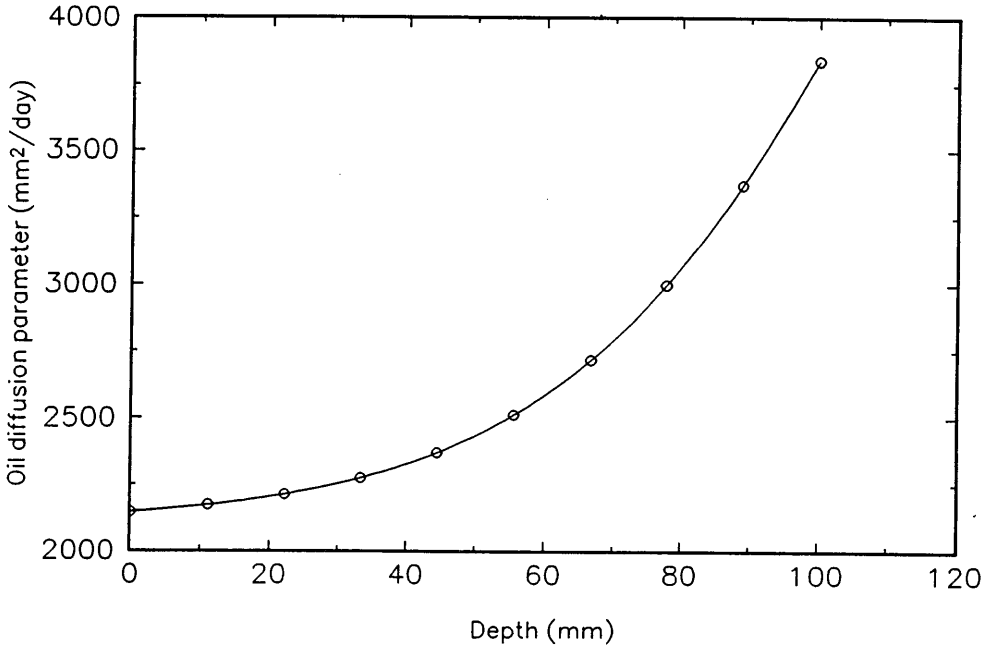


Figure 8.5 - Variation of oil diffusion with soil depth after 20 days of leaching in distilled water.

in the diffusion process. Despite the fact that the diffusion value is valid for a particular circumstance and under a specified condition, a comparison with other studies can be used to support the above observation. Comparing the oil diffusivity in this investigation ($D_{av.}$ = 2660 mm^2/day) with the oil diffusivity from a tar sand (a mixture of 85% sand and 15% montmorillonite and containing 15% bunker oil, by weight) leached with a surfactant, at a temperature of 50°C and head of 200 mm, examined by Yong et al. (1991) ($D_{av.}$ = 7420 mm^2/day), reveals that the oil diffusion in this case is only 3 times less than the obtained value by Yong et al. (1991b).

The predicted oil migration results (Figure 8.5) indicate that the diffusivity of oil increases significantly with the soil depth. This is due to the sharp increase in the oil migration profile which contributes to the increase in oil diffusivity.

8.5 Model Validation and Prediction

With the known material coefficients (diffusion, desorption, and coupling effect coefficients) for this particular test condition and using Equation (28), it is possible to determine the oil migration profile at a given time by applying the explicit finite difference method. In this regard, a FORTRAN program (see Appendix B), with a flow chart shown in Figure 8.6, was developed by the author to predict the variation of oil concentration with soil depth.

In order to validate the model, an experimentally measured oil migration profile after 40 days of leaching in distilled water in the laboratory was compared with a predicted oil profile (from the FORTRAN program) for the same period of time, as shown in Figure 8.7. The results of Figure 8.7 show that the predicted oil profile is much higher than the measured one. This leads to a decrease in the level of confidence in predicting the oil migration profile as the time progresses. The increase in the predicted oil migration profile is likely attributed to the incorporation of the non-dissolved phase of oil in the diffusion process. Also, since the dissolved oil represents a small fraction of the total oil concentration, the difference between the predicted and measured profile was shown to be substantial.

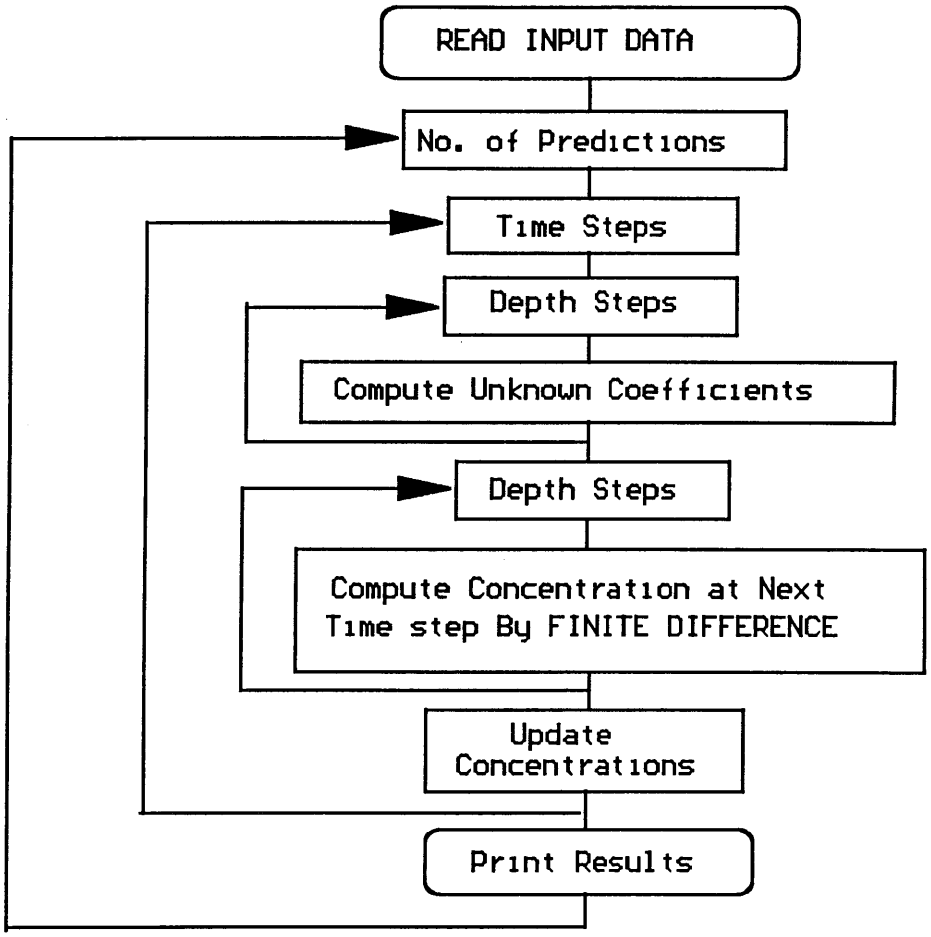


Figure 8.6 - Flowchart of oil concentration prediction program.

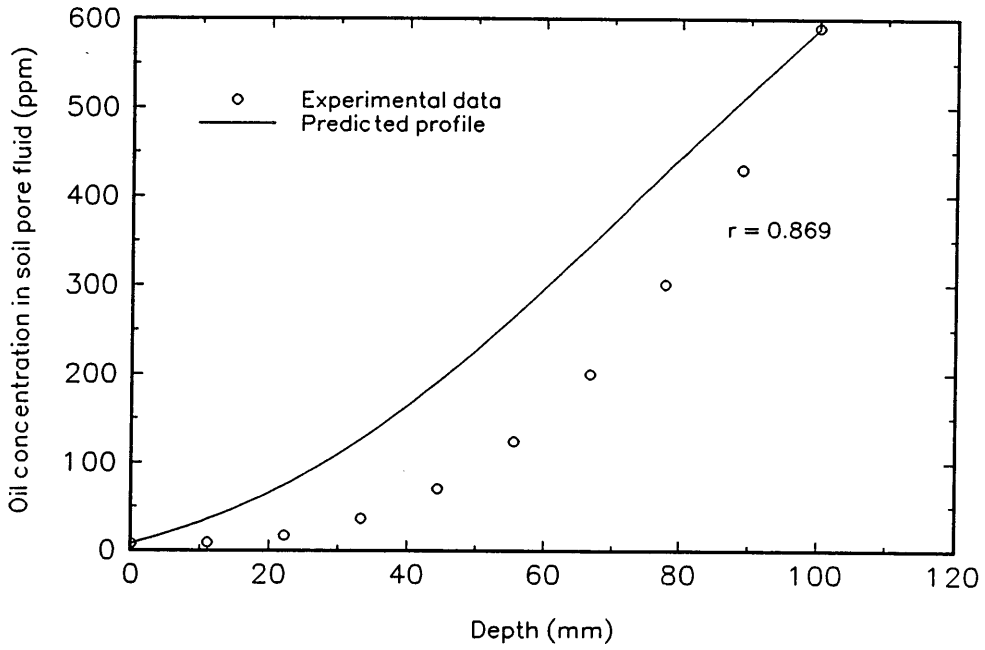


Figure 8.7 - Predicted and measured oil concentration profiles after 10 pore volumes (40 days) of leaching in distilled water.

CHAPTER 9
SUMMARY AND CONCLUSIONS

This research work investigated the feasibility of using Arabian oil residue as a means to stabilize the collapsible saline soils from Bahrain. Since oil residue can pose a threat to the surrounding environment, special emphasis on the environmental impacts associated with its application in soils was undertaken. The environmental study focused on evaluation of the: (a) oil retention characteristics and its bonding mechanisms with the soils, and (b) oil leachability potential and its migration behavior from the stabilized soils.

The required physical and chemical analyses were attained by an extensive laboratory testing program. In addition, a theoretical analysis was performed to evaluate the migration of oil from the stabilized soils. Observations and conclusions of this study, and their relation to the stated objectives of Chapter 1, are presented in the next section, followed by suggestions for further studies, and contributions to knowledge.

9.1 Summary and Concluding Remarks

9.1.1 Materials

The two natural soils used in this study are classified as saline calcareous silty sand soils, which are representative of the soil in Bahrain. These soils have low contents of soil organics and amorphous materials, but contain a substantial amount of organoclay minerals (about 10%, by weight) which contributed in the retention of oil in these soils. In addition, a third soil represents a washed soil obtained by dispersing one of the tested soils in distilled water prior to oil application to examine the effect of salinity reduction on soil performance. The soil washing process was found to enhance the activity of the soil.

The stabilizer used here was an oil residue sample, which is the heavy fraction remaining from the distillation process of crude oil. This oil residue is characterized as

an atmospheric Arabian type, which is a complex mixture of mostly saturates and aromatic hydrocarbons, and to a lesser extent of resins and asphaltenes. The low aqueous solubility of the oil residue, its high organic carbon partition coefficient, and its low volatilization potential enhanced the oil retention capability in the soils, and thus reduces its environmental mobility. The contribution of two different permeating solutions were also involved in testing: distilled water and saline water.

9.1.2 Geotechnical Aspects

The unconfined compression test results revealed a significant increase in the strength performance of the tested soil samples containing 4% oil residue, by weight, and 13 ± 1 % moisture content. However, as the content of oil residue increased above 4%, a reduction in the soil strength performance was observed. Moreover, the presence of oil residue in the soils prior to water addition showed a higher strength performance as compared to the presence of water in the soils prior to the oil residue addition.

Despite the lower strength performance of the leached samples as compared to the unleached samples, the stabilized leached samples still showed substantially higher strength performance as compared to the natural leached samples. A slight increase in the strength performance of the stabilized soil samples leached with distilled water was noted in contrast with the same samples leached in saline water.

The direct shear test results indicated that with 4% oil residue content, the cohesive component of the shear strength of the tested soils increased by more than 150% but a slight decrease, less than 18%, was observed in their angles of frictional resistance. The increase in the cohesive component was shown to be much higher than the reduction in the angle of frictional resistance, resulting in a substantial increase in the total shear strength of the stabilized soils. In addition, the presence of 4% oil residue was found to be sufficient to cover the entire surface of these soils with oil.

The CBR (California bearing ratio) results showed that the presence of oil residue in the soils under unsoaked conditions slightly reduced their CBR values. However, the CBR values of the soaked stabilized samples were slightly higher than their corresponding natural samples. Nevertheless, the changes in the CBR values of the leached stabilized samples were insignificant compared to the leached natural samples.

Viscosity of the oil residue, indirectly representative of the strength of the stabilized soil, appeared to be very sensitive to temperature; an increase in the oil temperature from 22°C to 30°C reduced its viscosity by about 50%. Initially, an increase in temperature was found to enhance the distribution, binding, and curing processes of oil in soils, resulting in an increase in the strength performance of the stabilized samples. The long-term strength performance of the stabilized samples was also expected to be enhanced under dry conditions (Dunn and Salem, 1973; Mitchell, 1993).

From these observations obtained from the geotechnical testing of the tested soils, the feasibility of using 4% of oil residue, by dry weight of soil, to stabilize the tested collapsible soils from Bahrain is shown. The presence of 4% oil residue has been found to significantly increase the cohesive components of the soil strength, and therefore enhance their total strength performance under both saturated and unsaturated conditions.

9.1.3 Geochemical Aspects

The variation in the surface charges of both the oil residue and tested soils (the interactive surfaces) is expected to be less sensitive within the natural soil pH range present in Bahrain.

The infrared spectra results indicated that the vibrational frequency peaks present in the oil residue were associated with the alkyl C-H group, the aromatic C-H and C=C groups, the carbonyl (C-O), and the sulphoxide (S=O) groups. The major frequency peaks found in the soils were assigned to the hydroxyl groups (silicate and water), the carbonate group, and the silanol and siloxane groups. The binding mechanisms between the two interactive surfaces were shown to be dominated by: Van der Waal's attraction, weak hydrogen bonding, water and cation bridging, and surface tension forces. The strength of the formed bonds were found to be relatively weak.

Leaching forces were shown to have insignificant changes in the shifts and absorbances of the frequency peaks of the soil-oil mixtures, indicating that most of the adsorbed oil was still bound to the surfaces of these soils. In addition, the increase in the oil residue content, above 4%, in these soils portrayed insignificant changes in their interactions and bondings with the oil.

The fluid retention capability of the soils, representative of the overall strength of bonding between the soil surfaces and its fluids (oil and water), was described in this study using the soil suction test. The tested natural soils were found to contain mostly rigid brittle bonds, which were dominated by salt cementation bonds. The presence of 4% oil residue content in the soils was shown to increase the adhesive bonding between the soil particles. However, a reduction in the fluid retention potential of the oil-soil-water system was observed as the oil residue content increased in the soils, indicative of their potential toward water repellent characteristics.

The soil washing process, i.e. removal of excess soluble salt, was shown to substantially affect the properties and behavior of the tested soil. The stabilized washed soil, from the Sanad site, showed a higher fluid retention capability than the stabilized natural soil, from the same site. However, the presence of salt was shown to slightly reduce the fluid retention characteristics of the soil-oil system. In addition, leaching forces were found to significantly reduce the fluid retention potential of the natural soils, indicative of the major loss in the cementing salt bonds of the natural soils due to the leaching process. Nevertheless, the influence of leaching revealed insignificant changes in the fluid retention behavior of soils containing 4% oil residue. Thus, the global bonding characteristics of the stabilized soils, containing 4% oil residue, were found to be relatively stable and insensitive to leaching forces, providing a good agreement with the results presented in the soil-oil interaction section (Section 5.1.2).

The adsorption-desorption isotherms of the stabilized soils, obtained from the soil suspension test, demonstrated the ability of the soils to retain oil at a slightly higher oil residue content than 4%. Moreover, this study showed that about 20% of the introduced oil was desorbed from the stabilized soils containing 4% oil residue. The amount of desorbed oil residue from the stabilized soil systems was found to be reduced in the cases of washed soil samples and in the presence of a saline solution.

9.1.4 Geo-environmental Aspects

The soil leaching study of the stabilized soils with 4% oil residue, designed to assess the retention and leaching behavior of the oil residue, indicated good oil retention in these samples. More than 90% of the oil by weight remained in the soil matrix after

ten pore volumes of leaching in the laboratory (i.e. 40 days). However, less than 3% of the oil by weight was detected in the leached effluents at the end of the leaching process (i.e. 10 pore volumes).

The leachability of oil residue, in this case, was partially attributed to the effect of the higher flow rate applied in the laboratory as compared to the rate expected in the field. Extrapolation of these results estimated that 6.5 years of actual field leaching, based on an annual precipitation rate of 75 mm/year in Bahrain, was required to leach out less than 3% of the oil from the stabilized soils. Since the oil residue will most likely be applied near the ground surface, the leached oil is expected to reach shallow depths after 6.5 years of field leaching.

Despite the severe conditions that the soil-oil mixtures are subjected to during laboratory testing, the depletion rate of the oil, expressed in terms of a reaction half-life, was observed to be relatively low. The half-lives of the oil due to continuous laboratory leaching and volatilization from its bulk form were estimated to be 3 and 20 years, respectively. The estimation of the half-lives was based on the loss of the low molecular fractions of the oil residue, which only represent a small portion of this oil. However, the heavy fractions of the oil are expected to have higher half-life spans than the ones estimated above.

The leaching test results revealed that the soil washing process prior to the application of the oil residue enhanced the oil retention capability of the soil, and significantly reduced its oil leachability potential. In addition, the presence of a saline environment was found to improve the oil retention characteristics of the tested samples. These observations agree with the results attained from the soil suspension test. Therefore, the use of the washed soils with 4% oil residue is preferable since these soils showed higher oil retention capability and thus are considered to be more environmentally friendly.

The leaching behavior of other constituents present in the stabilized soils, i.e. heavy metals and soluble salt, were also examined in this leaching study. The concentration of the heavy metals was found to be below the detection level. However, the salt leachability potential from the stabilized soils was shown to be slightly higher than the leachability of salt from the natural soils. This indicates the ineffectiveness of

4% oil residue to prevent upward migration of salt through the stabilized soils, which is one of the objectives of this research.

Besides the sorption and leaching processes, the contribution of other transport processes (such as volatilization, biodegradation, and photolysis) on the fate of oil residue in soil systems, together with the environmental considerations of the application of this oil, were addressed in Sections 6.3 and 6.4.

Prior to application of the oil residue in the field, two separate studies should be conducted in order to consider its use as an environmentally safe additive: (a) assessing the toxicity potential of the leached oil; and (b) evaluating the oil retention characteristics of the soil underneath the stabilized layer.

9.1.5 Oil Transport Modelling

Using a transport model and numerical computational techniques which combine the finite difference method and Powell's optimization procedure, the unknown material coefficients were computed from the experimentally measured oil migration profiles. The predicted results using this model indicated that oil diffusivity in the tested soil increases as soil depth increases. Moreover, the oil diffusivity in the pore fluid of the stabilized soil system was found to be relatively high. This is because only the dissolved fraction of the oil contributes in the diffusion process. However, the oil concentration used in this model is expressed in terms of both the dissolved and non-dissolved fractions of the oil.

The experimental results of the oil migration profiles in one of the stabilized soils, containing 4% oil residue, were compared with the corresponding theoretical predictions. The predicted results presented the contribution of the sorption, advection, diffusion, volatilization, and oil partitioning processes to predict the oil migration profiles with time and space in the stabilized soil. The predicted migration profiles were shown to be over-estimated as compared to the experimental migration profiles. Further studies toward sensitivity analysis should be addressed. In sensitivity analysis, the contribution of each of the involved transport processes can be quantified and thus the potential for a better prediction can be achieved.

9.2 Suggestions for Further Studies

Future studies should investigate:

(1) the toxicity of the individual constituents present in the leached oil prior to the application of the oil residue in the field.

(2) the retention characteristics of the leached oil in the clean soil underneath the stabilized layer.

(3) the potential use of additives (e.g. polymers, organic cations, clays) in the stabilized soils to: (a) enhance bondings and maximize oil retention in soils; and (b) reduce salt attacks to sub-structures, and as well to examine the influence of the presence of these additives on the strength performance of the stabilized system.

(4) the development of adequate laboratory techniques to measure the distribution of the different phases of oil in the stabilized soil system and incorporate their direct contribution in the transport model.

(5) the sensitivity of the developed model to the transport processes involved.

(6) the incorporation of volatilization, degradation, moisture, and temperature fluxes in the developed transport model.

(7) the actual contribution of the temperature on the geotechnical and geo-environmental performances of the stabilized soil.

9.3 Contributions to Knowledge

This study represents the following contributions toward a practical approach in the field of geo-environmental aspects of petroleum hydrocarbons (oil residue) which are expected to be used as a stabilizing agent for the collapsible saline soils in Bahrain:

(1) The concept of utilizing oil residue as a means to stabilize soils.

(2) Evaluation of characteristics and properties of soil-oil mixtures, which include:

   (a) Geotechnical performance

(b) Interaction and bonding mechanisms

(c) Interaction energy status

(3) Environmental impact assessments

(a) Identification of oil leachability potential and its impact on the mechanical properties and interaction performance of soils.

(b) Evaluation of the various transport processes involved and their impacts on the oil migration behavior of soils.

Although this study was conducted on a limited number of soils with the application of one type of oil residue, the results may well bear significant implications for other soils (not only the tested soils from Bahrain) as well as other types of oil residues (not only the used Arabian oil residue). Mixtures of soils having similar mineralogy and composition to those studied herein with oil residue possessing similar composition and property to the Arabian soil may exhibit comparable results.

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Appendices

```
      program TRANSMOD      Appendix A
c     ****************************************************************
c     *                                                              *
c     *         A Computer Program to Model the Transport            *
c     *         of Oil Residue in an Oil-Soil-Water System           *
c     *                                                              *
c     *  ========================================================    *
c     *                                                              *
c     *        using the explicit finite difference method           *
c     *                          and                                 *
c     *         non-linear optimization (Powell's) method            *
c     *                                                              *
c     ****************************************************************
c
c                     LIST OF VARIABLES
c                     =================
c
c        INPUT DATA
c        ==========
c     1  n        = number of unknown coefficients
c     2  n1+1     = number of nodes in the soil vertical direction
c     3  maxit    = maximum global iterations
c     4   m       = number of specified iterations
c     5  zmax     = maximum soil depth (mm)
c     6  zmin     = minimum soil depth (mm)
c     7  tmax     = final time   (days)
c     8  tmin     = initial time (days)
c     9  escal    = a scalar which is at least 0.5
c    10  difc     = initial value of maximum diffusion parameter (mm2/day)
c    11  pp       = stability requirement, less than 0.5
c
c    12  gcr      = universal gas constant   (Pa.m3/mole/k)
c    13  temp     = absolute temperature     (k)
c    14  amwt     = molecular weight of oil
c    15  akw      = soil permeability (mm/day)
c    16  poros    = effective porosity of the soil
c    17  rho      = dry density of the soil  (Mg/m3)
c    18  gamma    = specific weight of water (KN/m3)
c    19  hc       = vapor-liquid partition cofficient of the oil (dimensionless)
c    20  concfa   = concentration conversion factor for printout
c    21  timefa   = time conversion factor
c
c    22  x(n)     = initial value of each unknown coefficient
c    23  e(n)     = accuracy requirment of each unknown coefficient
c
c    24  cd(i)    = variation of oil concentration (ppm) with depth, at time tmin
c    25  cu(i)    = variation of oil concentration (ppm) with depth, at time tmax
c    26  hd(i)    = variation of head (mm) with soil depth
c
c
c
c        UNKNOWN COEFFICIENTS
c        ====================
c
c     x(1), x(2)  = diffusion/dispersion coefficients
c                   x(1) : (mm2/day)
c                   x(2) : (ml/g)
c     x(3), x(4)  = desorption isotherm coefficients
c                   x(3) : (mg/kg)
c                   x(4) : (ml/g)
```

```
c     x(5)         = osmotic coefficient          (mm5/g/s)
c     x(6)         = vapor coefficient            (mm5/g/s)
c     x(7)         = vapor restriction coefficient (mm5/g/s)
c
c
c        OTHER PARAMETERS
c        ================
c        c       = total oil concentration in the soil pore fluid
c        vx      = seepage velocity in the vertical direction
c        hdx     = hydraulic gradient
c        colx    = concentration gradient
c        ret     = desorption factor
c        crp     = oil restriction parameter
c        akcw    = oil restriction coefficient
c        vdp     = vapor density parameter
c        osm     = osmotic parameter
c
c
c        OUTPUT DATA
c        ============
c      x(i)        = final value of each unknown parameter
c      dz(i)       = diffusion parameter determined based on computed
c                    concentration at time tmax
c      ds(i)       = desorption parameter determined based on computed
c                    concentration at time tmax
c      zz(i)       = value of each depth interval
c      hd(i)       = varation of head with soil depth
c      cd(i)       = input concentration at time tmin
c      cu(i)       = input concentration at time tmax
c      cn(i)       = computed concentration at time tmax
c      dx          = distance between node n and n+1 in the vertical direction
c      dt          = time step interval
c      nt          = number of time steps
c      R2          = Cofficient of correlation
c      sumd        = total sum of differences  between input & computed
c                    concentrations at time tmax.
c     ==========================================================


      implicit real*8(a-h,o-z)
      dimension x(500),e(500),w(2000)

      common /data1/ co(2000),cn(2000),cd(2000),cu(2000),hd(2000),
     +               dz(2000),zz(2000),ds(2000)
      common /data2/ gcr,temp,amwt,akw,poros,rho,gamma,hc,pgt,gk,
     +               twodx,dx2,concfa,timefa
      character filen*60,filen1*60,filen2*60,filen3*60,aline*80


      write(*,900)
900   format(/1x,
     +'ŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸŸ'/1x,
     +'Ÿ                                                          Ÿ'/1x,
     +'Ÿ   TRANSMOD                                    06 MAY 94  Ÿ'/1x,
     +'Ÿ                                                          Ÿ'/1x,
     +'Ÿ        A Computer Program to Model the Transport        Ÿ'/1x,
     +'Ÿ        of Oil Residue in an Oil-Soil-Water System        Ÿ'/1x,
     +'Ÿ  ====================================================    Ÿ'/1x,
     +'Ÿ                                                          Ÿ'/1x,
     +'Ÿ        using the explicit finite difference method       Ÿ'/1x,
```

```
     +'Ý                           and                         Ý'/1x,
     +'Ý           non-linear optimization (Powell''s) method   Ý'/1x,
     +'Ý                                                       Ý'/1x,
     +'ÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝ')
      write(*,910)
910   format(/1x,
     +'A file containing the following lines of input is required:'/1x,
     +'       N,N1,MAXIT,M,ZMAX,ZMIN,TMAX,TMIN,ESCAL,DIFC,PP       '/1x,
     +'       GCR,TEMP,AMWT,AKW,POROS,RHO,GAMMA,HC,CONCFA,TIMEFA   '/1X,
     +'       E(i),  i=1,N                                         '/1x,
     +'       X(i),  i=1,N                                         '/1x,
     +'Name of input file?                                         ')
      read(*,'(a60)') filen
      open(10,file=filen,status='old',form='formatted')

      write(*,*) 'Enter name of output file:'
      read(*,'(a60)') filen1
      open(11,file=filen1,status='new',form='formatted')

      read(10,*) n,n1,maxit,m,zmax,zmin,tmax,tmin,escal,difc,pp
      read(10,*) gcr,temp,amwt,akw,poros,rho,gamma,hc,concfa,timefa
      read(10,*) (e(i) , i=1,n)
      read(10,*) (x(i) , i=1,n)

      gcr   = gcr*  7.46496E18/amwt
      gamma = gamma*7.46496E09
      rho   = rho/1000.
      pgt = poros/(gcr*temp)
      gk  = gamma/akw

      dx  = (zmax-zmin)/n1
      twodx = 2*dx
      dx2   = dx**2
      dt  = (pp*dx**2)/difc
      cav = 0.0
      exp = 2.718281828

      write(11,110) filen,filen1
      rewind(10)
29    read(10,'(a80)',end=39,err=39) aline
      write(11,'(a80)') aline
      goto 29
39    write(11,112)

110   format(78('-')/1x,
     +'Program: TRANSMOD',33x,'Latest Revision:  06 May 94'/78('-')//,
     +'Data   file: ',a60/
     +'Output file: ',a60//
     +78('*')/26x,'INPUT DATAFILE'/78('*')/)

112   format(78('*')/26x,'OUTPUT RESULTS'/78('*')//13x,
     +'ZZ(I)        CD(I)         CU(I)         HD(I)'/13x,
     +'(mm)         (ppm)         (ppm)          (m) '/)

c     Initial and Boundary Conditions
      do 13 i=1,n1+1
      zz(i)=zmin+dx*(i-1)
      cd(i)= 38.61540587 + 0.183276694*zz(i)**1.490608745
      cd(i)= cd(i) * 1.E-09
      cu(i)= 23.23591642 + 0.012984311*zz(i)**2.198180496
```

```
      cu(i)= cu(i) * 1.E-09
      cav=cav+cu(i)/(n1+1)
      hd(i)= 1400.0 - 14.0*zz(i)
      write(11,114)  i,zz(i),concfa*cd(i),concfa*cu(i),hd(i)*1.E-03
  114 format(i6,4f12.3)
   13 continue
      nt=(tmax-tmin)/dt
      write(11,115) dx,dt,n1+1,n,nt
      write(*,*)   'no of time step =',nt
115   format(/1x,
     +'Dx                  = ',f17.3/1x,
     +'Dt                  = ',f17.6/1x,
     +'No. of nodes        = ',i17/1x,
     +'No. of parameters = ',i17/1x,
     +'No. of time steps = ',i17)
      call optim(n,n1,dt,nt,maxit,escal,x,e,dx,w,tmin,cav,m)

      write(11,45)
      do 35 i=1,n1+1
      dz(i)= x(1)*exp**(x(2)*1.E03*cn(i))
      ds(i)= x(3)*1.E-06*exp**(-x(4)*1.0E03*cn(i))
      write(11,46) i,zz(i),concfa*cd(i),concfa*cu(i),concfa*cn(i),
     +dz(i),ds(i)*1.E06
   45 format(/
     +'CONCENTRATION OUTPUT'//11x,
     +'ZZ(I)        CD(I)        CU(I)',7x,
     +'CN(I)        DZ(I)        DS(I)'/12x,
     +'(mm)         (ppm)        (ppm)',7x,
     +'(ppm)    (mm2/day)      (mg/kg)'/)

   46 format(i4,6f12.3)
   35 continue
      close(10)
      close(11)
      write(*,920) filen1
920   format(//1x,
     +'ÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝ'/1x,
     +'                                                            '/1x,
     +'  Please see the following file for output:                 '/1x,
     +'                                                            '/1x,
     +'    ',a60                                                    /1x,
     +'                                                            '/1x,
     +'ÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝ')
      stop
      end

c     **********************************************************
c     *                                                        *
c     *   a subroutine to optimize the unknown coefficients    *
c     *                                                        *
c     *          using Powell's optimization method            *
c     *                                                        *
c     **********************************************************
      subroutine optim(n,n1,dt,nt,maxit,escal,x,e,dx,w,tmin,cav,m)
      implicit real*8(a-h,o-z)
      character*10 label
      dimension x(500),e(500),w(2000)
      common /data1/ co(2000),cn(2000),cd(2000),cu(2000),hd(2000),
     +               dz(2000),zz(2000),ds(2000)
      common /data2/ gcr,temp,amwt,akw,poros,rho,gamma,hc,pgt,gk,
```

```
     +                twodx,dx2,concfa,timefa
      write(*,*)  '... OPTIM called'
      iprint=1
      noluck=1
      ddmag=0.1*escal
      scer=0.05/escal
      jj=n*n+n
      jjj=jj+n
      k=n+1
      nfcc=1
      ind=1
      inn=1
      do 1 i=1,n
      do 2 j=1,n
      w(k)=0.0
      if((i-j).ne.0.0) go to 92
      w(k)=abs(e(i))
      w(i)=escal
   92 k=k+1
    2 continue
    1 continue
      iterc=1
      isgrad=2
      call explicit(n1,dt,nt,n,f,x,dx,iterd,tmin,cav)
      if(iterd.eq.m) return
      fkeep=abs(f)+abs(f)
  101 itone=1
      fp=f
      sum=0.0
      ixp=jj
      do 3 i=1,n
      ixp=ixp+1
      w(ixp)=x(i)
    3 continue
      idirn=n+1
      iline=1
      kline=1
  112 dmax=w(iline)
      dacc=dmax*scer
      if(ddmag.lt.(0.1*dmax)) dmag=ddmag
      if(ddmag.ge.(0.1*dmax)) dmag=0.1*dmax
      if(dmag.lt.(20*dacc)) dmag=20*dacc
      ddmax=10*dmag
      if(itone.eq.3) go to 184
      dl=0.0
      d=dmag
      fprev=f
      is=5
      fa=f
      da=dl
  124 dd=d-dl
      dl=d
  126 k=idirn
      do 4 i=1,n
      x(i)=x(i)+dd*w(k)
      k=k+1
    4 continue
      call explicit(n1,dt,nt,n,f,x,dx,iterd,tmin,cav)
      if(iterd.eq.m) return
      nfcc=nfcc+1
```

```
      if(is.eq.1) go to 191
      if(is.eq.2) go to 180
      if(is.eq.3) go to 176
      if(is.eq.4) go to 170
      if(is.eq.5) go to 141
      if(is.eq.6) go to 258
  141 if(f-fa) 147,142,150
  142 if((abs(d)-dmax).gt.0.0) go to 145
      d=d+d
      go to 124
  145 noluck=2
      go to 320
  147 fb=f
      db=d
      go to 154
  150 fb=fa
      db=da
      fa=f
      da=d
  154 if(isgrad.eq.1) go to 158
  155 d=db+db-da
      is=1
      go to 124
  158 d=0.5*(da+db-(fa-fb)/(da-db))
      is=4
      if(((da-d)*(d-db)).ge.0.0) go to 124
  161 is=1
      if((abs(d-db)-ddmax).le.0.0) go to 124
  163 d=db+(abs(ddmax))*sign(db,da)
      is=1
      ddmax=ddmax+ddmax
      ddmag=ddmag+ddmag
      if((ddmax-dmax).le.0.0) go to 124
      ddmax=dmax
      go to 124
  170 if((f-fa).ge.0.0) go to 155
  171 fc=fb
      dc=db
  173 fb=f
      db=d
      go to 193
  176 if((f-fb).le.0.0) go to 171
      fa=f
      da=d
      go to 193
  180 if((f-fb).ge.0.0) go to 191
      fa=fb
      da=db
      go to 173
  184 dl=1.0
      ddmax=5.0
      fa=fp
      da=-1.0
      fb=fhold
      db=0.0
      d=1.0
  191 fc=f
      dc=d
  193 a=(db-dc)*(fa-fc)
      b=(dc-da)*(fb-fc)
```

```
      if(((a+b)*(da-dc)).gt.0.0) go to 201
      fa=fb
      da=db
      fb=fc
      db=dc
      go to 163
  201 d=0.5*(a*(db+dc)+b*(da+dc))/(a+b)
      di=db
      fi=fb
      if((fb-fc).le.0.0) go to 207
      di=dc
      fi=fc
  207 if(itone.eq.1) go to 212
      if(itone.eq.2) go to 212
      itone=2
      go to 214
  212 if((abs(d-di)-dacc).le.0.0) go to 224
      if((abs(d-di)-(0.03*abs(d))).le.0.0) go to 224
  214 if(((da-dc)*(dc-d)).lt.0.0) go to 220
      fa=fb
      da=db
      fb=fc
      db=dc
      goto 161
  220 is=2
      if(((db-d)*(d-dc)).ge.0.0) go to 124
      is=3
      go to 124
  224 f=fi
      d=di-dl
      dd=sqrt((dc-db)*(dc-da)*(da-db)/(a+b))
      do 5 i=1,n
      x(i)=x(i)+d*w(idirn)
      w(idirn)=dd*w(idirn)
      idirn=idirn+1
    5 continue
      w(iline)=w(iline)/dd
      iline=iline + 1
      if((iprint-1).ne.0.0) go to 241
  235 write(11,*) ' Iterc=',iterc
      write(11,*) ' Printing from optim with iprint = ',iprint
      write(11,*) ' Value of f =',f
      do 13 j=1,n
      call outfix(j,label)
      write(11,515) j,x(j),label
515   format(1x,'X[',i3,']    = ',f12.3,2x,a10)
   13 continue
      if(iprint.eq.1) go to 241
      if(iprint.eq.2) go to 300
  241 if(itone.eq.1) go to 243
      if(itone.eq.2) go to 297
  243 if((fprev-f-sum).lt.0.0) go to 246
      sum=fprev-f
      jil=iline
  246 if((idirn - jj).le.0.0) go to 112
      if(ind.eq.2) go to 299
      fhold=f
      is=6
      ixp=jj
      do 6 i=1,n
```

```
      ixp=ixp+1
      w(ixp)=x(i)-w(ixp)
    6 continue
      dd=1.0
      go to 126
  258 if(ind.eq.2) go to 262
      if((fp-f).le.0.0) go to 287
      d=2*(fp+f-2*fhold)/(fp-f)**2
      if(((d*(fp-fhold-sum)**2)-sum).ge.0.0) go to 287
  262 j=jil*n+1
      if((j-jj).gt.0.0) go to 271
      do 7 i=j,jj
      k=i-n
      w(k)=w(i)
    7 continue
      do 8 i=jil,n
      w(i-1)=w(i)
    8 continue
  271 idirn=idirn-n
      itone=3
      k=idirn
      ixp=jj
      aaa=0.
      do 9 i=1,n
      ixp=ixp+1
      w(k)=w(ixp)
      if((aaa-abs(w(k)/e(i))).ge.0.0) go to 281
      aaa=abs(w(k)/e(i))
  281 k=k+1
    9 continue
      ddmag=1.
      w(n)=escal/aaa
      iline=n
      go to 112
  287 ixp=jj
      aaa=0.
      f=fhold
      do 10 i=1,n
      ixp=ixp+1
      x(i)=x(i)-w(ixp)
      if((aaa*abs(e(i))-abs(w(ixp))).ge.0.0) go to 10
      aaa=abs(w(ixp)/e(i))
   10 continue
      go to 299
  297 aaa=aaa*(1.+di)
      if(ind.eq.2) go to 319
  299 if((iprint-2).ge.0.0) go to 235
  300 kline=kline+1
      if(ind.eq.2) go to 306
      if((aaa-0.1).le.0.0) go to 320
      if((f-fp).lt.0.0) go to 307
      noluck=3
      go to 320
  306 ind=1
  307 write(*, *) '**it is going to change the second variable **'
      ddmag=0.4*sqrt(fp-f)
      isgrad=1
      iterc=iterc+1
      if((iterc-maxit).le.0.0) go to 101
      noluck=4
```

```
      if((f-fkeep).le.0.0) go to 320
      f=fkeep
      do 11 i=1,n
      jjj=jjj+1
      x(i)=w(jjj)
   11 continue
      go to 320
  319 if((aaa-0.1).gt.0.0) go to 321
  320 return
  321 inn=1
      go to 307
      return
      end

c     ************************************************************
c     *                                                          *
c     *    a subroutine to compute the unknown coefficients      *
c     *      using the explicit finite difference method         *
c     *                                                          *
c     ************************************************************

      subroutine explicit(n1,dt,nt,n,f,x,dx,iterd,tmin,cav)
      implicit   real*8(a-h,o-z)
      dimension x(500)
      character*10 label
      common /data1/ co(2000),cn(2000),cd(2000),cu(2000),hd(2000),
     +               dz(2000),zz(2000),ds(2000)
      common /data2/ gcr,temp,amwt,akw,poros,rho,gamma,hc,pgt,gk,
     +               twodx,dx2,concfa,timefa
      write(*, *) '... EXPLICIT called'

c     compute variation of concentration with time
      time=tmin
      iterd=iterd+1

      do 14 i=1,n1+1
      co(i)=cd(i)
   14 continue

      exp=2.718281828
      d1=(cu(1)-cd(1))/nt
      d2=(cu(n1+1)-cd(n1+1))/nt
      akcw  = x(5)*timefa*pgt
      const = gk*akcw
      osm   = const*x(5)*timefa/2.
      crp   = const  +  1
      vdp   = (const*x(6)*timefa - x(7)*timefa/poros)*hc
      icount = 0
      write(11,655) osm,crp,vdp
655   format(/1x,
     +'OSM = ',e20.10/1x,
     +'CRP = ',e20.10/1x,
     +'VDP = ',e20.10/)

      do 3 n2=1,nt
      if (n2.ge.ncount) then
       ncount = ncount + 250
       write(*, *) '...n2 =',n2
      endif
```

```
      if (n2.ge.nt) write(11,674)
      do 1 i=2,n1
      ret   = 1 + (rho*x(3)*1.E-06*x(4)*1.E03*exp**
     +        (-x(4)*1.E03*co(i))/poros)
      dw1   = x(1)*exp**(x(2)*1.E03*co(i))
      dw2   = x(2)*1.E03*dw1
      hdx   = (hd(i+1) - hd(i-1))/twodx
      co1x  = (co(i+1) - co(i-1))/twodx
      co2x  = (co(i+1) - 2*co(i)+co(i-1))/dx2
      co2x2 = (co(i+1)**2 - 2*co(i)**2 + co(i-1)**2)/dx2
      vx    = -(akw/poros)*hdx - (x(5)*timefa+x(6)*timefa*hc)*co1x

      aa1   = crp*vx*co1x
      aa2   = osm*co2x2
      aa3   = vdp*co1x**2
      aa4   = dw2*co1x**2 + dw1*co2x
      cn(i) = co(i) + (dt/ret)*(aa4-aa3-aa2-aa1)

      if (n2.ge.nt) write(11,675) i,co(i),hd(i),vx,ret

    1 continue
      if (n2.ge.nt) write(11,676)

  674 format(3x,
     +'i          co(i)              hd(i)',16x,
     +'vx                ret'/)
  675 format(i4,4e18.10)
  676 format(' ')

      cn(1)=co(1)+d1
      cn(n1+1)=co(n1+1)+d2
      do 2 i=1,n1+1
      co(i)=cn(i)
    2 continue

      time=time+dt
      if(n2.ne.nt) go to 3
      do 33 i=1,n1,50
      difc   = x(1)*exp**(x(2)*1.E03*cn(i))
      ss     = difc*dt/(dx**2)
      write(11,433) ss,difc
  433 format(/1x,
     +'=============================================================='/1x,
     +'STABILITY          = ',f10.6/1x,
     +'DIFFUSION          = ',f10.3,'   (mm2/day)')

   33 continue
    3 continue

c     Determine cofficient of correlation
      sumd = 0.0
      s2y  = 0.0
      s2ye = 0.0
      do 51 i=1,n1+1
      sumd = sumd + abs(cu(i)-cn(i))
      s2y  = s2y  + (cu(i)-cav  )**2
      s2ye = s2ye + (cu(i)-cn(i))**2
   51 continue
      sumd = sumd*concfa
      f    = sumd
```

```
      r2    = (1-s2ye/s2y)
      write(*, *) 'iterd          ',iterd
      write(11,510) iterd,r2,sumd
510   format(1x,
     +'ITERD              = ',i10/1x,
     +'R2                 = ',f10.6/1x,
     +'SUMD               = ',f10.6,'   (ppm)     '/1x,
     +'============================================================')
      do 37 j=1,n
      call outfix(j,label)
      write( *,515) j,x(j),label
      write(11,515) j,x(j),label
*15   format(1x,'X[',i3,']     = ',e20.10,2x,a10)
515   format(1x,'X[',i3,']     = ',f12.3,2x,a10)
   37 continue
      write(*, 525) sumd,ss,difc
525   format(/1x,
     +'SUMD               = ',f10.6,'  (ppm)     '/1x,
     +'STABILITY          = ',f10.6/1x,
     +'DIFFUSION          = ',f10.3,'  (mm2/day)'/)
   40 format(1x,50(f8.5,1x))
   41 format(2x,'time = ',f12.3)
   45 format(i3,2x,i3,2x,3(f10.5,2x))
      return
      end
      subroutine outfix(j,label)
      implicit real*8(a-h,o-z)
      character*10 label

      label              = '          '
      if (j.eq.1) label = '(mm2/day) '
      if (j.eq.2) label = '(ml/g)    '
      if (j.eq.3) label = '(mg/kg)   '
      if (j.eq.4) label = '(ml/g)    '
      if (j.eq.5) label = '(mm5/g/s) '
      if (j.eq.6) label = '(mm5/g/s) '
      if (j.eq.7) label = '(mm5/g/s) '
      return
      end
```

```
------------------------------------------------------------------------------
 Program: TRANSMOD                                  Latest Revision:  06 May 94
------------------------------------------------------------------------------

Data   file: transmod.dat
Output file: transmod.out

*******************************************************************************
                            INPUT DATAFILE
*******************************************************************************

 7    9    1    1  100.0     0.0     20     4    0.50    1200.   0.10
  8.314510      293.0    900.0     .864      0.44     1.50     9.807    0.03
 1.0E09     8.64E04
   .1         .1          .1          0.001       .1          1                .1
 2057.459   1800.191   9881.518    15.616    13627.518    1.188111635E06  -7010.380


      read      n,n1,maxit,m,zmax,zmin,tmax,tmin,escal,difc,pp
      read      gcr,temp,amwt,akw,poros,rho,gamma,hc,concfa,timefa

      read      (e(i) , i=1,n)
      read      (x(i) , i=1,n)
*******************************************************************************
                            OUTPUT RESULTS
*******************************************************************************

             ZZ(I)        CD(I)        CU(I)        HD(I)
             (mm)         (ppm)        (ppm)         (m)

     1         .000       38.615       23.236       1.400
     2       11.111       45.252       25.819       1.244
     3       22.222       57.264       35.091       1.089
     4       33.333       72.744       52.141        .933
     5       44.444       91.019       77.638        .778
     6       55.556      111.698      112.083        .622
     7       66.667      134.520      155.884        .467
     8       77.778      159.295      209.385        .311
     9       88.889      185.873      272.889        .156
    10      100.000      214.135      346.666        .000

Dx                 =          11.111
Dt                 =         .010288
No. of nodes       =              10
No. of parameters  =               7
No. of time steps  =            1555

OSM =       .1278922891E+10
CRP =       .3172420286E+01
VDP =       .6731451216E+10

  i          co(i)              hd(i)              vx                ret

  2    .2987796839E-07    .1244444444E+04    .2426619525E+02    .1525810697E+01
  3    .4007931734E-07    .1088888889E+04    .2257471658E+02    .1525726940E+01
  4    .5554126358E-07    .9333333333E+03    .2015795276E+02    .1525600017E+01
  5    .7835849834E-07    .7777777778E+03    .1692198880E+02    .1525412771E+01
  6    .1107126835E-06    .6222222222E+03    .1295662756E+02    .1525147377E+01
  7    .1542297253E-06    .4666666667E+03    .8621883858E+01    .1524790628E+01
```

8	.2092119518E-06	.3111111111E+03	.4499592954E+01	.1524340235E+01
9	.2742479979E-06	.1555555556E+03	.1175923973E+01	.1523807984E+01

STABILITY	=	.178779	
DIFFUSION	=	2145.346	(mm2/day)
ITERD	=	1	
R2	=	.999478	
SUMD	=	17.674196	(ppm)

X[1]	=	2057.459	(mm2/day)
X[2]	=	1800.191	(ml/g)
X[3]	=	9881.518	(mg/kg)
X[4]	=	15.616	(ml/g)
X[5]	=	13627.518	(mm5/g/s)
X[6]	=	1188111.635	(mm5/g/s)
X[7]	=	-7010.380	(mm5/g/s)

CONCENTRATION OUTPUT

	ZZ(I) (mm)	CD(I) (ppm)	CU(I) (ppm)	CN(I) (ppm)	DZ(I) (mm2/day)	DS(I) (mg/kg)
1	.000	38.615	23.236	23.236	2145.346	9877.933
2	11.111	45.252	25.819	29.872	2171.128	9876.910
3	22.222	57.264	35.091	40.079	2211.390	9875.335
4	33.333	72.744	52.141	55.549	2273.841	9872.950
5	44.444	91.019	77.638	78.377	2369.233	9869.431
6	55.556	111.698	112.083	110.746	2511.387	9864.444
7	66.667	134.520	155.884	154.278	2716.114	9857.740
8	77.778	159.295	209.385	209.276	2998.788	9849.277
9	88.889	185.873	272.889	274.325	3371.333	9839.278
10	100.000	214.135	346.666	346.666	3840.244	9828.169

```
      program TRANSPRE              Appendix B
c     ****************************************************************
c     *                                                              *
c     *         A Computer Program to Predict the Transport          *
c     *         of Oil Residue in an Oil-Soil-Water System           *
c     *         using the Explicit Finite Difference Method          *
c     *                                                              *
c     ****************************************************************
c
c                       LIST OF VARIABLES
c                       =================
c
c        INPUT DATA
c        ==========
c     1  n        = number of unknown coefficients
c     2  n1+1     = number of nodes in the soil vertical direction
c     3  zmax     = maximum soil depth (mm)
c     4  zmin     = minumum soil depth (mm)
c     5  tmax     = final time (days)
c     6  tmin     = initial time (days)
c     7  difc     = initial value of maximum diffusion parameter
c     8  pp       = stability requirement, less than 0.5
c
c     9  grc      = universal gas constant
c    10  temp     = absolute temperature
c    11  amwt     = molecular weight of oil
c    12  akw      = soil permeability
c    13  poros    = effective porosity of the soil
c    14  rho      = dry density of the soil
c    15  gamma    = specific weight of water
c    16  hc       = vapor-liquid partition coefficient of the oil
c
c    17  x(n)     = Final value of each unkown coefficients,
c                   as descibed below:
c        x(1), x(2)  = diffusion/dispersion coefficients
c        x(3), x(4)  = desorption isotherm coefficients
c        x(5)        = osmostic coefficient
c        x(6)        = vapor coefficient
c        x(7)        = vapor restriction coefficient
c
c    18  hd(i)    = variation of head with soil depth
c    19  cd(i)    = variation of concentration with soil depth, at time tmin
c    20  concfa   = concentration conversion factor for printout


c        OTHER PARAMETERS
c        ================
c        dx       = distance between node n and n+1 in the vertical direction
c        dt       = time step interval
c        nt       = number of time steps
c        c        = total oil concentration in the soil pore fluid
c        vx       = seepage velocity in the vertical direction
```

```
c        hdx     = hydraulic gradient
c        co1x    = concentration gradient
c
c        ret     = desorption factor
c        crp     = oil restriction parameter
c        akcw    = oil restriction coefficient
c        vdp     = vapro density parameter
c        osm     = osmotic parameter
c
c        OUTPUT DATA
c        ============
c        zz(i)       = value of each soil depth interval
c        cd(i)       = input concentration at time tmin
c        cu(i)       = Experimently measured concentration
c                      at a given time (i.e tmax)
c        cc(i,j)     = computed concentration at a given time
c                      (i.e tmax) based on the calibrated model
c     ============================================================

      implicit real*8(a-h,o-z)
      common /data1/ co(2000),cn(2000),cd(2000),cu(2000),x(500),
     +cc(100,200),hd(2000),ds(2000),zz(2000)
      common /data2/ gcr,temp,amwt,akw,poros,rho,gamma,hc,pgt,gk,
     +               twodx,dx2
      character filen*60,filen1*60,filen2*60,filen3*60,aline*80

      write(*,900)
900   format(/1x,
     +'ÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝ'/1x,
     +'Ý                                                              Ý'/1x,
     +'Ý TRANSPRE                                        6 MAY 94     Ý'/1x,
     +'Ý                                                              Ý'/1x,
     +'Ý       A Computer Program to Predict the Transport            Ý'/1x,
     +'Ý       of Oil Residue in an Oil-Soil-Water System             Ý'/1x,
     +'Ý       using the Explicit Finite Difference Method            Ý'/1x,
     +'Ý                                                              Ý'/1x,
     +'ÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝ')
      write(*,910)

910   format(/1x,
     +'A file containing the following lines of input is required:'/1x,
     +'          N,N1,ZMAX,ZMIN,TMAX,TMIN,DIFC,PP                    '/1x,
     +'          GCR,TEMP,AMWT,AKW,POROS,RHO,GAMMA,HC,CONCFA,TIMEFA'/1X,
     +'          X(i),  i=1,N                                        '/1x,
     +'Name of input file?                                           ')
      read(*,'(a60)') filen
      open(10,file=filen,status='old',form='formatted')

      write(*,*) 'Enter name of output file:'
      read(*,'(a60)') filen1
      open(11,file=filen1,status='new',form='formatted')
```

```
      read(10,*) n,n1,zmax,zmin,tmax,tmin,difc,pp
      read(10,*) gcr,temp,amwt,akw,poros,rho,gamma,hc,concfa,timefa
      read(10,*) (x(i),i=1,n)

*-----------------------------------------------------------------------
*     ADJUSTMENT TO INPUT
      x(2) = x(2) * 1.0E+03
      x(3) = x(3) * 1.0E-06
      x(4) = x(4) * 1.0E+03
      x(5) = x(5) * timefa
      x(6) = x(6) * timefa
      x(7) = x(7) * timefa
*-----------------------------------------------------------------------

      gcr   = gcr*  7.46496E18/amwt
      gamma = gamma*7.46496E09
      rho   = rho/1000.
      pgt = poros/(gcr*temp)
      gk  = gamma/akw

      dx  = (zmax-zmin)/n1
      twodx = 2*dx
      dx2   = dx**2
      dt  = (pp*dx**2)/difc
      exp = 2.718281828

      write(11,110) filen,filen1
      rewind(10)
29    read(10,'(a80)',end=39,err=39) aline
      write(11,'(a80)') aline
      goto 29
39    write(11,112)

110   format(78('-')/1x,
     +'Program: TRANSPRE',33x,'Latest Revision:   6 May 94'/78('-')//1x,
     +'Data   file: ',a60/1x,
     +'Output file: ',a60//
     +78('*')/26x,'INPUT DATAFILE'/78('*')//)

112   format(78('*')/26x,'OUTPUT RESULTS'/78('*')//)

      do 13 i=1,n1+1
      zz(i)=zmin+dx*(i-1)
      cd(i)= 38.61540587 + 0.183276694*zz(i)**1.490608745
      cd(i)= cd(i) * 1.E-09
      cu(i)= 7.120277141 + 0.001992419*zz(i)**2.733336742
*     cu(i)= 23.23591642 + 0.012984311*zz(i)**2.198180496
      hd(i)= 1400.0 - 14.0*zz(i)
   13 continue
```

```
      NT=(TMAX-TMIN)/DT
      write(11,115)  dx,dt,n1+1,n,nt
      write(*,*)   'No of time step =',nt

115   format(/1x,
     +'Dx                = ',e17.10/1x,
     +'Dt                = ',e17.10/1x,
     +'No. of nodes      = ',i17/1x,
     +'No. of parameters = ',i17/1x,
     +'No. of time steps = ',i17/)

      CALL EXPL(N1,DT,NT,DX,TMIN,TMAX,N4)

      write(11,144)
      do 35 i = 1, n1+1
      write(11,145)  i,zz(i),concfa*cd(i),cu(i),concfa*cc(i,n1+1)
   35 continue
      write(11,148)

144   format(78('=')/11x,
     +'ZZ(I)       CD(I)       CU(I)       CC(I)'/12x,
     +'(mm)       (ppm)       (ppm)       (ppm)'/)
145   format(i4,4f12.3)
148   format(78('='))
*=============================================================================
*          ZZ(I)       CD(I)       CU(I)       CC(I)
*           (mm)       (ppm)       (ppm)       (ppm)
*
*  1        .000      61.772      42.366      42.366
*=============================================================================

      write(*,920) filen1
920   format(//1x,
     +'ÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝ'/1x,
     +'                                                                '/1x,
     +'  Please see the following file for output:                     '/1x,
     +'                                                                '/1x,
     +'    ',a60                                                        /1x,
     +'                                                                '/1x,
     +'ÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝÝ')
      end

C     ************************************************************              C
C     *                                                          *              C
C     *         A SUBROUTINE TO CUMPUTE CONCENTRATION            *              C
C     *                    AT A GIVEN TIME                       *              C
C     *                                                          *              C
C     *       USING THE EXPLECIT FINITE DIFFERENCE METHOD        *              C
C     *                                                          *              C
C     ************************************************************              C
```

```
      SUBROUTINE EXPL(N1,DT,NT,DX,TMIN,TMAX,N4)
      implicit real*8(a-h,o-z)
      common /data1/ co(2000),cn(2000),cd(2000),cu(2000),x(500),
     +cc(100,200),hd(2000),ds(2000),zz(2000)
      common /data2/ gcr,temp,amwt,akw,poros,rho,gamma,hc,pgt,gk,
     +               twodx,dx2

C     COMPUTE CONCENTRATION THROUGH TIME

      TIME=TMIN
      DO 14 I=1,N1+1
      CO(I)=CD(I)
   14 CONTINUE

      EXP=2.718281828
      N3=NT/10
      IF(NT.LT.8)  N3=1

      D1=(-67.0717837+109.9245144*exp**(-TMAX/101.7447998))*1.E-09
      D1=(D1-CD(1))/NT
      D2=(-111.293155+298.7863735*exp**(TMAX/46.8330369))*1.E-09
      D2=(D2-CD(N1+1))/NT

      akcw  = x(5)*pgt
      const = gk*akcw
      osm   = const*x(5)/2
      crp   = const  +  1
      vdp   = (const*x(6) - x(7)/poros)*hc

      DO 3 N2=1,NT
      DO 1 I=2,N1
      ret   = 1 + (rho*x(3)*x(4)*1.E00*exp**(-x(4)*1.E00*co(i))/poros)
      dw1   = x(1)*exp**(x(2)*1.E00*co(i))
      dw2   = x(2)*1.E00*dw1
      hdx   = (hd(i+1) - hd(i-1))/twodx
      co1x  = (co(i+1) - co(i-1))/twodx
      co2x  = (co(i+1) - 2*co(i)+co(i-1))/dx2
      co2x2 = (co(i+1)**2 - 2*co(i)**2 + co(i-1)**2)/dx2
      vx    = -(akw/poros)*hdx - (x(5)+x(6)*hc)*co1x
      aa1   = crp*vx*co1x
      aa2   = osm*co2x2
      aa3   = vdp*co1x**2
      aa4   = dw2*co1x**2 + dw1*co2x
      cn(i) = co(i) + (dt/ret)*(aa4-aa3-aa2-aa1)
    1 continue

      cn(1)=co(1)+d1
      cn(n1+1)=co(n1+1)+d2
      if(n2/n3*n3-n2.ne.0) go to  15
      n4=n4+1
```

```
      do 16 i=1,n1+1
      cc(i,n4)=cn(i)
   16 continue
      write(11,222) n4, time
      write( *,222) n4,time
222   format(1x,'Time in days: ',i5,f12.4)
   15 do 2 i=1,n1+1
      co(i)=cn(i)
   2  continue
      time=time+dt
   3  continue

      do 51 i=1,n1+1
   51 continue
      return
      end
```

```
-------------------------------------------------------------------------------
 Program: TRANSPRE                                    Latest Revision:   6 May 94
-------------------------------------------------------------------------------

 Data   file: prednew.dat
 Output file: prednew.out

*******************************************************************************
                            INPUT DATAFILE
*******************************************************************************


7    9    100.    0.0    40    4    1200    0.10
8.31451  293.0   900.0   0.864   0.44   1.50    9.807   .03   1.0E09   8.64E04

2057.459    1800.191    9881.518   15.616   13627.518    1.188111635E06    -7010.380


 Read       n,n1,zmax,zmin,tmax,tmin,difc,pp
 Read       gcr,temp,amwt,akw,poros,rho,gamma,hc,concfa,timefa
 Read       (x(i),i=1,n)
*******************************************************************************
                            OUTPUT RESULTS
*******************************************************************************


 Dx                 =    .1111111111E+02
 Dt                 =    .1028806584E-01
 No. of nodes       =                 10
 No. of parameters  =                  7
 No. of time steps  =               3499

 Time in days:      1       7.5802
 Time in days:      2      11.1708
 Time in days:      3      14.7613
 Time in days:      4      18.3519
 Time in days:      5      21.9424
 Time in days:      6      25.5329
 Time in days:      7      29.1235
 Time in days:      8      32.7140
 Time in days:      9      36.3045
 Time in days:     10      39.8951
===============================================================================
           ZZ(I)        CD(I)        CU(I)        CC(I)
            (mm)         (ppm)        (ppm)        (ppm)

   1         .000       38.615        7.120        7.201
   2       11.111       45.252        8.558       35.416
   3       22.222       57.264       16.684       74.896
   4       33.333       72.744       36.088      126.999
   5       44.444       91.019       70.715      191.228
   6       55.556      111.698      124.153      265.118
   7       66.667      134.520      199.756      345.063
   8       77.778      159.295      300.700      427.493
   9       88.889      185.873      430.020      509.631
  10      100.000      214.135      590.638      589.664
===============================================================================
```

RETENTION AND TRANSPORT OF OIL RESIDUE IN A SANDY LOAM SOIL

Raymond N. Yong, Lamya F. Mohammed, and Abdel M. O. Mohamed

Raymond N. Yong[1], Lamya F. Mohammed[2], and Abdel M. O. Mohamed[3]

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RETENTION AND TRANSPORT OF OIL RESIDUE IN A SANDY LOAM SOIL

REFERENCE: Yong, R. N., Mohammed, L. F., and Mohamed, A. M. O., **"Retention and Transport of Oil Residue in a Sandy Loam Soil,"** Analysis of Soils Contaminated with Petroleum Constituents, ASTM STP 1221, Tracey A. O'Shay and Keith B. Hoddinott, Eds., American Society for Testing and Materials, Philadelphia, 1994.

ABSTRACT: The behaviour of a natural soil obtained from Bahrain, containing oil residue as a stabilizing agent has been experimentally investigated to determine the effectiveness of the mixture, particularly with respect to leaching forces. The experimental work focuses on the examination of interaction mechanisms, retention potential and leaching behaviour. The results show good attenuation of the oil residue in the tested soils. This is attributed to low aqueous mobility of the oil and good interaction behaviour. The bondings between oil and soil surfaces are shown to be dominated by Van der Waal's attraction, weak hydrogen bonding and cation and water bridging.

KEYWORDS: Soil stabilization, leaching, partition coefficients, infrared spectra, functional groups, oil-soil interaction processes, fluid holding capacity.

The problem of collapsible soils is well known, and exists in many parts of the world where soil type, texture, climate, and regional controls favour the formation and retention of salt-crystallized cementation bonds. In the Arabian Gulf region, the collapsible soil consists of medium to fine-sized particles cemented by crystallized salt, with a strong potential for loss in strength under wet conditions. To combat the problem, various methods have been proposed [1, 2], not the least of which is stabilization of the soil matrix. The common types of soil stabilizers include cement, lime, bitumen, organic polymers, and fly ashes [3, 4].

Because of the significant presence of a very active petroleum industry in Bahrain, the use of oil residue (residuum) for stabilization appears as a very propitious use of a "native" product. Oil residue is the heavy fraction remaining undistilled in the fractionation process of crude oil. From the initial study of the stability and mechanical properties of the soil mixed with various proportions and types of oil residues, it is clear

[1] William Scott Professor, Civil Engineering Department, Director, Geotechnical Research Centre, McGill University, 817 Sherbrooke St. West, Montreal, Quebec, Canada, H3A 2K6.

[2] Lecturer, Civil Engineering Department, University of Bahrain, P.O.Box: 32038, Isa Town, State of Bahrain.

[3] Associate Director, Geotechnical Research Centre, Adjunct Professor, Civil Engineering Department, McGill University, 817 Sherbrooke St. West, Montreal, Quebec, Canada, H3A 2K6.

that whereas stability can be achieved with a 4% addition of oil residue [5], long-term stability which requires proper retention of the additive and bondings achieved, constitutes the primary problem. It is expected that the effects of rainfall and groundwater fluctuation would provide the opportunity for migration of oil residue from the stabilized soils, and hence poses a threat to the surrounding environment in the form of surface and groundwater contamination. Since oil residue contains toxic substances (hydrocarbons and heavy metals), its leachability from the stabilized soil can cause a significant threat to human health and all living creatures. This constitutes another important consideration for high oil retention capability of the stabilized soil.

A proper knowledge of the various mechanisms of interaction between oil and soil surfaces is important in predicting the oil retention capability of the soil, and also the long-term behaviour of oil. Interaction mechanisms are influenced by soil constituents, the type of petroleum hydrocarbon and the presence of water. Previous studies [6 - 9] have shown that the presence of surface-active constituents in the soil matrix, such as organics, amorphous materials and clay minerals, can significantly enhance its interaction with oil. In addition, the solubility and octanol-water ratio of oil residue play a major role in interaction behaviour. However, the presence of water on soil surfaces, prior to the introduction of oil, interferes with soil-oil bonding.

This study focuses attention on the investigation of: (a) the nature of interactions between soil and oil residue; (b) the retention potential of adsorbed fluids (oil and water) to soil surfaces; (c) the leachability behaviour of non-adsorbed or desorbed oil residue from the soil, and (d) the fate of the oil residue in the stabilized soil.

MATERIALS AND METHODS

Soil Sample

The composition and properties of the tested natural soil, obtained from the eastern part of Bahrain (Sanad) by the Ministry of Works (Geotechnical Division) in Bahrain, are given in (Table 1). Measurement of specific gravity and consistency limits were performed according to ASTM D 854, test method for specific gravity of soils, and ASTM D 4318, test method for liquid limit, plastic limit, and plasticity index of soils, respectively, and particle size analysis was conducted using the method described in ASTM D 422, method for particle-size analysis of soils. Determinations of compaction parameters and permeability coefficient (at maximum dry density) were carried out following ASTM D 698, test methods for moisture-density relations of soils and soil-aggregate mixtures using 5.5-lb (2.49-kg) rammer and 12-in. (305-mm) drop, and ASTM D 2434, test method for permeability of granular soils, respectively. The pH and conductivity measurements of 1:10 soil-water extract were conducted according to ASTM D 1293, test methods for pH of water, and ASTM D 1125, test methods for electrical conductivity and resistivity of water, respectively, and cation exchange capacity (C.E.C.) was determined at natural soil pH using the silver thiourea method [10]. The ethylene glycol-monoethyl ether (EGME) method without sample pretreatment [11] was used for determination of specific surface area, and the rapid titration method [12] was used for determination of carbonate content. Organic content determination involved the wet oxidation method [13], and amorphous material determination was performed using the method described by Segalen [14]. Sample preparation for X-ray diffraction and analysis were performed following the procedures described by Moore and Reynolds [15].

TABLE 1--Selected properties and composition of the tested soil from Bahrain.

Properties	Value[1]	Variation Range[2]	Properties	Value[1]	Variation Range[2]
Geotechnical			Chemical		
Specific gravity	2.7	...	Soil pH (1:10 soil/water)	7.8	7.2 - 8.5
Consistency limits			Soil Conductivity (1:10 soil/water; ds/m)	1.5	0.25 - 10
liquid limit (%)	21	...	C.E.C. (cmol/kg)	24	...
plastic limit (%)	16	...	Surface Area (m^2/kg)	$40X10^{-3}$	...
Soil Gradation			Organic Content (w%)	1.3	0 - 4
sand (w%)	63	50 - 90	Carbonate Content (w%)	28	4 - 50
silt (w%)	25	5 - 35	Amorphous Silica (w%)	0.3	...
clay (w%)	12	0 - 20			
effective diameter D_{10} (mm)	0.02	...	Mineralogical Composition (by X-ray analysis)		
Soil Texture	sandy loam	sandy to loamy soils			
Compaction					
maximum dry density (Mg/m^3)	1.78	...	Quartz, Calcite, Dolomite, Feldspar, Palygorskite, Montmorillonite, Illite, Kaolinite.		Quartz, Calcite, Dolomite, Feldspar, Halite, Palygorskite, Smetite.
optimum moisture content (%)	14	...			
Permeability (m/s)	$1x10^{-8}$	...			

1 Experimentally measured values obtained based on average of triplicate samples.
2 Variation range values were obtained from Doornkamp et al. [40].

From soil gradation analyses, the soil sample can be classified as a sandy loam. As can be seen from (Table 1), the values of cation exchange capacity (C.E.C.) and specific surface area are representative of the presence of the high carbonate content. The soil organic content and amorphous materials content are considered to be low. The clay mineral fraction, which represents 12% by soil weight is dominated by expandable type minerals (e.g., montmorillonite and palygorskite).

Oil Residue Samples

The oil residue used for the study was provided by the Bahrain Petroleum Company (BAPCO), and is classified as atmospheric Arabian oil residue. This oil residue is the bottoms remaining from the fractional distillation of crude oil, and is a complex mixture consisting mostly of saturates and aromatic hydrocarbons, and to a lesser extent, resins, asphaltenes, and heavy metals. The typical composition and properties of Arabian oil residue are presented in (Table 2).

Previous studies on the properties of Arabian oil residue [16 - 18] indicate that the typical oil residue has a high boiling point, a high molecular weight and a complex structure. These studies also show that the main types of hydrocarbons present in oil residue include: (a) paraffinic (i.e., n-hexadecane); (b) cycloparaffinic (i.e., methyleycyclohexane); (c) monocyclic aromatic (i.e., butylbenzen); (d) polycyclic aromatic (i.e.,naphthalene, pyrene, phenanthrene, and chrysene); (e) heterocyclic compounds (i.e., quinoline, dibenzofuran, and benzothiophene). Moreover, the polycyclic aromatic hydrocarbon represents the major constituent of the Arabian oil residue.

For this study, the tests on the oil residue sample received from BAPCO which were conducted at room temperature (22±2 °C), included determination of specific gravity, viscosity, hydrocarbon concentration, water solubility, and volatilization ratio. The specific gravity was measured in pycnometer following the method described in ASTM D 891, test methods for specific gravity, apparent, of liquid industrial chemicals by pycnometer method, and oil viscosity was determined using a Contraves Rheomat 15 rotating cylindrical viscometer, and the method described by the Institute of Petroleum (Method IP 72, [19]). Determination of total petroleum hydrocarbon present in the oil residue was conducted using Soxhlet extraction method [20], and its water solubility was determined by preparing a saturated aqueous solution of the oil residue, then measuring the oil concentration in the extracted soluble parts (of the aqueous solution) using an Infrared spectrophotometer (ASTM E1148, test methods for measurement of aqueous solubility, [21]). Determination of the volatilization ratio, i.e., the ratio of the volatilized fraction weight to the oil residue weight, will be discussed later when the problem of oil transformation is addressed. The organic carbon partition coefficient (K_{oc}) and octanol-water ratio (K_{ow}) were estimated from empirical relations described by Means et al. [8], and Chiou et al. [22], respectively. The vapour pressure (P_v) and Henry's law constant (K_h) were both estimated from Mackay [23].

The results shown in (Table 2) indicate that the oil residue has a low water solubility, low volatilization ratio, high organic carbon partition coefficient, and a density slightly less than that of water, indicating, thereby, a behaviour similar to a non-polar organic compound in soil. Moreover, from these results, one would expect that this oil residue would have a high retention potential in soil.

TABLE 2--Properties of Arabian oil residue.

Properties	Value[3]	Variation Range[3]
Physical		
Specific Gravity	0.97[1]	0.94-0.99
Viscosity (m^2/s)	40E-6[1]	20-90
Boiling Point (°C)	> 370	370+
Chemical		
Elemental Composition (w%)		
Carbon	82	82-84
Hydrogen	11	11-12
Sulfur	4	2.5-5
Oxygen	2	1- 2
Nitrogen	< 1	< 1
Metal Concentration (ppm)		
Vanadium	40	20-110
Nickel	15	6- 28
Iron	10	6- 20
Hydrocarbon Types (w%)		
Saturates	26	15-35
Aromatic	49	45-53
Resin	15	13-18
Asphaltene	10	3-12
Hydrocarbon Conc. (w%)	93[1]	
Molecular Weight (g/mole)	> 1000	
Physico-chemical		
Water Solubility (ppm)	< 10[1]	Low Solubility
Organic Carbon partition coefficient (log)	3.6[2]	
Octanol-water Ratio (log)	4.3[2]	High Partitioning
Volatilization Ratio (w%)	5[1]	
Vapor Pressure (KPa)	4E-4[2]	Low Volatility
Henry's Law Constant ($atm-m^3/mole$)	4E-4[2]	

[1] Experimentally measured values at a room temperature of 22±2 °C, based on average values obtained from triplicate samples.
[2] Estimated values based on empirical relations.
[3] Other values and variation range were obtained from studies conducted on oil residue by Ali and Bukhari [16] and Ali et al. [17].

Sample Preparation

To ensure that the soil samples to be tested were as close to uniform as possible, the natural soil was air dried, ground, and sieved to finer than 4.75 mm mesh. This constituted the source batch from which all samples were derived. One batch of the soil was used to determine the

"natural" soil properties and behaviour. For the oil-stabilized test samples, a test batch of the soil was mixed with the oil residue. Since a previous study by Mohammed [5] had shown that the resultant unconfined compressive strength of the stabilized soil was obtained with a 4% addition of oil, this was the amount used for all the tests conducted for this study. In the procedure followed, soil samples were first mixed thoroughly with oil residue at 4% by dry weight of soil and then mixed with water at the optimum moisture content. The additional of oil residue to dry soil simulates an actual field condition in most arid regions. The oil-soil mixture samples were left to cure in closed glass containers for 24 hours. Volatilization of oil from the mixtures during this curing period is negligible since oil residue consists of mainly heavy forms of hydrocarbons.

Testing Procedures

The experimental program consisted of four parts. The first part involved the determination of the properties of the soil sample and oil residue, as shown in (Tables 1 and 2). In the second part, the possible bonding mechanisms of the soil and oil residue were evaluated. In the third part, the retention of soil fluids (oil and water) in the soil sample, under various pressures, was measured. The final part examined the retention capacity and leachability behaviour of the oil residue in the soil. In all the experiments followed, the preparation and testing were performed at a room temperature of 22±2 °C. Moreover, triplicate samples were used in all experiments, except for the leaching test, whereby duplicate samples were used. The reported results consist of the calculated average values.

Interaction and Bonding -- Infrared spectrophotometry was used for evaluation of possible bonding mechanisms. Preparation and interpretation of infrared analysis were performed according to the methods described by White and Roth [24] and ASTM E 204, practice for identification of material by Infrared Absorption Spectroscopy using the ASTM code band and chemical classification index. The analyses were also performed on the oil sample, natural soil, and both leached and unleached soil-oil mixtures. Only the fine portion of the soil samples, finer than 0.075 mm mesh, was tested.

The infrared tests were conducted on dried soil samples using the pressed-pellet method. The pellets were prepared by mixing 2% of the sample (by weight) with buffering material (potassium bromide, KBr). The sample-KBr mixture was then ground into a homogenous fine powder. Approximately 200 mg of the mixture powder was placed in a special mould, an evacuable KBr die connected to a vacuum pump. With a pressure of 670 MPa applied to the mould and maintained for 10 minutes, a clear disc (pellet) of 13 mm diameter and 1 mm thickness was formed. This pellet was then placed in a suitable sample holder and analyzed by infrared spectrophotometry using a model Michelson-100, manufactured by Bomem. A similar procedure was used for determining the infrared spectra of oil residue. Only 0.5% of the oil by weight was used in the preparation of oil-KBr pellet. A blank sample of pure KBr was also tested as "background" along with the other samples.

Retention of soil fluids -- Retention of pore fluids by the soil (soil suction) was determined using a pressure plate apparatus. The test was conducted on the soil sample and its mixture with oil before and after leaching. The test procedure followed the method described by Yong and Warkentin [25]. The samples were compacted to their maximum dry densities in lucite rings of 38.1 mm diameter and 12 mm height. The change in moisture content of the tested samples was monitored under various suctions. Each sample was subjected to two cycles (desorption and absorption) in the suction range between pF 0.0 and pF 3.8 (where suction pF is the logarithm value of the water head in cm). For each pF stage, an equilibrium had to be established between the applied pressure and the

energy at which liquid was retained in the soil sample.

Leachability behaviour -- The leachability behaviour of the soil-oil mixture was examined using leaching column test. The test procedure followed the methods described by Fuller [26] and Yong et al. [27]. In this test, lucite chambers of 50 mm diameter and 100 mm height were used as leaching cells. The test was performed on duplicate samples obtained from natural soil and soil-oil mixture. During the preparation of each cell, the sample was subsequently compacted until its maximum dry density was reached. The compacted samples were then leached with distilled water (pH = 6) under a hydraulic gradient of 10. During the leaching period, effluents were collected until 10 pore volumes of leachate were recovered.

The concentration of oil, some heavy metals, and salt were measured in each collected pore volume. The electrical conductivity of the collected effluents was measured according to the test methods for electrical conductivity and resistivity of water, ASTM (D 1125), and the salt concentrations of the effluents were estimated from electrical conductivity based on the empirical relationship given in Brown et al. [28]. Moreover, the typical heavy metals present in this oil residue include: vanadium, nickel, iron, and lead. The measurement of the concentration of these heavy metals in the collected effluents was conducted using Atomic Absorption Spectrophotometry.

Determination of oil concentration -- The oil in the effluents collected from the leaching columns and the oil present in the soil pore fluids were extracted, measured, and reported in terms of total petroleum hydrocarbon, using infrared spectrophotometry. Preparation and analysis were performed according to the Partition-Infrared Method (ASTM D 3921, petroleum hydrocarbons (oil/grease) content of water/wastewater). In this test, each fluid sample was first acidified with hydrochloric acid to pH 2. The sample was then transferred to a "separating" funnel and mixed with carbon tetrachloride (CCl_4) at a ratio of 1:10 of the sample volume. Following this, the sample was shaken for 15 minutes and left to separate into two layers. The CCl_4 sample was extracted and placed in a 10 mm path-length cell and analyzed using an infrared spectrophotometer. The absorbance of the sample at a frequency of 2930 cm^{-1} was measured. A typical band for petroleum hydrocarbon (C-H group) is present at this frequency. A blank sample of pure CCl_4 as well as standards (of known concentration of oil residue) were also tested along with the other samples. The concentration of oil in the sample was then determined by comparing the sample absorbance at the above frequency to the absorbances of the standards at the same frequency.

The amount of oil adsorbed to the soil at the end of leaching was measured by Soxhlet extraction method [20]. The soil sample was oven dried, then ground and placed in a thimble. The thimble was placed in the extractor and washed several times with trichlorotrifluoroethane(freon). The oil content was then determined as the ratio of the difference between the weight of the sample before and after washing to the weight of the dry soil.

RESULTS AND DISCUSSION

Infrared Spectra

The infrared spectra of the oil residue, natural soil, and soil-oil mixture (Figs. 1 and 2), and the corresponding main assignments of various frequency peaks present in the oil residue and soil are summarized in (Tables 3 and 4), respectively. Each reported infrared spectrum represents a composite of multiple scans. The major vibrational frequencies present in the oil are associated with the alkyl C-H group, aromatic C-H and C=C groups, and the carbonyl group. The dominant frequencies found in soil are assigned to the hydroxyl group, the carbonate group, and the silanol and siloxane groups.

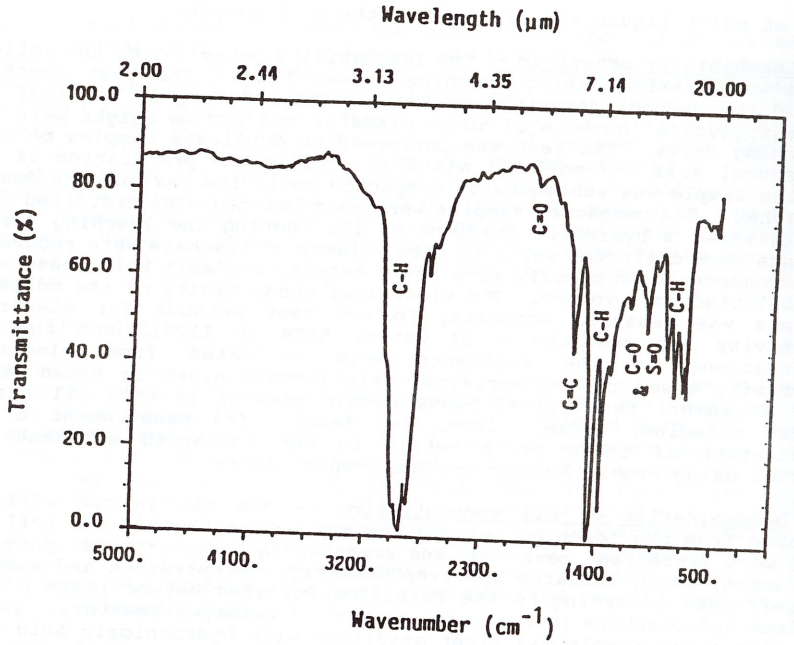


FIG. 1--Infrared spectra of oil residue. This spectrum is a composite of multiple scans.

TABLE 3--Characteristic infrared absorption frequencies present in the tested oil residue.

Wavenumber (cm^{-1})	Intensity	Peak Assignment
2850-2960	Very Strong	C-H stretch
2960		methyl group (CH_3)
2930		methylene group (CH_2)
2860		CH_2 & CH_3
2710	Weak	C-H stretch (aldehyde)
1700	Very Weak	C=O stretch (aldehyde & ketone groups)
1600	Strong	C=C stretch (aromatic) & some C=O stretch
1380-1460	Very Strong	C-H bending
1460		methyl (asymmetric)
1380		methyl (symmetric)
1030	Weak (sharp)	C-O stretch & some S=O stretch
730- 860	Strong	C-H (aromatic)
860,810,740		out of plane bending

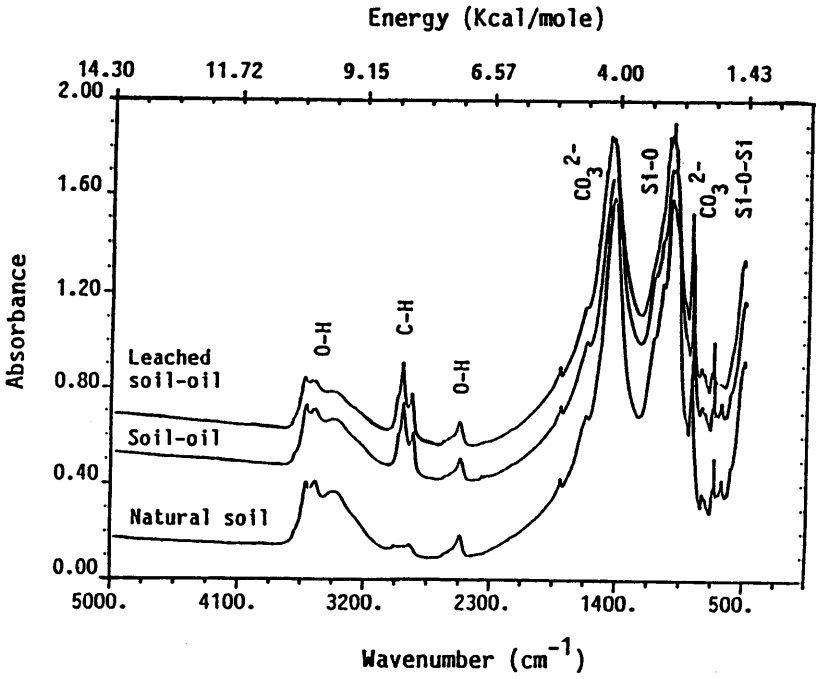


FIG. 2--Infrared spectra of silt and clay fractions of the tested soil and its mixture with oil residue. These spectra are composites of multiple scans.

TABLE 4--Characteristic infrared absorption frequencies found in silt and clay fractions of the tested soil.

Wavenumber (cm^{-1})	Intensity	Peak Assignment	Frequency Range[1]
3390 - 3620	Broad	O-H stretch	3330-3630
2522	Weak	Bonded O-H stretch	2500-3390
1443	Very strong	CO_3^{2-} stretch	1490-1410
1027	Very strong	Si-O stretch	1100- 970
874	Sharp	CO_3^{2-} bend	875- 860
803	Very weak	Si-O-Si stretch	800- 600
713	Weak (sharp)	CO_3^{2-} bend	750- 680
661	Very weak	SO_4^{2-} bend	680- 580
469	Broad	Si-O-Si bend	540- 400

[1] Frequency range based on data obtained from White and Roth [24].

However, when the soil interacts with the oil residue, the vibrational frequencies of the mixture differ from that of the oil-free soil. The extent of the shifts of the frequencies is a measure of the interaction between them. The higher shifts toward the positive frequencies indicate the formation of strong bonds whereas, the smaller shifts in the frequencies are interpreted in terms of simple Van der Waal's attractions [6, 29].

Bonding Mechanisms

One can speculate that at least three different situations can co-exist in an oil-soil-water mixture: (1) oil may adsorb onto the surfaces of the soil constituents, (2) oil may form bonds which link (aggregate) some of the soil particles, and (3) oil may exist separately in the soil pore fluid (Fig. 3). In turn, one expects that within the pore fluid of soil, oil can exist in three separate phases: dissolved, liquid (non-aqueous phase liquid: NAPL) or gaseous. It is envisaged that the three situations described will co-exist and that the proportions of each (situation) will obviously depend on the interacting constituents and conditions leading to the development of the oil-soil mixture. Since the oil residue consists of large molecules with long chain lengths, it is expected that the primary mode of interaction will be via van der Waal's attraction forces. As the number of contact points between the oil residue and soil particle surfaces increases, in addition to the larger van der Waal's interactions [6, 7, 30], significant binding interactions of alkyl groups (oil) with surface oxygens or hydroxyls (soil or water) and exchangeable cations will also occur, as can be observed from the infrared spectra (Fig. 4).

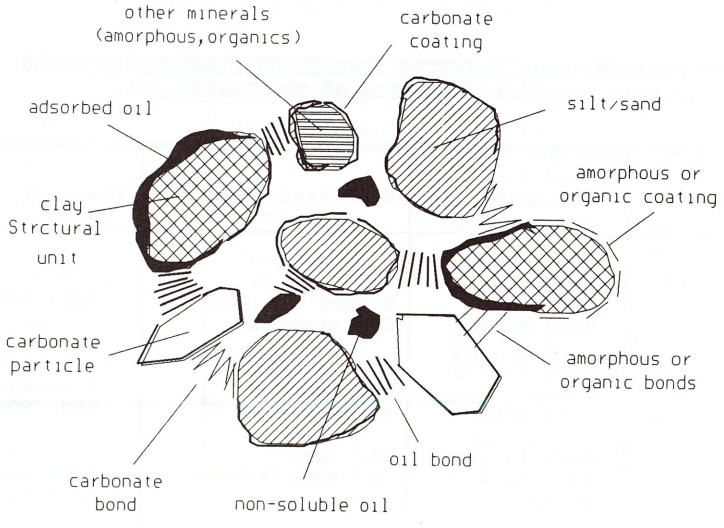


FIG. 3--Hypothetical presentation of soil-oil mixture.

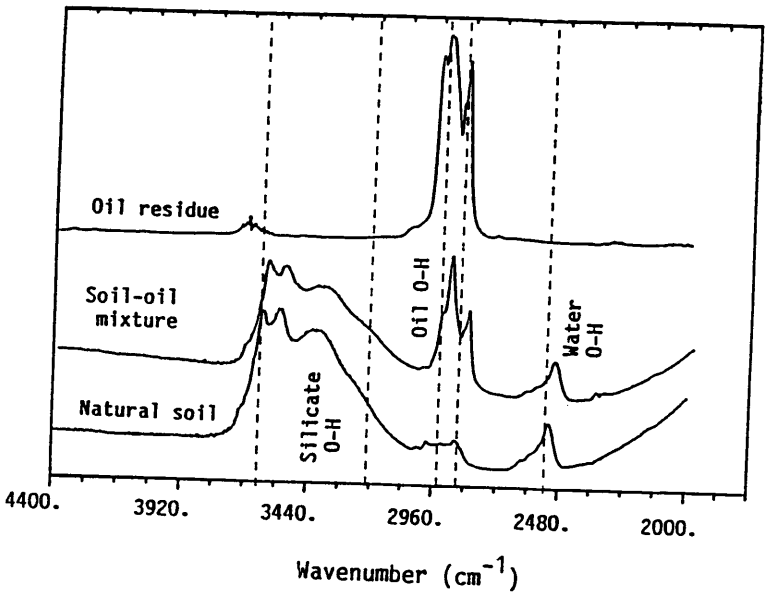


FIG. 4--Infrared spectra of oil residue, soil and their mixtures. These spectra are composites of multiple scans.

The adsorbed oil on the soil particle surfaces is characterized by the appearance of C-H stretching (alkyl group) at three different frequencies: 2853, 2924 and 2953 cm^{-1}, in the mixture spectra (Fig. 4). The alkyl C-H bands are shifted to lower frequencies (-7 cm^{-1} shift) in the mixture, as compared to their frequencies in the oil, in all likelihood due to the formation of weak hydrogen bonding between the hydrogens of C-H group and the oxygens or the hydroxyls of the silicate layer. The lower shift in the frequencies of the alkyl group indicates that the newly formed bonds have lower energy than the original C-H bond [31 - 33].

The broad frequency present in the range between 3390 and 3620 cm^{-1} of the natural soil is attributed to O-H stretching (hydroxyls within the silicate structure), and the shift in the hydroxyl group of the mixture to lower frequency (-5 cm^{-1} shift) is due to intercalation (penetration of oil into the interlayer spacing of the silica and alumina sheets), due to weak hydrogen bonding between the hydroxyls of the silicate layer and alkyls or carbonyls of the intercalated oil. Intercalation of oil leads to reduction in both frequency and energy of the new bond and hence an increase in the interlayer spacing of the tested soil. The frequency peak at 2522 cm^{-1} of the natural soil spectra which is due to the water hydroxyl group, undergoes a slight reduction in the frequency (-6 cm^{-1}) in the mixture spectra. One attributes this to water hydroxyls interacting with either oxygens of the silicate layers or oil carbonyls through hydrogen bonding. Water bridging between the silicate surface and either the oil or calcite surfaces is a likely possibility, as is cation bridging because of the presence of exchangeable cations in the soil system. Moreover, surface tension is another bond that will be produced due to water bridging [34, 35].

The small shift observed in the frequency assigned to the silanol group, from 1027 cm^{-1}, in the mixture, to 1024 cm^{-1}, in the soil, can be due to the fact that oxygens in the silica sheet interact weakly with the hydrogen from alkyl groups or hydroxyl groups. The small shifts in most of the frequencies indicate that van der Waal's attractions are dominant [7, 33]. A comparison of the infrared spectra of the soil-oil mixture before and after leaching shows insignificant changes in the frequency peak shifts and absorbances, indicating thereby that most of the adsorbed oil is still bound to the soil surfaces.

In summary, the major types of binding mechanisms between oil and soil surfaces include: van der Waal's attraction, weak hydrogen bonding, and water and cation bridging. A schematic picture of the interactive mechanisms involved is shown in (Fig. 5).

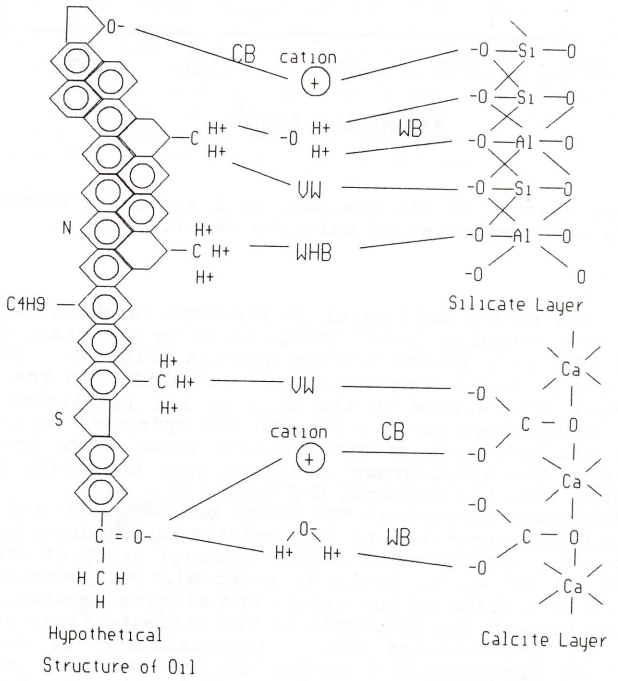


FIG. 5--Illustration of interaction bonding-mechanisms between oil residue and soil surfaces. Oxygens in silicate layer can be replaced with hydroxyls. VW, Van der Waal's attraction; WHB, weak hydrogen bonding; WB, water bridging; CB, cation bridging.

Fluid Retention/Soil Suction

Soil suction tests, measuring fluid retention capability in the soils (soil-fluid characteristic), were conducted to assess the strength of bonding between soil surfaces and both water and oil. The results of the tests (Figs. 6a and 6b) portray the variation of moisture contents with soil suction in two cycles (measured in terms of pF, where pF = log to base 10 of pressure expressed as cms. of water) both in the desorption and absorption processes of the soil suction test. The moisture contents of all samples are seen to drop significantly at a suction range from pF1 to pF1.5 -- indicative of air-entry into the test samples.

The soil fluid characteristic of the natural soil is slightly higher and shows a sharper drop in its moisture content as compared to the soil-oil mixture (Fig. 6a). The presence of oil in the mixture sample does not permit formation of the classical Gouy electrical double layer formed in soil-water systems. The addition of oil to soil may enhances its cohesion through binding mechanisms at the contact points between particles, in contrast to the situation in the natural soil where salt cementation bonds (e.g., carbonate, halite) are dominant. The salt bonds which are rigid brittle bonds are seen to be responsible for the sudden drop in moisture contents at approximately pF1 [36].

A comparison of soil fluid characteristics (curves) of the natural soil and soil-oil mixture, both leached with distilled water, shows that the mixture sample has a slightly higher fluid retention capability than the soil sample (Fig. 6b), likely due to the effect of leaching on the interparticle bonds formed in each case. The natural soil sample appears to have lost most of its cementing salt bonds during the leaching process [37], whereas the mixture sample appears to have retained most of its cohesive bonds. Comparing the soil fluid characteristics of both leached and unleached soil-oil mixtures shows insignificant changes in their retention behaviour, providing thereby a good agreement with the results of the previous section.

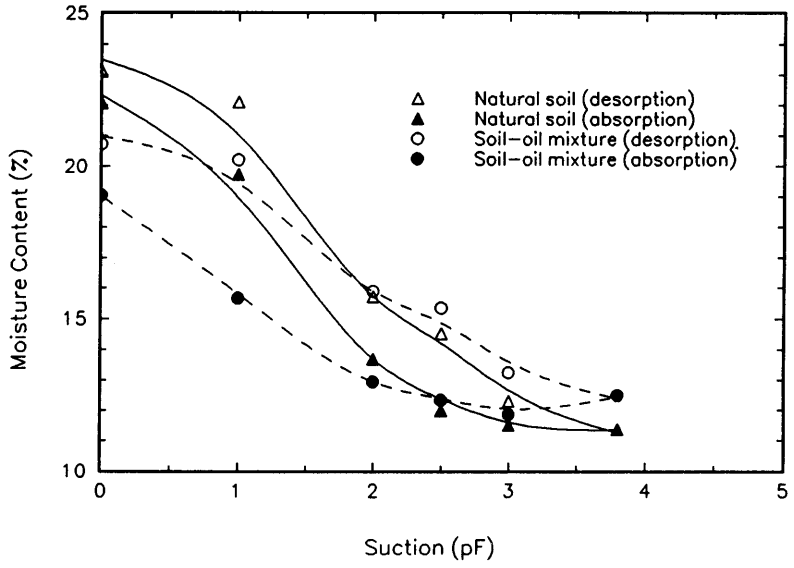


FIG. 6a--Fluid retention curves for unleached samples.

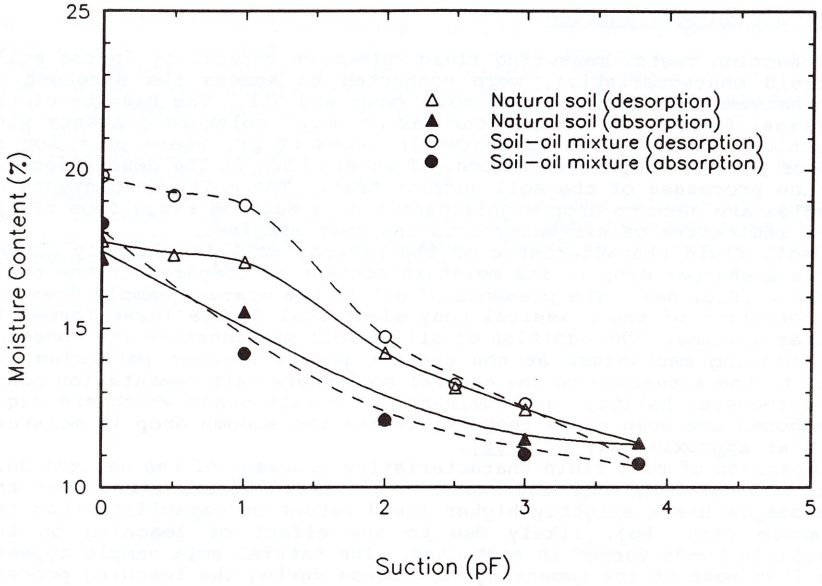


FIG. 6b--Fluid retention curves for leached samples.

Leachability of Soluble Salts (ions)

The presence of high salt content in the natural soil (chloride, sulfate, sodium and calcium), and their high solubilities make it important to assess their potential for leaching -- i.e., leachability potential and effect of oil presence in soil on leachability. (Fig. 7) shows the relative salt concentration (C/Co, ratio of the effluent salt concentration C to the initial salt concentration of the soil Co) in the collected effluents in relation to the cumulative pore volume for both the natural soil and the soil-mixture samples. The salt concentrations in the collected effluents are seen to decrease sharply in the early pore volume discharges, followed by a steady and gradual decrease to residual values.

Leachability of Heavy Metals

The measured concentrations of the heavy metals (vanadium, nickel, iron, and lead) in the collected effluents were below the detection level. This is mainly due to their presence at low concentrations in the stabilized soil system and the high pH of the soil pore fluid. Based on stabilizing the soil with 4% oil residue, the concentrations of vanadium, nickel, and iron in the soil were 1.64 mg/kg, 0.62 mg/kg, and 0.40 mg/kg, respectively. In addition, the mobilities of the tested heavy metals are expected to be very low in alkali environment [30]. This is because the solubilities of such metals substantially reduce under saline-alkali environment, as in this case (pH = 7.8). A large portion of these heavy metals are expected to precipitate into insoluble forms under alkali conditions, resulting into low environmental threat [38, 39].

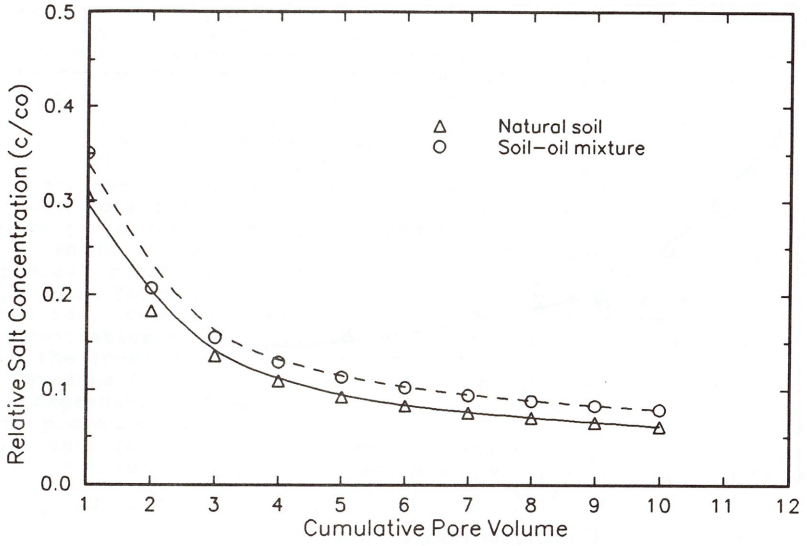


FIG. 7--Relative salt concentration in effluents collected during leaching.

Leachability of Oil

Oil transport from the soil-oil mixture due to rainfall is expected to be low because of the low aqueous solubility of the oil, its high structural form, and the relatively low permeability of the soil-oil mixture. As can be seen from (Fig. 8) which portrays the relative concentration of oil (C/Co) for the duplicate samples in relation to the cumulative pore volume, the ratio is extremely low, but nevertheless follows the same pattern demonstrated by the results (Fig. 7). One can assume that the rapid reduction in oil concentration in the initial stages of leaching can be attributed to the removal of soluble and lighter fractions of oil present in the soil pore fluid.

To estimate the amount of oil penetration into the substrate from the soil-oil mixture due to rainfall infiltration, one can use the average annual precipitation rate in Bahrain (approximately 75 mm/year [40]) and compare this with the laboratory rate. The rainfall occurs primarily during the winter months, so that the average temperature during the rainfall is very near the tested temperature of 22±2 °C. In this leaching study, a flow rate of approximately 14 mm/day (5100 mm/year) was used, which when extrapolated to include the field rate provides one with a value of about 2.2% of the oil leaching from the soil-oil system after 7 years of field leaching, reaching a depth of 100 mm below the ground surface after 7 years.

The leachability of 2.2% of oil residue was partially attributed to a relatively higher flow rate applied to the samples tested in the laboratory as compared to actual field conditions. A higher flow rate may allow greater momentum to be transferred from the leaching water to the oil in the pore fluid, thereby providing more kinetic energy to reduce the interfacial tensions between the oil and water. This may enhance the mobility of a large portion of the oil in the pore fluid [41].

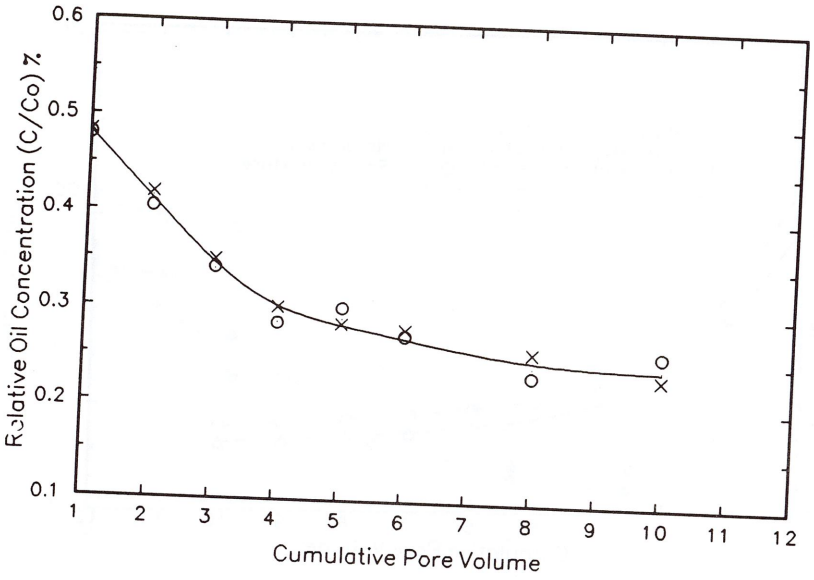


FIG. 8--Relative oil concentration in effluents collected from leaching test.

Oil Mass Balance

The results of the oil mass balance (in the soil) at the end of the leaching process (Fig. 9) indicate that significant amounts of oil are retained in the leached soil. More than 90% (by weight) of the oil remains in the soil matrix after 10 pore volumes of leaching. However, only 2.2% of the oil was detected in the collected effluent at the end of the leaching process. A comparison of the initial oil concentration used with the measured concentration at the end of the test shows a difference of approximately 4% by weight, -- in all likelihood due to volatilization and degradation of portions of the oil residue.

Transformation of Oil

Oil residue has the potential to volatilize from oil-soil-water mixtures depending on several physical and chemical parameters. These parameters include: (a) properties of oil residue such as melting point, vapor pressure, and Henry's law constant; (b) environmental conditions such as temperature, soil type, soil moisture content, and concentration and depth of incorporation of oil. Volatilization rate can be significantly enhanced for (a) hydrocarbons with high vapor pressure and high Henry's constant; (b) sandy soils in arid regions; (c) shallow depth soils mixed with high oil concentration [23, 42, 43].

Because of the high melting point and low vapor pressure of the oil residue used in this study, its volatilization rate is expected to be low. To determine the potential for volatilization of oil residue, triplicate oil residue samples were left exposed to the atmosphere (at a temperature of 22±2 °C). From the measured changes in their weights (in relation to elapsed time), calculations were made which show that approximately 5% of oil residue by weight will be volatilized over a period of 1.5 years.

However, in an oil-soil-water mixture under the same temperature condition, it is expected that the volatilization rate will be lower, due in part to adsorption of some of the oil to soil particle surfaces and also to low Henry's constant of the oil residue. In arid regions with high temperatures, as in Bahrain (27±3 °C) [40], the volatilization of oil from a similar soil system can be substantial. Higher temperature results in higher vapor pressure, lower viscosity, and higher aqueous solubility of the oil. This can lead to an increase in the Henry's constant and thus an increase in volatilization of the oil residue [44].

The potential for the oil residue to be transformed into another compound (degradation) under certain environmental conditions is strongly influenced by various processes, including adsorption, volatilization, chemical reactions, photolysis, and microbial degradation. The site-specific factors which could also affect its transformation include physical, chemical, and biological characteristics of the soil, the concentration of the oil, the length of time the oil has been in the soil, and the local ground water regime.

Studies [45, 46] have shown that the optimum environmental conditions for degradation of petroleum hydrocarbon include: (a) sufficient moisture; (b) presence of suitable microorganisms; (c) presence of soil macro-nutrients (e.g., phosphate, ammonia, and organic carbon); (d) presence of micro-nutrients (e.g., amino acids and vitamins); (e) warm temperatures; (f) neutral soil pH; (g) a good aeration site; (h) low molecular weight of hydrocarbons, and (i) high oil concentrations in soil, > 4 % by weight [47]. Accordingly it is expected that degradation of oil residue in the soil-oil mixture is expected to be relatively low due to: (a) the low moisture content in the soil (b) the high molecular weight of the oil residue; (c) the low content of soil macro-nutrients; (d) high soil salinity; and (e) low probability of existence of suitable microorganisms and micro-nutrients in arid regions.

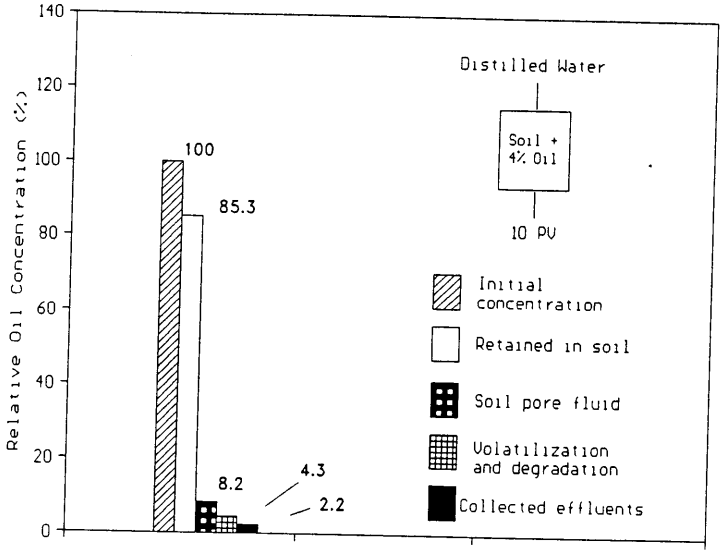


FIG. 9--Oil mass balance for the tested sample at the end of leaching.

Temperature Effect

Temperature has a significant role on the behavior of oil residue in soil. In this study, all the laboratory experiments were performed at a room temperature of 22±2 °C. However, in actual field conditions, where oil residue is expected to be used (Bahrain), the average annual temperature is slightly higher (27±3 °C). An increase in temperature is expected to enhance soil interaction mechanisms, reduce fluid retention, and increase oil leachability [30, 48, 49]. A rise in temperature increases both water solubility and vapor pressure of oil, which affect their concentration in the soil void, and hence enhances their interactions [48]. An increase in temperature reduces the dielectric constants of the fluids, thereby resulting in a further restriction in the formation of the Gouy electrical double layers in this system. This can lead to an increase in the attractive forces of the system and a tendency for higher soil permeability [49]. Moreover, the reduction in oil viscosity and the increase in water solubility of the oil are another contributing factors in the increase of oil leachability with temperature.

CONCLUDING REMARKS

The experimental study of the tested sandy loam soil at 22±2 °C (obtained from Bahrain) stabilized with oil residue, designed to assess the retention and leaching behaviour of oil residue, shows good oil retention in the tested sample, with about 93.5% of the oil by weight remaining in the soil matrix at the end of leaching. This can be partially attributed to the nature of bonding formed between the oil and the soil surfaces; these bonds were shown to be dominated by Van der Waal's attraction, weak hydrogen bonding and cation and water bridgings. The low aqueous mobility of the oil and the surface activity of the soil were also seen to contribute to oil retention. The bonds formed were found to be relatively weak but stable (insensitive to leaching). Only 2.2% of oil was detected in the leached effluents at the end of testing; extrapolation of these results show that seven years of actual field leaching are required to remove this 2.2% of oil. In addition, the leachability of 2.2% of oil residue was partially attributed to the effect of the higher flow rate applied in the laboratory as compared with the one expected in the field.

The results of this study indicate that oil residue has a potential to leach from the stabilized soil and can pose an environmental threat due to its toxic behavior. Further studies toward the application of additives (e.g., polymers or organic cations) to the stabilized soil should be considered. These additives would be expected to enhance the bonding between oil and soil surfaces and thus maximize oil retention in soil [50, 51]. Moreover, toxicity assessment of the leached oil should be also studied in future work prior to the application of oil residue in the field.

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