SEPTEMBER 2019

Ph.D. in Civil Engineering

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HASAN KALYONCU UNIVERSITY GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES

EFFECTS OF MINERAL ADMIXTURES ON SOM PROPERTIES OF CRUDE OIL POLLUTED SAND

Ph.D. THESIS IN CIVIL ENGINEERING

BY

FARMAN KHALIL GHAFFOORI

SEPTEMBER 2019

Effects of mineral admixtures on some properties of crude oil polluted sand

Ph.D. Thesis

In Civil Engineering Hasan Kalyoncu University

Supervisor

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September 2019

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GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES INSTITUTE PhD ACCEPTANCE AND APPROVAL FORM

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Document no: ENS.FR.32 Release date: 26.03.2018 Rev no/ Date: 00/--

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

FARMAN KHALIL GHAFFOORI

ABSTRACT

EFFECTS OF MINERAL ADMIXTURES ON SOME PROPERTIES OF CRUDE OIL POLLUTED SAND

GHAFFOORI, Farman Khalil Ph.D. in Civil Engineering Supervisor: Prof. Dr. Mehmet KARPUZCU September 2019, 203 pages

This thesis presents a study on environmental pollution by crude oil in a contaminated area. Mineral admixtures such as ground granulated blast furnace slag and fly ash are used to stabilize polluted soil. The overarching goal of this study is to evaluate the addition mineral admixtures to improve the polluted soil by crude oil. This study focused on the Erbil-Gwear main road location close to the Lajan village. Since there are several refinery stations in this area it is paramount to study the environmental issues. Samples of sandy soil were artificially mixed with various percentage of crude oil namely 0%, 2%, 4%, 6%, 8%, 10%, 12%, 14% and 16% in relative to their dry weight to observe the influences of crude oil contamination on some properties of sand samples. To investigate the effect of mineral admixture on the contaminated soil samples by crude oil several mixtures were prepared. For instance, mixtures were mixed by the addition of 0%, 4%, 6% and 8% crude oil with GGBFS and FA admixtures with the amount of 0%, 10% and 15% were utilized in this study. The compaction and direct shear tests were utilized in this study. The results of this research show that specific gravity, the optimum moisture content and the maximum dry density were decreased while the percentage of crude oil content was increased. The results of friction angle were fluctuated with increasing crude oil. Apparent cohesion (c) values were increased up to a certain point and then slightly decreased with increasing the percentage of crude oil addition. Mineral admixtures provide an improvement in compaction and the strength properties of polluted soil. Moreover, the statistical analysis was used to demonstrate the significant differences of each factor used in this research.

Keywords: Soil pollution, crude oil, multivariate regression, GGBFS, FA

ÖZET

HAM PETROLLE KİRLENMİŞ KUMLU ZEMİNLERİN BAZI ÖZELLİKLERİ ÜZERİNE MİNERAL KATKILARIN ETKİSİ

GHAFFOORI, Farman Khalil Doktora Tezi, İnşaat Mühendisliği Bölümü Tez Danışmanı: Prof. Dr. Mehmet KARPUZCU Eylül 2019, 203 Sayfa

Bu tez, ham petrol ile kirlenmiş bir alanda çevre kirliliği üzerine bir çalışma sunmaktadır. Ayrıca, tez çalışmasında öğütülmüş granül yüksek fırın cürufu (GGBFS) ve uçucu kül (FA) gibi mineral katkılar kirlenmiş zemini stabilize etmek için kullanılmıştır. Bu çalışmanın temel amacı ise, ham petrol ile kirlenmiş zemini geliştirmek için mineral katkıların değerlendirilmesidir. Çalışma, Lajan köyüne yakın Erbil-Gwear anayol lokasyonu üzerine odaklanmıştır. Bu alanda birkaç rafineri istasyonu bulunduğundan, çevre konularını incelemek de oldukça önem arz etmektedir. Kumlu zeminlerin bazı özellikleri üzerinde ham petrol kirlenmesinin etkilerinin gözlemlenebilmesi için, kumlu zemin numuneleri laboratuvar ortamında kuru ağırlıkça %0, %2, %4, %6, %8, %10, %12, %14 ve %16 ham petrol içerecek şekilde ham petrol ile karıştırılmıştır. Ayrıca, mineral katkıların etkilerinin değerlendirilmesi için, ham petrol ile kirlenmiş zemin numuneleri ve mineral katkılar farklı oranlarda karıştırılarak çeşitli karışımlar hazırlanmıştır. Örneğin, bu çalışmada kirlenmiş zeminler %0, %4, %6 ve %8 oranlarında GGBFS ile ve %0, %10 ve %15 oranlarında FA ile karıştırılmıştır. Bu çalışmada sıkıştırma ve basit kesme testleri kullanılmıştır. Bu araştırmanın sonuçları, ham petrol yüzdesi arttığında özgül ağırlık, optimum nem içeriği ve maksimum kuru yoğunluğun azaldığını göstermektedir. Sürtünme açısı sonuçları ise artan ham petrol yüzdesine bağlı olarak dalgalanmıştır. Görünen kohezyon (c) değerleri ise belirli bir noktaya kadar artmış, daha sonra ham petrol yüzdesinin artmasına bağlı olarak az miktarda azalmıştır. Bununla birlikte mineral katkıların kullanılması da, kirlenmiş zeminin sıkıştırma ve dayanma özelliklerinde iyileşme sağlamıştır. Ayrıca, çalışmada kullanılan her bir faktörün farklılıkların öneminin gösterilmesi için istatistiksel analiz yapılmıştır.

Anahtar Kelimeler: Zemin kirlenmesi, ham petrol, çok değişkenli regresyon, GGFBS, uçucu kül

То

My mum

My wife

And

(Rezdar, Noor and Renwar)

All my family

ACKNOWLEDGEMENTS

First of all, I want to express my gratitude and thankfulness to the God almighty who is a creator, the sovereign, and the sustainer of the universe and creatures.

This thesis would not have been possible without the continuous inspiration and monitoring of my supervisor, Professor Dr. Mehmet KARPUZCU.

I want thanks to Dr. Adem YURTSEVER. Also, my thanks to all jury members for them support for me. My special thanks are reserved to Dr. Ali Rashid KHOSHNAW encourages study with me without his support it was impossible.

My special thanks are reserve for my mother, father, sisters and brothers. All my family, they have given me an endless enthusiasm and encouragement. I would like to thank to Erbil construction laboratory (ECL). My special thanks are reserve to Mohamed Moafak ARBILI, and Dr. Diler SABAH. My great appreciation for my wife Gashaw and my children Rezdar, Noor and Renwar they support me during my study. Finally, I would like to express my sincere gratitude to anyone who helped me throughout the preparation of the thesis.

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LIST OF SYMBOLS AND ABBREVIATIONS

API	American Petroleum Institute
AASHTO	American Associate Society for High way Transportation Organization
ASTM	American Society for Testing Materials
ANOVA	Analysis of variance
BOD	Biochemical Oxygen Demand
CBR	California Bearing Ratio (%)
А	Total Cross-Sectional Area (mm ²)
DO	Dissolved Oxygen
Dr	Relative Density (%)
EC	Electrical Conductivity (dS/m)
ECL	Erbil Construction Laboratory
EPA	Environmental Protection Agency
GGBFS	Ground Granulated Blast Furnace Slag
GPS	Geographical Position System
GLM	General Linear Model
IOC	International Oil Company
FA	Fly ash
FAO	Food and Agriculture Organization
OMC	Optimum Moisture Content (%)
с	Apparent cohesion (kPa)
Gs	Specific gravity
Yd	Dry density (g/cm ³)
pН	Power of Hydrogen
SEM	Scanning Electron Microscopy
USCS	Unified Soil Classification System
USEPA	Environmental Protection Agency in the United States
φ	Angle of internal friction (°)

MDD	Maximum Dry Density (g/cm ³)
NDP	National Development Plan
NSS	Not Statistically Significant
OM	Organic Matter
SM	Silty Sand
SP	Poorly Graded Sand
SS	Statistically Significant
SW	Well Graded Sand
TDS	Total Dissolved Solids
TH	Total Hardness (mg/l)
TPH	Total Petroleum Hydrocarbon
TSC	Technical Service Contract
TSS	Total Suspended Solids
UCS	Unconfined Compression Strength (kPa)
VOC	Volatile Organic Compounds
WHO	World Health Organization
XRF	X-Ray Fluorescence
LL	Liquid Limit (%)
PL	Plastic Limit (%)
Cu	Coefficient of Uniformity
D	Sample Diameter (mm)
Q	Quantity of Flow
ppm	part per million
q	Flow Rate (ml/min)
t	time (min)
W	Water content (%)
As	Arsenic
Al	Aluminum
Cd	Cadmium

Cu	Copper
Zn	Zinc
Fe	Iron
Mn	Manganese
Pb	Lead
Ni	Nickel
Cr	Chromium
Hg	Mercury
Ν	Nitrogen
Р	Phosphorus
Κ	Potassium
NO ₃	Nitrate
SO_4	Sulfate
SO ₃	Sulfur trioxide
Al ₂ O ₃	Aluminum oxide
Al ₂ O ₃ CaCo ₃	Aluminum oxide Calcium carbonate
CaCo ₃	Calcium carbonate
CaCo ₃ CaO	Calcium carbonate Calcium dioxide
CaCo ₃ CaO Fe ₂ O ₃	Calcium carbonate Calcium dioxide Iron (III) oxide
CaCo ₃ CaO Fe ₂ O ₃ SiO ₂	Calcium carbonate Calcium dioxide Iron (III) oxide Silicon dioxide
CaCo ₃ CaO Fe ₂ O ₃ SiO ₂ MgO	Calcium carbonate Calcium dioxide Iron (III) oxide Silicon dioxide Magnesium oxide
CaCo ₃ CaO Fe ₂ O ₃ SiO ₂ MgO Co	Calcium carbonate Calcium dioxide Iron (III) oxide Silicon dioxide Magnesium oxide Cobalt
CaCo ₃ CaO Fe ₂ O ₃ SiO ₂ MgO Co U	Calcium carbonate Calcium dioxide Iron (III) oxide Silicon dioxide Magnesium oxide Cobalt Uranium
CaCo ₃ CaO Fe ₂ O ₃ SiO ₂ MgO Co U Se	Calcium carbonate Calcium dioxide Iron (III) oxide Silicon dioxide Magnesium oxide Cobalt Uranium Selenium
CaCo ₃ CaO Fe ₂ O ₃ SiO ₂ MgO Co U Se Sr	Calcium carbonate Calcium dioxide Iron (III) oxide Silicon dioxide Magnesium oxide Cobalt Uranium Selenium Strontium
CaCo ₃ CaO Fe ₂ O ₃ SiO ₂ MgO Co U Se Sr Ca	Calcium carbonate Calcium dioxide Iron (III) oxide Silicon dioxide Magnesium oxide Cobalt Uranium Selenium Strontium Calcium

CHAPTER 1 INTRODUCTION

1.1 General

Pollution of soils by crude oil could influence chemical, physical and mechanical characteristics of the soils. Soil contamination could take place because of many activities such as petroleum transportation facilities, damaged pipeline, corroded tanks, oil drilling processes, tanker accidents, leakage of crude oil and natural seepage.

In Erbil province, oil production is a recent process. It has been proved that oil refineries and companies have caused environmental pollutions in the region. The soils of surrounding areas have been polluted by spilling the crude oil. Oil productions exist remarkably in several locations in Erbil such as Koya, Taqtaq, Khurmala, Kawrgosk and Gwear. This study focuses on the Erbil-Gwear main road close to Lajan village where there is several oil refineries across this area. Industrial activity is needed for the socioeconomic development of a country. Refined products of crude oil like petroleum, diesel are major resources for industrial work. Mineral admixtures are used in this study to stabilize polluted soil and to reduce pollution in the soil.

Based on experimental and theoretical works done by various researches, for example, Abousnina (2015) confirmed that the geotechnical properties of soil, such as, liquid limit, plastic limit, cohesion, angle of internal friction or shear strength, compressibility etc. based on the soil type, degree of saturation, soil structure, void ratio, stress history and pore fluid quality. There is a great possibility of effects on the above mentioned properties because of change of pore fluid of soil polluted by crude oil.

The main aim of this study is to consider the impact of crude oil contamination on the properties of sandy soil. Some laboratory tests included compaction and direct shear test have carried out to contaminated and uncontaminated samples. The sandy soil samples are artificially polluted with different ratio of crude oil 0%, 2%, 4%, 6%, 8%, 10%, 12%, 14% and 16% in relative to their dry weight to observe the influence of

crude oil contamination of soil with respect to behavior of sandy soil properties. Mineral admixture such as ground granulated blast furnace slag and fly ash are used in this study to stabilize polluted sandy soil. Various percentage of GGBFS and FA 0%, 10% and 15% are mixed with 0%, 4%, 6% and 8% crude oil in 36 mixtures to evaluate effect of mineral admixture on polluted soil. Four groups are used each group for one percentage of crude oil and each group consist of nine mixes. Results of each groups are showed for compaction parameters such as optimum moisture content and maximum dry density. Also, parameters of direct shear apparent cohesion and friction angle demonstrated in the results.

1.2 Objective and scope of the thesis

The main purpose of this research is to evaluate the impact of petroleum pollution on the geotechnical characteristics of sandy soil. Hydrocarbon contaminants may follow a complex pathway from source to aquifers. These contaminants may move through the unsaturated zone in the vapor phase to travel down to the aquifer. The rate of hydrocarbon movement from the source of contamination to the aquifer is controlled by several factors such as hydraulic conductivity of soil/sediment, temperature, moisture, and related physical parameters. Permeability is a time-depended phenomenon and is a function of the velocity of fluid flow, geometry of the aquifer layers, and physical and chemical interactions. Therefore, accurate quantification of the rate of contaminant permeation across the geological materials is an essential requirement for the design and implementation of any remediation method.

The purpose of this research is to come up with more comprehension of the characteristics of the exposed soil to crude oil pollution causing the change of its physical characteristics. The findings of this research can be used as a guide for other researchers to enhance their comprehension of the soil properties when petroleum products are added to them.

The originality and objective of the study are utilizing mineral admixture to improve and stabilize oil polluted soil. Main scopes of the thesis are illustrated in the following:

- 1. To determine the effect of crude oil contamination on the properties of sandy soil.
- 2. To investigate experimentally the percolation of crude oil in sand.
- 3. Utilizing mineral admixture such as ground granulated blast furnace slag and fly ash in mixtures with different percentage.

- 4. To evaluate the impact of mineral admixture on polluted soil by crude oil.
- 5. To conduct compaction and direct shear tests on mixtures with various ratio of crude oil and mineral admixtures.
- 6. To determine the differences in the geotechnical behavior of clean and oil contaminated sand.
- 7. To determine flow and penetration of crude oil in the field and in the laboratory.
- 8. To provide a comprehensive basis for soil behavior contaminated with crude oil bases on the data collected and analyzed.
- Evaluate impact of crude oil on various type of planting in Erbil province close to refiner's area.
- 10. Use statistical analysis ANOVA program to evaluate significant of parameters and response. Moreover, used Minitab program to find nonlinear regression equation for used parameters.
- 11. To provide guidance and information for engineers and researchers.

1.3 Introduction of crude oil

Crude oil is a combination of hydrocarbons that occur naturally. This can be refined to many different products such as diesel, gasoline, jet fuel, kerosene, among other products called petrochemicals. Crude oil is accumulated in different permeable rock structures in the earth's crust and can be extracted from the rocks for use as fuel or processing. The products are named corresponding to their contents and origins and are classified in accordance with their specific gravity. Crude oils are heavier and produce more heat while burning. However, they have the lowest API. According to Helmenstine (2014), petroleum is a complex combination of hydrocarbons in addition to other chemicals. The components differ widely depending on the place that the crude was formed and how it was formed. It however has the same characteristic properties and components. The hydrocarbon compounds in the crude oils include paraffins ranging from pentane to pentadecane (C5 – C15), alkylparaffins, naphthenes, alkylbenzenes and nuclear aromatics. Other associated matters are natural gases, hydrocarbon waxes, and salt water. Crude oils also contain a variety of other chemical constituents comprising of sulphur, oxygen, carbondixode, nitrogen and trace metals. Crude oils, are usually characterized by some of the chemical and physical properties, which have been found to have a critical role in the defining of the nature of the oil's geological aspects as well as their environment of origin (Chinenyeze and Ekene, 2017).

A study by Khamehchiyan et al. (2007) observed that the primary physical properties of crude oil included American Petroleum Institute (API) gravity, viscosity, salt content, specific gravity and pour point. Lastly, crude oils serve as vital tools for the analysis of environmental elements, the relationship between crude oils that have similar geologic ages and the renewal of historical temperature of the oils.

Crude oil value is determined by the paraffin wax and sulfur content and API gravity. A group of heavier and highly dense compounds in oil known as asphaltenes are comprised of metals, sulfur and other elements (Podgorski et al., 2013). In hydrocarbons, a growth in the number of carbon results in the decrease of solubility and the vapor pressure. All of the mentioned compounds are found in crude oil and they all lead to contamination in one way or another. The constituents of unrefined petroleum differ depending on the location from which they were extracted. Petroleum from Iraq has a different chemical composition from crude oil pumped in California.

1.3.1 Hydrocarbons in crude oil

The type of hydrocarbon primarily categorizes crude oil. Paraffin is the most prevalent hydrocarbon in petroleum products. Specific liquid paraffin is characterized by heaviest and high value. In addition to the fact that naphthalene is a critical part of all products related to a liquid refinery. However, it likewise contains a portion of the heavy asphalt-like remains of refinery procedures. Aromatics mainly constitute a small amount of most petroleum. Benzene is the most prevalent aromatic, and it is commonly used as a base in the crude oil sector.

The percentage of four main types of hydrocarbons found in crude oil.

- i. Paraffin (15-60%)
- ii. Naphthenes (30-60%)
- iii. Aromatics (3-30%)
- iv. Asphaltic (remainder)

The hydrocarbons primarily are alkanes, cycloalkanes, and aromatic hydrocarbons.

1.3.2 Elemental composition of petroleum

The hydrocarbons are composed of nitrogen, oxygen, and sulfur. They make up a significant variety of multiplex molecular structures, some of which cannot be easily determined. Even though there are considerable differences between the ratios of the organic molecules, the basic composition of petroleum percentage by weight is well-defined.

- i. Carbon (83 to 87%)
- ii. Hydrogen (10 to 14%)
- iii. Nitrogen (0.1 to 2%)
- iv. Oxygen (0.05 to 1.5%)
- v. Sulfur (0.05 to 6.0%)
- vi. Metals (< 0.1%)

The color and viscosity of petroleum differs remarkably in different places. A majority of crude oil is dark brown or black in color, but it also appears as green, red, or yellow. Since petroleum is a combination of such widely assorted components, its physical characteristics also differ widely. Its looks, for instance, varies from no visible color to black. The specific gravity (the proportion of the weight of equal volumes of unrefined petroleum and pure at standard conditions) is potentially the most important physical aspect. Distilled water is randomly allocated an API gravity of 10°. Lighter liquids such as oil have API gravities arithmetically higher than 10. Petroleum can be categorised as heavy, medium and light, with regard to their API gravity. This has been illustrated below:

- Heavy crudes range from 10 to 20° API gravity
- Medium crudes range from 20 to 25° API gravity
- Light crudes have above 25° API gravity

Petroleum can be classified as "sweet" or "sour". This is reliant on the quantity of sulfur in the crude oil. It can occur as an element or as a compound such as hydrogen sulfide. Sweet petroleum has lesser sulfur contents than sour petroleum. It is meaning that the weight of sweet crudes is at most 0.5% and that of sour crudes is at least 1%. Sulfur is

extracted from petroleum because its compounds such as sulfur oxide can have detrimental effects when released on the environment.

1.4 Petroleum pollution in soils

In the past few years, public awareness on the environmental concerns brought about by pollution has been increased. Scientists and environmentalists worldwide are met with the obstacle of quelling the damaging impacts of environmental pollution. Oil spillages on soil and water, pipeline leakages, underground and surface fuel storage tanks, carefree waste disposal, and mismanagement of sludge, constitute the main sources of petroleum pollution in the environment.

Soil pollution, as a result of oil exploration proceedings, has rapidly become a significant environmental problem (Chukwujindu et al., 2008; Bosco et al., 2005). There is no doubt that the issue of petroleum contamination of soil and water has become a bone of contention and is gaining attention because of the detrimental health and environmental impact that it has (Ribes et al., 2003). Future generations face the threat of issues arising from the impacts of the current irresponsible attitude towards the environment. Petroleum is used to make refined crude oil products and they have the capacity to pollute the ecosystem. In fact, there are various chemicals in petroleum and their products. Practically, it is difficult to measure each one separately. Nevertheless, it is beneficial to calculate the Total Petroleum Hydrocarbon (TPH) amount at the chosen site.

The analytical goal for each crude oil spill site is to evaluate the amount of pollution and to efficaciously and safely detach the pollutant from the soil with the aim of returning the soil back to a functional form. Attempts for complete removal may not be practically attainable either due to cost or source, then the objective is to remediate the soils to the concentration amounts that would not be harmful to flora and fauna (ATSDR, 1999; Torres et al., 2005). The way to handle, dispose or reuse non-hazardous petroleum contaminated soils has received attention.

The variety of pollutants is constantly changing due to agrochemical and industrial evolution. This variety, and the alteration of organic constituents in soil by biological activity into diverse metabolites, makes soil surveys to determine the pollutants as both arduous and dear. The impacts of soil pollution also depend on soil properties because these control the potency, bioavailability, and residence period of pollutants.

The phrase "contaminated land" holds important implications in several territories and nations. In these particular territories, polluted land is a unique tag allotted to a land site where soil contamination has been suspected. Moreover, these contaminants are highly likely regarded to be a great menace to the ecosystem and to human health. The categorization of the severity of the several threats presented by the polluted land is not always easily conducted. This is due to the fact that the concurrence on the level of danger and risk factors is not always unanimously established. This, to a large degree, is caused by unawareness or lack of knowledge of: (a) the inherent features and distribution of the contaminants in the polluted soil, and (b) the characteristics, degree, and extent of the different threats posed by the contaminants. The nature of the land environment needs to be considered in order to for us to fully acknowledge the different ecosystem and health risks arising from the contaminants found on the soil and in the sub-surface of polluted lands. Land pollution can result in adverse consequences. It is of the utmost importance for people to be well- of the destiny of the contaminants in the soil strata below the earth's surface. In order to achieve a simple, representation of this, the underlying soil strata would generally be pinpointed as the substrate substance. Figure 1.1 is an illustration of a diagrammatic representation of the possible pathways to biotic receptors whereby contaminants in a polluted land may travel. The extents of risk posed by the contaminants moving along these pathways, and the procedures impacting the destiny of the contaminants along these pathways, would become one of the many primary aspects that will decided the course of action needed to reduce or do away with the threat completely. This requires deliberation for the eradication, minimization, containment, and the mitigation of contaminants, among other available options. One of the main aspects is risk management, i.e., the control of the contaminant threat such that the menace is minimized to tolerable limits as authorized by laws and consented practice.

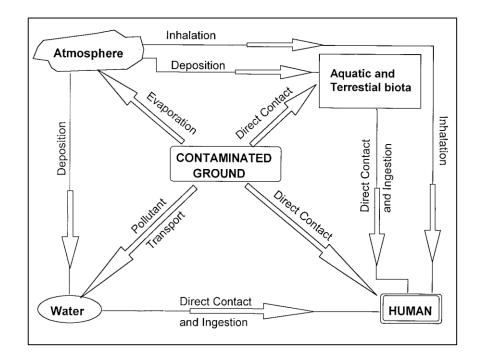


Figure 1.1 Pathways from contaminated ground to biotic receptors (Yong, 2000)

1.5 Constituents of the problem

The basic purpose of the material illustrated in this research is to enhance a better comprehension of the different components of the issue broadly described as land pollution. Figure 1.1 shows how the effects of land pollution are felt in several ways. The basic understanding needed is the nature and the dissemination of the contaminants into the polluted ground. This is essential in the determination of whether or not these contaminants are detrimental to the immediate environment and the different biotic types that reside therein. Figure 1.2 shows the fundamental components of the land pollution issue. The following are the main bits of information needed:

- Types of the different contaminants that exist in the substance;
- Distribution and partitioning of the contaminants in the substance;
- Possibility for movement or transformation in constitution and concentration of the contaminants;
- Work of the substance material with respect to contaminant "bonding", distribution, transformation, and movement of contaminants;
- How hazardous the contaminants are;
- Environmental mobility of the contaminants; and

• Fundamental components needed to design and implement rectification of the polluted land

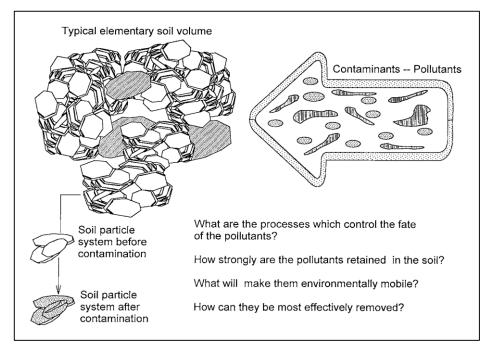


Figure 1.2 Pollutant-soil interaction problem (Yong, 2000)

The study material produced is contrived to give the fundamental components which make up the contaminant soil system in the substance. The basic question is: "What are the procedures that influence the persistence and destiny of contaminants?" Why do we need to know more about these procedures? Because:

• This gives us the comprehension of the longevity of the bonding association between contaminants and soil solids;

• Control of the pollutants in the polluted soil would be more efficaciously implemented; and

• Rectification methodology and technology and contamination alleviation can be properly developed and efficaciously implemented.

1.6 Problem statement and justification

The effects of pollution have continued to negatively impact the environment. These are mainly due to industrialization practices and population increase (Goel, 2009). Natural resources such as land is the major cause of the increasing rate in population and overcrowding issues especially in the cities and major towns. Waste disposal is perceived as the biggest environmental challenge that is brought about by overcrowding.

Contamination is an overall issue and its potential in affecting soundness of the human populace is extraordinary (Khan and Ghouri, 2011). The effect of contamination in the region of stuffed urban areas and from mechanical effluents and cars has achieved an aggravating greatness and is exciting open mindfulness (Begum et al., 2009). Unreasonable levels of contamination are making a great deal of harm human and creature wellbeing, plants including tropical downpour woods just as the more extensive condition (Khan and Ghouri, 2011). Contamination is the reason for some disease, which influence the old as well as the youthful and the lively and all creatures and plants (Kanmony, 2009). The WHO report brings up that twenty million kids overall experience the ill effects of contamination which has turned out to be basic as a result of overpopulation (Kanmony, 2009).

The natural occurring materials which cause water contamination include: gases, soils, minerals, among others. Water sources continue to be less and not sufficient enough in many areas to attend to the ever-growing needs of an expeditiously increasing population and this scarcity has led to the over-exploitation of water resources resulting in their salinity, increased contamination, and eutrophication due to intensive agricultural practices (Al-Weher, 2008). Several estimation show that at least 50 nations with an area of approximately 21 million hectares have fully or partially contaminated water. This low quality water has detrimental effects on human health, aquatic life, and plants that use this water (Khan and Ghouri, 2011).

The existence of heavy metals at detection quantities and crucial components at increased concentration leads to hazardous impacts if it remains unprotected from the human population (Fong et al., 2008). The understanding of heavy metal retention in soil, where the metals originated from, and their potential interactions with soil characteristics are a primacy in many environmental watches (Qishlaqi and Moore, 2007). The amassing of heavy metals in soils used for agricultural purposes is a big problem due to food safety problems and possible health risks in addition to its dangerous impacts on the soil.

In recent years, the primary concern has been heavy metals that result from accumulation of contaminated water, air, and soil in the bio-systems which lead to pollution of the food chain (Begum et al., 2009). Continuous use of unprocessed manures and waste-waters has residue elements from metals which remain in the soils in depositing great levels of toxins. Spraying the soil with waste-water continuously reduces its capacity to retain the

heavy metals. Since repeated use of the waste-water and fertilizers affect mostly the surface soils, the heavy metals further leak into the ground-water available for the plants' usage (Papatilippaki et al., 2008). Application of high amounts of fertilizer has nitrates and heavy metals which pollute ground-water for plant irrigation (Mico et al., 2006). Simeonov et al., (2010) cite that heavy metals such as Cd and Pb are toxic to plants and animals, even in tiny doses. Lead negatively affects physical development and additive thresholds. Exposure to lead also decreases visual sharpness causes brain damage, and neurological problems, which can result to loss (Simeonov et al., 2010). Getting in contact with Cd elements can result to cancer of the skin, complains of absorption, among many other diseases that chemical irritation cause (Kumar, 2009).

Manganese danger influences the focal sensory system, visual response time, hand dauntlessness and eye-hand coordination (Calkins, 2008). A disorder named manganese described by sentiments of shortcoming and dormancy, tremors, a masklike face and mental aggravation. Respiratory impacts have additionally been noted in specialists incessantly uncovered by inhalation. Weakness and loss of libido have likewise been noted in male laborers harassed with manganese (Calkins, 2008). Zinc danger is uncommon, yet at focuses in water up to 40 mg/l, may instigate lethality described by manifestations of fractiousness, pain and muscular solidness (Al-Weher, 2008).

1.7 Organization of the thesis

Chapter 1 General description, object of the research, scope of the thesis and introduction of crude oil.

Chapter 2 presents a review of the significant literature for this work. Literature review for previous similar works.

Chapter 3 Materials and experimental procedures.

Chapter 4 Environmental impact for polluted area.

Chapter 5 Flow and penetration crude oil on soil.

Chapter 6 Results and discussion.

Chapter 7 summarizes the conclusions and provides some recommendations for future work.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

A majority of the environmental and ecological problems are brought about by oil spillage while in transit on land or during oil excavation procedures. These issues could also have numerous impacts on soil properties such as: shear strength, compressibility, among others. Pollution brought about by oil has negative impacts on the engineering properties, with the incorporation of the reduction of the holding capacity of bases with no great depth and revealing the structure stability into morbidity of unsymmetrical settlements. A majority of researchers have outlined the advantageous effects of oil contamination on shear strength.

2.2 Background

The researchers Al-Sanad et al., (1995) evaluated compaction and permeability tests on clear and oil contaminated sandy soil, varied up to 6%, Kuwaiti sands to evaluate the impact of oil pollution on the geotechnical characteristics. The findings showed decreasing unimportant porosity and strength, increasing compressibility, and increasing compaction properties and CBR values with the existence of oil up to 4% by weight. With the aim of finishing the assessment, (Al-Sanad and Ismael, 1997) followed through the aging impacts on the Kuwaiti soil that is polluted by oil. The findings revealed a growth of robustness and stiffness of the polluted soil samples in a duration of six months (Puri, 2000). The findings revealed that the level of friction reduced from 25 to 20% and the value of hydraulic conductivity relies on the density of the pollutant oil.

According to research conducted by Khamehchiyan et al., (2007) on sandy, clay soils through laboratory testing, with these soil specimens obtained from a coastal region, he discovered that there were a number of limitations when it came down to the addition of petroleum to these samples. Some of the limitations of this research were: Atterberg limits, porosity, strength, maximum water content, and maximum dry density. The polluted specimens were prepared by combining the soils with petroleum in the quantities of 2%, 4%, 8%, 12%, and 16% by dry weight. The non-polluted and polluted clay were contrasted with (Ur-Rehman et al., 2007). The tests conducted were the uniaxial compressibility, direct shear, compaction, porosity, and Atterberg limits. Ur-Rehman et al., (2007) conducted several laboratory tests with the inclusion of all fundamental and advanced geotechnical tests like the Scanning Electron Microscopy (SEM) method, organic carbon tests, pH, and Cation Exchange Capacity technique, standard Proctor compaction test, untrained uniaxial compression tests, and one dimensional consolidation tests. All of these tests were conducted so that the physical and chemical nature of the soils, compaction properties, assessment of strength, and compressibility could be determined. At low pressure, the shear strength of the soil was less than that of the non-polluted soil samples, and while the strength was a bit more than that of the non-polluted sample at high pressure. The pollution has negatively affected the plasticity of the clay.

2.3 Contaminated soil

A study by Al-sanad and Ismael (1997) proved that an increase in the amount of pollutant in soil results in the increase of the stiffness and aging of the soil. Increase and decrease in temperature also affects polluted sandy soil (Aiban, 1998). The outcome of the two separate studies done on sandy soil indicated that there is irreparable deformation of polluted sand as the temperature increases.

It has been determined that oil leakage on soil has both beneficial and detrimental effects on its properties and characteristics (Naeini and Shojaedin, 2014). A series of shear strength tests were conducted whereby the impact of soil pollution on the liquefaction ability of sandy soil is assessed. The samples are prepared by combining the Firoozkuh sand with petroleum in 4%, 8%, and 12% by dry weight. The findings indicate that even up to 8% of soil pollution is enough to increase soil liquefaction resistance and the liquefaction resistance reduces with an increase in the pollution percentage.

2.4 Geotechnical properties of sandy soil

Petroleum spillage has become an everyday occurrence in some areas where the exploration of crude petroleum is rampant (Akinwumi et al., 2014). This has adverse effects on the ecosystem by causing soil pollution. This experimental assessment has the objective of evaluating the impact of soil pollution by petroleum by adding the pollutant to lateritic clay soil so that the effects of pollution on the properties of clay soil such as

plasticity, porosity, and shear strength are determined The soil sample was polluted by incorporating differing amounts of petroleum to it. Specific gravity, Atterberg limits, compaction, California Bearing Ratio (CBR) and porosity tests were done on the polluted and non-polluted specimens. Capillarity, the plasticity limit index of the soil grew as the contaminant was added. In contrast to this, the moisture retaining content, specific gravity, porosity, CBR, and the optimum dry unit weight reduced as the contaminant was being added. Polluted soil needs stabilization and rectification before it is used in construction.

According to Nasehi et al., (2016) noted that soil pollution through gas oil leakage may alter the properties and characteristics (mechanical and chemical) of soil. Crude oil transportation, corroded pipes, refinery plants, and storage tanks enhance gas oil leakage. This study's primary objective is to put the effects of soil pollution by gas oil into consideration and determine its impact on the geotechnical properties of some soil samples. The impact of gas oil pollution on the geotechnical properties is closely studied on the following soil samples SP (low quality sand), CL (clay soil with low plasticity), and ML (silt). The non-polluted samples will undergo a number of experimental tests how their properties change when contaminated. The tests done on them are the compaction, direct shear, plasticity, and unconfined compression strength (UCS). The specimens are artificially polluted with 3%, 6%, and 9% of gas oil respectively relative to their dry weight. The outcome of these tests shows that there is a reduction in the friction angle, maximum dry density, and optimum moisture content and improvement in soil cohesion and plasticity of CL and ML with increase of the contaminant. The field emission SEM technique revealed that the increase of clay soil particles prolongs the time it takes for fabric flocculation to take place and therefore, it is a primary aspect for improving the unconfined compression strength in clay soil.

Furthermore, Puri (2000) assessed the geotechnical properties of the polluted soil through the use of laboratory tests and discovered that some of the soil's properties, such as compaction and angle of internal friction, were affected by pollution. Shin and Das (2001) evaluated the bearing capability of unsaturated polluted soil and realized that the optimum bearing capability of the soil on the surface rapidly decreased due to pollution. Ratnaweera and Meegoda (2005) conducted compression tests that were not confined on fine-grained soils (using Glycerol, Acetone, and Propanol as pollutants) and came to the conclusion that pollutants reduce the strength and stress-strained pattern of the soils. Khamehchiyan et al., (2007) conducted tests to examine the impact of petroleum pollution on the geotechnical properties of sandy and clay soils. The outcome of this study showed that contamination causes a decrease in their porosity, optimum dry weight, and maximum water content. Olchawa and Kumor (2007) evaluated the impact of diesel oil on the compressibility of soil and discovered that their compressibility increases with increase in the amount of the pollutant present in them. Olgun and Yildiz (2010) investigated the impact of petroleum pollution on the geotechnical properties of clay soil with high plasticity and came to a realization that the soil's liquid limit and consolidation parameters reduced while its strength increased and the dielectric constant of pore fluid also decreased.

2.5 Influence of oil contamination on the mechanical properties of soil

Crude oil leakage pollutes the soil and alters its physical and mechanical properties. The physical properties of soil include: color, texture, structure, consistency, and density. While the chemical properties include: the pH and cation exchange capacity. Soil horizons are discrete layers that constitute a soil profile and they run parallel to the ground. Jia et al. (2011) conducted a test and discovered that clay fraction tends to be higher in the heavily contaminated specimens while their Atterberg limits grew with increase in oil pollution. In-situ penetration tests revealed a decrease in soil strength with depth for the heavily contaminated specimen.

One of the most important soil properties that are essential for planning, designing and examining applications related to engineering properties is the shear strength of the soil. Other geotechnical engineering aspects include foundations, embankments, slopes, and retaining walls. Shear strength involves the maximum stress that can be endured by a soil before it reaches a case of failure (Sabbar et al., 2017). The shear strength of soil is a shared impact of interlocking forces and the friction between the soil grains that exist within the granular soils. With this regard, the shear strength of soil is derived from the general aspect of the cemented soil particles as well as their consistency within fine soils. A study by Nazir (2011), which examined the impacts of pollution from motor oil to the characteristics of over-consolidated clay, found that there is a significant reduction in the total strength and in the soil limits of plastic and liquid wastes. This was because the pollutants increased over a three months, including the swell index that was noted to have increased over a six months period. Khosravi et al., (2013) evaluated the consequences

of pollution on the properties of kaolinite and revealed that the pollutants make the cohesion of the kaolinite salts to increase and there was a reduction in the compressibility of the different soil types and the internal angle of friction. His research is a part of a wide program with the objective of enhancing a better comprehension of the effects of pollutants on soil properties. The tests conducted were: consolidation, direct shear, Atterberg limits, basic properties, and unconfined compression tests, which were carried out on polluted and non-polluted kaolinite samples. The polluted samples were prepared by adding various gas oil components to kaolinite. The findings of these tests show that the contaminant increases soil cohesion and reduces their compressibility and friction angle. The aim of this experiment is to show that the crude oil polluted sites can use other ways of treating these sites. Shear strength properties, for instance the internal friction angle and cohesion, investigated by such tests, as the direct shear box, ring shear, standard penetration test, cone penetrometer, van shear and triaxial apparatus.

The investigations carried out by Evgin et al. (1996); Amor (1990); Evgin and Das (1992); Al-Sanad et al. (1995) considered two states of initial relative density for the sand: (loose and dense) and two liquids for saturation: (water and oil). In the result of Cook et al., (1992) performed direct shear tests on dry and oil polluted Mississippi River sand where crude oil was utilized as the soil contaminant. These tests were performed utilizing distinctive degrees of oil contamination, S_0 , initial relative densities, D_r , and total normal pressures with the fundamental goal to explore the conceivable negative impacts of the presence of oil in the pore spaces on the strength-deformation behavior, and the angle of internal friction. The information from the direct shear tests conducted in the research facility were utilized to obtain shear stress versus horizontal displacement plots for the examples of clean dry sand, and furthermore for crude oil contaminated sand examples.

The decline in the friction angle is a component of both the initial relative density of sand and the level of crude oil saturation. For the scope of parameters considered by (Cook et al., 1992) the rate decline in the values of angle of friction ranged from 17.6% to 25% when contrasted with its value at a similar relative density in the dry situation. Furthermore, for a given level of oil saturation, the reduction in friction angle is bigger for sand at a higher relative density. Apparently, the outcomes of (Cook et al., 1992) demonstrate that shear strength parameters of sand are unfavorably influenced by oil pollution. On other hand Al-Sanad et al., (1995) also carried direct shear tests on Jahra sand to examine the influence of relative density, type of oil, and percent contamination on the effective strength parameters. Experiments were carried out at relative densities of 30%, 60%, and 90%. For four kinds of oil, the percent oil contamination changed somewhere in the range of 2% and 6% by weight. The tests were performed in a shear box 100mm x 100mm x 20mm with a rate of shear equivalent to 0.75 mm/min utilized for every one of the tests. In the results of the examination it tends to be presumed that oil pollution prompts reduction strength. Nonetheless, the progressions are not huge in connection to the level of oil. The decrease in the angle of friction was 2 for specimen arranged at a relative density of 60% and mixed with 6% of heavy crude oil. Heavy crude oils influence the strength parameters of sand more than light gas oil and benzene at all relative densities.

The relationship between relative density and the angle of friction for clean and contaminated sand at different percentage of oil demonstrated that the decrease of the friction angle with heavy crude oil more than light gas oil. This decrease was apparent for all relative densities from loose to very dense conditions.

2.6 Summary of previous work

Many researchers dealt with impact of crude oil contamination on geotechnical properties of clay and sandy soil. In Table 2.1 below showed work of the several researchers based on type of soil, different percentage of oil utilized in them investigations, which type of oil used and the main geotechnical tests used in the study. It is a guide line to good understand of all works as a summary and brief key to decide for select type of test and identify percentage of crude oil used.

No.	Researcher	Soil type	Oil %	Oil type	Tests	Country
1	AL-Sanad et al., (1995)	Sand (SP)	0,2,4,6	Crude oil	Spec. Grav.+Atter. Lim. + Compa.+CBR+ Constant head pearmeability+tria xial + Direct shear & consolidation	Kuwait
2	Khamehchi yan et al., (2007)	SM , SP & CL	0,4,8,12,1 6	Crude oil	Atter. Lim. + Compa. +Direct shear + Uniaxial compr. & pearmeability	Iran
3	Nazir, (2011)	Clay (CH)	UD Sample	Motor oil	Atter. Lim. + Permeability. +Unconfined compr.& Compressibility Properties	Egypt
4	Elisha, (2012)	Soft Clay	case study	Crude oil	Atter. Lim. Compa. + UU triaxial + Sorption +Swelling.	Nigeria
5	Ijimdiya, (2013)	CL by USCS	0,2,4,6,8	Motor oil	Particle size distribution+Unco nfined compressive+ Void ratio+ Mv & Cv.	Nigeria
6	Akinwumi et al., (2014)	Lateriti c Clay	0,2,4,6,8, 10	Crude oil	Spec. Grav. +Atter. Lim. + Compa.+CBR & pearmeability	Nigeria
7	George et al., (2015)	Sand 60% &clay 32%	0,4,8,12	Diesel oil	Atter. Lim. + Compaction. +Unconfined compressive & CBR.	India
8	Pandey and Bind (2014)	Soil Clay (CL) Indian standar d	0,4,8,12,	engine oil	Atter. Lim. + Compaction	India

 Table 2.1 Summary of previous works on contamination.

9	Abousnina et al., (2015)	Fine Sand	0.0.5,1,2, 4,6,8,10,1 5,20	light Crude oil	Direct Shear Cohesion + Frictional angle + Compressive Strength	Austtrali a
10	Nasehi et al., (2016)	fine & coarse grained	0,3,6,9,12	gas oil	Atter. Lim. +Compa. +Direct shear + Unconfined compr.	Iran
11	Harsh et al., (2016)	Clays and sands	0,3,6,9	Crude oil	Spec. Grav. +Att. Lim. + Swelling	India
12	Pradeepan et al., (2016)	clay (CL)	0,4,8,12,1 6	Diesel oil	Atter. Lim. + Compa. +Unconfined compr.	India

2.7 Pollution

Pollution is the introduction of substances into water, soil or air, or any other part of the ecosystem, which have harmful effects on the environment. This can happen naturally or be caused by human activities (Singh, 2006). It can be classified as point source and non-point source contamination (WHO, 1998). The causative agents of pollution or contamination are referred to as pollutants or contaminants respectively. These agents are defined as materials that cause pollution when introduced to the ecosystem (Singh, 2006; Rashid, 2010).

The Environmental Protection Agency in the United States (USEPA, 1999) stated that the retractions procedures include a wide array of biological, chemical and physical procedures that act on the pollutants to decrease their morbidity, mass, movement, and concentration. Some of these procedures are radioactive decay, volatilization, absorption, dilution, and anaerobic and aerobic biodegradation (Rittman, 2004).

2.8 Environmental pollution in Iraq

The number of population and rapid urbanization has being expanding around the world, particularly in the developing countries, which had a yearly urban development rate of

3.6% somewhere in the range of 1950 and 2005, versus just 1.4 % in developed countries (Aubry et al., 2012). This surge has led to elevating demand for food, shelter and employment. Population of Iraq has tripled since 1970, growing from 10 to 30 million, around 71% of which is living in urban areas. 47% of the urban people are currently living in slum-like conditions. It is expected that the population will increase to approximately 50 million by 2030 (NDP, 2010).

The Iraqi country faces a variety of environmental problems, such as, draught, desertification, oil refineries, factories, water pollution and shortage, discharges of sewage into rivers, fertilizer and pesticide contamination of the soil, air pollution in urban areas and inefficient solid waste management (USEPA, 2004). NDP (2010) reported that 39% of the agricultural lands of Iraq suffers from decreasing in crop land. Consequently, a noticeable amount of heavy metals and other chemicals are released into the water, soil and air. Smoke from oil-well fires and burning oil trenches during the recent war caused localized soil contamination.

In order to good understand the oil impact on the soil properties in Iraq and sources, dangers and treatments of oily soil pollutants. In one hand, pollution by oil product activity and its transportation by pipe line networks and tankers are the sources for pollution, in other hand, main source of pollution by crude oil in Iraq is the wars, Kuwait war, 1991, American war 2003 (Mutter and Lamy, 2014) and ISIS war.

In 1991 the environmental disaster happened in Iraq and Gulf region due to Kuwait war. The war prompted consume and spillage a huge number of huge amounts of oil and its product to the Iraqi environment. It was happened that as a result of the Kuwait war, air contamination is the most influenced, followed by pollution of soil and water (Kalidar, 1994). Jubouri, (2000) conducted Soil investigation at different depths and showed higher rates of hydrocarbons up to 20% in the areas close to oil facilities. The toxins spread to a radius of around 7 km, yet there is no evidence of ground water pollution (Jubouri, 2000). Because of the lack of treatment units, oil contamination additionally affects the Iraqi rivers. The contaminations concentration that discharged to waterways were 89 mg/l of unrefined petroleum, 1.4 mg/l Ammonia and 460 mg/l of COD (Kalidar, 1994). Amid the post-war in Kuwait and so as to control the oil wells.

After the last war in 2003 known as American war, a lot of environmental problems were emerged. The oil pollution become an important aspect in the Iraqi environment pollution due to the following reasons (Mutter and Lamy, 2014):

a) Before and during the war:

i. In planning to the war before starting, the Iraqi government prepared fuel tanks under and over the ground close to every governmental administrative office. In the meantime, there are extra oil storage in little tanks by the general population in houses and gardens.

ii. With the starting war, the Iraqi army burned thousands of tons (around 540 m³ for each day) of black oil and other types of oil to mislead the enemy air forces (Mutter and Lamy, 2014).

iii. The oil facilities, pipeline networks and storage tanks of fuel were focused on around multiple times and fired in excess of $63,000 \text{ m}^3$ of unrefined petroleum, 2.5 million units of gas and in excess of $82,000 \text{ m}^3$ of other oil based goods.

b) After the war:

i. The huge amount of crude oil leaked and spread as a resultant of vandalism of the pipelines while the proceeding of the destroy infrastructure in oil framework and, oil and gas pipelines.

ii. Oil contraband and the going with waste when transport, and loading oil and so forth.iii. Many fuel pumps damaged and destroy in filling stations reason to polluted the area around to their.

iv. Electric power problems that urge inhabitants to secure diesel and gas generators. These applications add to the contamination of the earth somehow.

2.9 Physicochemical studies of soil

Soil is a fundamental natural resource that is considered to be irreplaceable and it has a fundamental role in the regulation of climate, biodiversity maintenance and the production of food. It is also the main linkage between the hydrosphere, the atmosphere and the geosphere. Soil is a key component of natural and agricultural environment, and plays a significant role in growing, decomposing and recycling of all biological communities (Alloway, 2004). Potentially toxic elements are considered the significant most hazardous materials in soil and water contamination. They can be passed to,

dispersed through and accumulated in biological organisms and then may be transported through the food chain to human population as a final consumer. As it is known, that trace elements are present in soil in various chemical forms with difference solubility and bioavailability. Although some trace metals including Cu, Zn, Fe and Mn, are essential for all living organisms on earth, some others, As, Cd and Pb, not only have unknown function in plants, animals and human but also are toxic for biological organisms (Peijnenburg et al., 2007).

At a global scale, the most commonly known soil pollutants include the chlorinated hydrocarbons and heavy metals such as lead that is normally found in lead paints, chromium, aeronautics fuel and cadmium, which is mostly present in battery-powered batteries.

Most of the pollutants that end up in the soil environment include chemical substances and the heavy metals such as copper and lead that are let out from old pluming water system (Rashid, 2010). The study also found that most of the compost from municipal waste including the leachate tend to increase the levels of the organic matter in soil. It also increases the amounts of the available soil micronutrients Fe, Mn, Cd, Cu, Pb, Zn, and Ni and the macro- nutrients N, P, and K. The soil content of CaCO₃ is also reduced owing to the leachate acidic pH that in turn lowers the productivity of soil including the crop yield. Moreover, the leachate from waste has been found to have an impact of the chemical and physical properties of the soil (Roghanian et al., 2012). It encourages the aggregation of soil, a decrease in surface crusting of the soil, raises the organic matter in the soil and it also lowers the pH levels in soils that are calcareous.

With adding leachate to soil, the amount of soil Cl, soluble sulfate and soluble bicarbonate increases and leaching and time passing decreases their amount. As per physical-chemical and mineralogical properties, soils can have incredible ability to hold particles and mixes through ingestion and appearance responses on particles surfaces. Natural issue, Fe and Mn oxides and mud minerals can frame buildings and adsorb a few metals because of the surface charge of these materials (Langmuir, 1997).

Muhammed (2008) conducted an ecological study on the Tasluja cement plant and mining site, Sulaimani-Iraq. The results of physiochemical parameter were as follows: the mean soil temperature was 23.45 °C, pH values was ranging from 7.4 to 9.2, the EC values was ranging from 12 to 125 μ s/cm, sulphate concentration value was ranging between 128 and

680 mg/kg, while Fe, Zn, Cu, Mn, Co, Ni, Cd and Pb were estimated for soil systems, trace metals were showed in different modes during the study period. While a study by Muhammed (2008) in Halabja city revealed that the available phosphorus ranged between 3 and 8 mg/kg while the amount of total phosphorus ranged between 176.65 and 415.49 mg/kg. Total calcium carbonate ranged between 23.19 and 34.48 % which indicates that all soils were considered to be calcareous soils. Generally, soil samples varied in organic matter contents which ranged from 0.41 to 2.37 % but pH value of the soil samples ranged between 7.41 and 7.81 and the soil was located between slightly to moderately alkaline.

More dominant soluble cations which can be ordered were $Ca^{+2} > Mg^{+2} > Na^+ > K^+$ but the most dominant soluble aninon was HCO₃ which resulted from dissolving CaCO₃ followed by Cl. Chemical and physical characteristics of two study soils show that these soils contained higher amounts of calcium carbonate of more than 10%, while the EC of these soils were less than 1.2 ds/m. The pH of these two study soils is more than 7.2. The soils available phosphate were 10.62 and 9.02 µg/g in Darbandikhan and Arbat locations (Rashid, 2010). In addition, a study by Mohammed (2013) revealed the high concentration of Ca in all soil samples was expected because it was characterized as highly calcareous and the concentration of PTEs was found to be Mn> Fe> Sr> Ni > Zn > Cr > V > Cu > Pb > Co > U > Se > Mo > Cd. Although relatively high concentrations of Ni and Cr were found at all sampling areas, yet they were close to threshold level, mean concentrations of trace elements in the soil samples in the different studied areas were all below the soil guideline value.

Krishna and Govil (2004) observed that the levels of metals in soils around the industrial areas were found to be significantly higher than their normal concentration in soil. On the other hand, the study done by Rashad and Shalaby (2007) on the dispersion and deposition of heavy metals around polluted area showed that the mean pH value, EC, organic matter, Ca, Mg, Na and Cl were 7.9, 4.8 ds/m, 2.8%, 4.5 meq/l, 3 meq/l, 11.8 meq/l and 7.3 meq/l respectively; while mean concentration of Cd, Cu, Ni, Cr and Zn were $5.1\mu g/g$, 97.11 $\mu g/g$, 12.21 $\mu g/g$, 11.2, $\mu g/g$ and 1101 $\mu g/g$ respectively.

A study done by Raman and Narayanan (2008) revealed that pH, EC, Pb, Cd, Cu, Mn, Cr, Ni and Hg value in the soil were varied between 6.3 and 7, 180.2 to 622 μ mhos/cm, 7.43 to 51.52 mg/kg, 0.17 to 0.40 mg/kg, 25.28 to 43.08 mg/kg, 32.74 to 110.8 mg/kg, 6.50 to 44.28 mg/kg, 4.68 to 9.52 mg/kg and 0.029 to 0.20 mg/kg) respectively. While a

study done by Oyedele et al., (2008), investigated that the mean value of pH, organic matter, potassium, sodium, calcium, magnesium were 7.5, 3 mg/kg, 2 mg/kg, 0.57 mg/kg, 12.3 mg/kg, 6.4 mg/kg respectively. Lead for instance increased with depth from 37.9 ug/g to 102.1 μ g/g.

The concentrations of Zn and Cu diminished with expanding soil profundity which means that their low versatility. Soil organic matter substance of the surface soil extended from 2.7 to 4.2% in the wet season and from 3.0 to 6.2% in the dry season. While, Singh et al., (2008) assessed the impact of polluted soil; the result showed that the pH of all samples ranged between 7 to 7.5, the percentage of organic matter was between 6 to 19 %, chlorides and sodium in MSW varied between 0.02 to 0.4 mg/g and 0.02 to 0.1 mg/g respectively, Calcium and nitrate content of soil samples was in the range of 0.11 to 0.1 mg/g and 0.08 to 0.092 mg/g respectively. Sulphate, potassium and phosphate of soil samples were within a range of 0.085 to 0.11 mg/g, 0.1 to 0.95 mg/g and 0.0016 to 0.004 mg/g respectively.

A study by Schenato et al., (2008) on heavy metals in polluted area in southern Brazil, investigated the average concentration of Pb, Cu,Cr, Cd, Ni, Zn and Hg found it to be 20 mg/kg, 120 mg/kg, 113 mg/kg, 0.2 mg/kg, 97 mg/kg, 72 mg/kg,0.02 mg/kg. While the average concentration of pH and total organic carbon were 6.1% and 0.2% respectively. Also Adefemi and Awokunmi (2009) studied the impact of polluted soil by solid waste disposal; high concentrations of Cu, Mn, Fe, Pb, and Zn were found in the soil samples. Whereas, Adjia et al., (2008) revealed these levels to be were out of the critical level for agriculture for the high concentrations of Pb and Zn, Cd, Cu and Zn, but the levels of Ni in urban wastes from all sites were lower than the critical level; the level of Ca ranged from 12.59 to18.45 g/100 g whereas the levels of Mg ranged from 2.80 to 3.5 g/100 g.

According to Banar et al., (2009) carried out a research on soil heavy metal pollution in Eskisehir/Turkey. They discovered that the mean concentrations of Cr, As, Pb surpassed the threshold and natural background values, while the highest concentrations of Ni, Cu, and Zn surpassed the specified threshold limit. Soil pH fluctuated from 5.7 to 8.9 and was acidic to close to neutral and basic in nature. Likewise, Ogbonna et al., (2009) illustrated that the soils were moderately acidic. Moreover, above permissible values of heavy metals were observed in all the locations of the waste dumpsites. A study conducted by Awokunmi et al., (2010) investigated the ranges of concentrations of cobalt, chromium,

copper, iron, lead, manganese, nickel and zinc which between 105 and 810 mg/kg, 900 and 2000 mg/kg, 18.00 and 133.10 mg/kg, 1100 and 10,920 mg/kg, 3500 and 6860 mg/kg, 20 and – 2210 mg/kg, 18 and 335 mg/kg and 350 and 3052 mg/kg in all locations on all dump sites. Also, Okeyode and Rufai (2011) revealed that levels of the metals in soils were significantly higher than their normal concentration in soil. In addition, a study conducted by Rashad et al., (2011) showed relatively high pH and CaCO₃ content and low organic matter content at the soil surface.

A study done by Amuno (2011), showed some degrees of contamination with metals like Pb, Zn, Ba, Sr, Se; while the rates of, Mn, and Cu were lower contrasted with their particular normal shale substance and in this way demonstrating no advancement of any sort. What's more, the examination led by Parth et al., (2011) conducted that soils in the downstream and region of Hyderabad city dumpsite were significantly polluted by metals with their rates past the threshold value. The normal concentrations of As, Cr, Pb was found to surpass the prescribed threshold limit, while the highest groupings of Cu, Ni and Zn surpassed the recommended edge limit. Soil pH shifted from 5.7 to 8.9 and was acidic to close impartial and antacid in nature.

Beyene and Banerjee (2011) in their study in Addis Ababa city on the trace element in a solid waste disposal site collected some soil samples from the nearby open land and from the dumpsite and found that the concentration of heavy metals such as nickel, zinc, lead and cobalt exceeded the internationally acceptable soil limit. Chineyre et al., (2013) assessed the quality of soil in the Njoku Sawmill. They found out the mean values of soil temperature was 33.6 °C, pH of the heavily polluted points was 7.3, organic matter and nitrate were 6.47 % and 18.82 mg/kg respectively; while sulphur and phosphate were 158.48 mg/kg and 9.61 mg/kg respectively. On the other hand, calcium, magnesium, sodium and potassium were 13.01mg/100g, 10.41 mg/100g, 130 mg/100g and 23 mg/100g respectively.

2.10 Physicochemical studies of water

Water can be polluted from different sources, the major sources of water contamination are industrial, chemical, physical, organic, thermal wastes, municipal, and agricultural pollutants (EPA, 2000). The potential sources of water are precipitation, penetration of surface water, water permeating from adjoining area and ground water in contact with the fill. One of the primary concerns with ground - water pollution is that it might last longer

underground for a lot of years. This is in complete differentiation to surface water contamination which can undoubtedly be remediated (Rao and Shantaram, 2003).

Environmental effect of polluted water is usually caused by the run-off of the toxic compounds going into surface water and groundwater. The pollutants mobility in soils can significantly relies on physical, chemical and biological reactions (Rao and Shantaram, 2003). World Health Organization and Ministry of Health (1998) conducted a survey on physio-chemical and bacteriological drinking water source in Erbil province, the PH values were always observed above 7.0, Whereas concentrations of sodium, calcium, potassium and total dissolved solid ions ranged between 3.0 and 33.5 mg/l, 18 and 55 mg/l, 0.6 and 3.0 mg/l and 100 and 424 mg/l respectively.

Another study carried out by Mustafa (2006) on the impact of wastewater on the Tanjaro environment concluded that generally Tanjaro River, Qliasan stream and ground water are polluted with sulfate, nitrate, nitrite, ammonia, ammonium and heavy metals such as cadmium, copper, nickel, lead and zinc. On the other hand, Ahmad and Mustafa (2008) concluded that the majority of the water wells 63% of the groundwater in Sulaimaniyah city is polluted with NO₃, in which nitrate is more than 10 mg NO₃/l.

Moreover, Hawrami (2010) study on drinking water quality in Duhok Province revealed the metals Cd, Pb and Ni were higher than the permissible limit, according to the WHO guide line, while chromium was lower than the permissible limit, therefore, the water is not safe for drinking and causes adverse health effect on population. Rashid (2010) investigated the estimation of the physico-chemical parameters of water from the waste disposal called Tanjaro which is located in the Sulaimani city. In all different sources, the potential of mean hydrogen ion ranged between 7.8 and 8.2 in Tanjaro river standing and well water samples respectively; EC, total hardness, BOD₅ and DO mean values was 876.4, 781.9 and 1125 μs/cm, 224.7, 233.8 mg.CaCO₃.l⁻¹ and 90.2 mg.CaCO₃.l⁻¹, 3.7, 2.4 and 1.1 mg.1⁻¹ and 4.43, 4.16 and 2.65 mg.1⁻¹ for standing and running Tanjaro river, and well water samples respectively. The average mean concentration values of sodium, potassium and magnesium were 53.6, 84.5, 5144.3 and 120.92 mg.1⁻¹, 29.4, 20.73, 1861.5 and 1.18 mg.l⁻¹ and 22.6, 20.77, 354.2 and 17.3 mg.l⁻¹ in Tanjaro river standing, running leachate and well water respectively. The average mean concentration values of chlore was 35.4, 24.48, 3459.4 and 17.42 mg.l⁻¹ for Tanjaro river standing, running , leachate and well waters respectively. On the other hand the most of the studied samples from the river showed pollution by heavy metals except Zn, Cu, Al and Fe which exceeded permissible recommended values due to impact of sewage waste water from Sulaimani city, location of landfill site adjacent to the river, and anthropogenic activities. Levels of heavy metals were relatively high in well water adjacent to landfill sites. Nearly all well water samples were exceeding the permissible recommended values for drinking purpose except Fe, Mn and Al.

Studying the components of water in pollution involves analyzing leakages of waterwaste and sewages. Pollution environment, leakages of chemicals from factories into farms, and use of unprocessed fertilizers affects soil nutrients necessary for growing plants. Heavy metals, which are found in Nigeria, possess high levels of iron, zinc, cadmium, and nickel which pollutes lands for growing crops thus affecting the production of food in the province (Ikem et al., 2002). However, Adefemi et al., (2007) conducted a research in Ekiti state, Nigeria. They explored the evaluation of the physico-chamical status of water from four main dumps. They inferred that a critical look at the physicochemical parameters of the water tests from all the dams in contrast with the WHO standard. Furthermore, they demonstrated that the water tests still fall inside the stipulated scope of worthiness and subsequently the water can be treated for domestic purposes. Moreover, a study by Schenato et al., (2008) on heavy metals in municipal solid waste landfills in southern Brazil revealed that the concentration of some metals such as Pb and Ni are above the maximum values allowed, while Cr and Cd are below the detection limit of the methods used.

Another study conducted by Raman and Narayanan (2008) revealed that the pH of water samples in dump sites area varied from 5.24 to 6.59; total alkalinity values varied from 40 to 260 mg.l⁻¹; hardness of water sample varied from 450 mg.l⁻¹ to 669 mg.l⁻¹. Calcium concentration varied from 107 to 169 mg.l⁻¹ and magnesium concentration varied from 22.5 to 60.1 mg.l⁻¹. The nitrate and phosphate concentration varied from 22.35 to 26.37 mg.l⁻¹ and 0.11 to 0.16 mg.l⁻¹ respectively. Several physico-chemical characteristics of surface water including magnesium, sodium and calcium concentrations were 120 ppm and 300 ppm, 200 ppm respectively. BOD ranged between 5 to 10 mg.l⁻¹, also Alkalinity ranged between 40 to 80 mg.l⁻¹ (Kassenga and Mbuligwe, 2009). While, Ololade et al., (2009) studied some physico-chemical parameters in waters near solid waste disposal areas from various sources. The mean ground water pH was 6.54 but the mean surface water pH was 6.79; nitrate ranged from 7.40 to 8.80 mg.l⁻¹ and 8.04 to 10.2 mg.l⁻¹ in

samples from ground and surface water respectively. The concentrations of chloride ranged from 202 to 304 mg.1⁻¹ and 143 to 190 mg.1⁻¹, the concentration of Sulphate ranged from 75 to 130 mg.1⁻¹ and 63 to 71 mg.1⁻¹ in samples from ground and surface water respectively. Rajkumar et al., (2010) studied the physicochemical analysis of ground water near Erode municipal solid waste disposal areas. They found the values of water pH, EC, total dissolved solids and alkalinity to be 7.1 to 8.2, 410 to 3830 μ s.cm⁻¹, 267 to 2345 mg.1⁻¹, 210 to 675 mg.1⁻¹ respectively; sodium and potassium concentrations ranged between 0 to 437 mg.1⁻¹, 4 to 76 mg.1⁻¹ respectively; calcium and magnesium concentrations were 28 to 188 mg.1⁻¹, 5 to 209 mg.1⁻¹ respectively; while chlorides concentration ranged between 28 to 759 mg.1⁻¹.

Majolagbe et al., (2011) investigated the quality assessment of ground water in the vicinity of dump sites in Ifo and Lagos, Southwestern Nigeria. They found that the mean values of water temperature, pH, EC, total dissolved solids, alkalinity and total hardness were 28.75 °C, 6.67, 1.01 ms.cm⁻¹, 474.25 mg.l⁻¹, 135.46 mg.l⁻¹ and 97.1 mg.l⁻¹ respectively; while chloride, sodium magnesium concentrations were ranged between 92.78 to 162.07 mg.l⁻¹, 39.92 to 308.78 mg.l⁻¹, 4.72 to 192.24 mg.l⁻¹ respectively; but Pb, Fe, Cu, Cd, Zn concentration ranged between 0.001 to 0.003 mg.l⁻¹, 2.06 to 2.27 mg.l⁻¹, 0.02 to 0.012 mg.l⁻¹, 0.01 to 0.005 mg.l⁻¹, 0.14 to 2.43 mg.l⁻¹ respectively. In addition, the study of Beyene and Banerjee (2011) also found that the pH of the soil was between 5.68 and 5.72. These levels were determined to be an indication of acidity and it also showed that there is a high concentration of heavy and toxic metals. The study assessed the spread of heavy metals profile particularly in the groundwater network near a solid waste disposal site in Malaysia. The results of the study showed that there were significant presence and high levels of heavy metals including Pb, Mn, Zn, Fe and Cd. The concentration levels of the metals were higher compared to the standard and permissible levels of concentration as provided by the (WHO, 2007) standards for drinking water. The increase of the heavy metals has also resulted to a high uptake of metals by some of the crops that were under examination.

On the other hand, Aderemi et al., (2011), investigated the assessment of ground water contamination by leachate. In all the wells, the mean hydrogen ion value of 4.2 was recorded, thus the groundwater investigated in this study was below the WHO permissible limits for potable water. The Na ranged between 15.73 to 325 mg.l⁻¹. The concentration of iron metal in samples collected from groundwater and was between 0.18 and 0.91 mg.l⁻

¹, all of which are above the WHO acceptance levels in almost 75% of the collected samples. Zinc metal was also detected in the collected water samples with values that were from ND to 0.02mg.l⁻¹. These concentrations are far lower than the WHO permissible levels. The sampled ground water did not detect any components of lead and cadmium metals.

Akinbile and Yusoff (2011) studied the assessed the groundwater quality in Akure -Nigeria. The parameters determined included; pH ranging from 5.7 to 6.8 and indicating toxic pollution; temperature, ranging from 26.5 to 27.50 °C; concentrations of iron, nitrate, nitrite and calcium, ranging from 0.9 to 1.4 mg.l⁻¹, 30 to 61 mg.l⁻¹, 0.7 to 0.9 mg.l⁻¹ ¹ and 17 to 122 mg.l⁻¹ respectively. For heavy metals, zinc ranged between 0.3 and 2.3 mg.l⁻¹ and lead ranged from 1.1 to 1.2 mg.l⁻¹. Shanthi and Meenambal (2012) studied the physicochemical analysis of ground water near Coimbatore. They found the values of water temperature, pH, EC, total dissolved solids, dissolved oxygen and BOD were 25.12 to 27.18 °C, 7.03 to 7.89, 512 to 951 µs/cm⁻¹, 545 to 996 mg.l⁻¹, 3.78 to 6.43 mg.l⁻¹, 1.1 to 3.7 mg.l⁻¹ respectively. Calcium and magnesium concentrations were 108 to 264 mg.l⁻¹ ¹ and 34 to 67 mg.l⁻¹ respectively. Alkalinity, chlorides, total hardness were 78 to 187 mg.l⁻¹,114 to 287 mg.l⁻¹,149 to 305 mg.l⁻¹ respectively; while nitrate concentration was up to 20.1 mg.l⁻¹. On the other hand, in a study conducted by Afolayan et al., (2012) revealed the temperature of the groundwater samples ranged from 24.8 to 26.7 °C. The pH, EC and dissolved oxygen of the groundwater samples was ranged between 5.98 to 12.19, 0.17 to 9.94 us.cm⁻¹ and 3.18 to 4.41 mg.l⁻¹ respectively. While total hardness and concentration of Cl ranged between 6 to 126 mg.l⁻¹ and 5 to 474 mg.l⁻¹ respectively. Nitrate was generally less than the WHO standard limit.

While according to a study conducted by Dibakar et al., (2012) revealed the pH and EC and total hardness were within the permissible limit declared by WHO. Several physicochemical characteristics of water including total hardness and BOD ranged from 96 to 552 mg.l⁻¹ and 2.2 to 2.6 mg.l⁻¹ respectively, the chloride content ranged from 14.97 to 182.56 mg.l⁻¹, the average of total alkalinity varied from 18.20 to 142 mg.l⁻¹ and nitrate concentration was found to be in the range of 4.2 to 24.18 mg.l⁻¹, chloride ranged between 1174.2 and 135.6 mg.l⁻¹ (Jhamnani and Singh, 2009).

2.11 Effect of mineral admixtures on soil properties

Investigation on how to reduce the bad effects of sandy soil shows that it is possible when mixed with other chemical combinations. The chemical properties essential for mixture with sand include clay, fly ash, lime, silica fume, cement and slag. Waste matter (slag) is attractive for engineering because of the economic and environment benefits. Scholars also investigated two different types of sandy soils, one mixed with slag contents weighing 2%, 4%, and 6% while the other sample was clean sand only (Sabbar et al., 2017). The research also made use of two types of tests to examine the influence of slag in sandy soil which were unconsolidated undrained triaxial and the direct shear tests.

Engineers use slag because of its positive impact on the environment. When contractors use slag in construction, it produces low levels of carbon dioxide in the air. Slag is residue from metals such as iron, lead, steel, and zinc, among other metals. Other engineers, like the structural and geotechnical ones, also use slag in their constructions (Yi et al., 2013). Slag provides stronger concrete than cement, which makes it preferable by geotechnical engineers who use it widely to improve the clay soils. However, the idea that the slag improves sand is still under further investigations. When it comes to the mixture with water, Portland cement reacts faster than metal residue, which requires an additional chemical activator to blend entirely (Ouf, 2001). The fact is that one ton of cement especially Portland cement generates over 0.90 tons of carbon dioxide. Making use of slag is beneficial to the environment and construction workers because it emits low levels of carbon dioxide, which makes it safe for use. Moreover, construction engineers prefer to use slag rather than other metal residues because it reduces the cost of production thus increasing the chances for high productivity. Matsuda et al., (2008) describe GBFS as a component that is light weight, high permeability. The GBFS are useful in back-filling of sand, quay-wells, and making light-weight wall. Mixing substance activators with slag, increases the strength and stability of shear sand (Yi et al., 2013).

According to USCS, fly ash is non-plastic of fine silt which, when blended with soil develops cementations bonds. The bonds result from pozzolanic reaction (Zumrawi, 2015). The cement-like bond is due to an intrinsic property, which hardens under favorable temperatures and application of mechanical pressure to the soil. Mixing fly ash with clay in different proportions brings forth another form of cement suitable for construction because it produces fine concrete (Mir and Sridharan, 2014).

2.12 Statistical analysis

Numerous statistical researches aim to determine the relationship between dependent and independent variables. The dependent variables in this study are the oil leakages and the independent is germination. ANOVA which is the evaluation of variance determines the confidence levels as well as the level of significance in the provided data. Using means and standard deviations of the independent and dependent variables, it is possible to calculate the variance using the means to make ANOVA analysis possible. Algin (2018) used the ANOVA evaluation to determine the significance of design factors and their responses. ANOVA is also performed to identify the level of effectiveness of the independent variables on the design responses. In the results obtained p-values for which if it is higher than 0.05, the parameter is rejected as an insignificant factor on the response at 95% confidence level. This study will use the analysis to find out the relationship between oil and water in agricultural activities, that is, planting. ANOVA requires the calculation of p-value to be able to determine the level of significance and confidence of the oil spills in plants. ANOVA produces statistically significant (SS) analysis using 95% level of significance and calculation of the F-distribution test. In the attempt to find the regression and correlation from compaction of soil properties and mechanical pressure, the use of 95% level of confidence, p value, and the f-value must be used to make ANOVA easy to explain. According to Oluremi et al., (2017) utilized Minitab R15 program for statistical analysis parameters obtained in them results MDD, OMC, UCS, SEO, CI, PI and PF by utilized ANOVA according to compactive efforts produced statistically significant (SS) and using 95% level of significance and F-distribution test as shown in Table 2.2.

Most analysis uses geotechnical engineering components including the plasticity index, among others to conclude on the effort index values which vary between -1, 0, and 1. The standard applicable in measuring the effort index for the study includes WAS, BSL, and BSH. The effort index, which is mainly in form of percentages, shows the most significant effect using positive coefficients while the weak coefficients are in negative values. Therefore, correlation coefficients values denoted as (R^2) show a good relationship between the unconfined compressive strength (UCS) and parameters in equation 2. However, value of $R^2 = 66.8\%$ implies that the relationship between the independent and dependent parameters is strong at the rate of 0.67. The regression equation is:

Variable	Source of variation	Degree of freedom	F _{CAL}	P-value	F _{CIRT}	Remark
UCS 14	SEO Compositivo	5	2.167	0.13948	3.326	SS
Day Curing	Compactive Effort	2	23.521	0.00017	4.103	SS
Maximum	SEO Commonstinue	5	56.682	5.17E-07	3.326	SS
Dry Density	Compactive Effort	2	204.72	7.7E-09	4.103	SS
Optimum	SEO	5	6.253	0.006994	3.326	SS
Moisture Content	Compactive Effort	2	32.624	4.14E-05	4.103	SS
Plasticity	SEO Compactive Effort	1	5.99	0.034408	4.965	SS
Index		10	-	-	-	SS
Percentage	SEO Compactivo	1	7.476	0.021043	4.965	SS
Fine	Compactive Effort	10	-	-	-	SS

Table 2.2 Analysis of variance for unconfined compressive strength. (Oluremi et al.,

(2)

2017)

Another variable that is essential in ANOVA analysis is the use the means of the dependent and independent factors among the groups (Nwankwo, 2014). Using sample means is significant in this study because they are rarely the same implying that the end results of the study will be reliable, easy to understand, as well as easy to evaluate. The process of data collection is the reason why the variances and means of the data on plants, soil types, and oil types are different. Therefore, ANOVA is useful in group data analysis because it helps to compare the variability between and within groups. ANOVA also evaluates the variance for physicochemical parameters, which calculates the correlations between parameters which are the soil types, water types, and oil types over time. The P-value of this study is at 0.05, which is essential in the calculation of regression and correlations. In general, this study focuses on the treatment with fertilizer increased soil pH and electrical conductivity for two kinds of soil. The data to analyze is from the IBM SPSS Statistics 19 software which is the current method of recording statistical information in the Windows. The results illustrated in Table 2.3. Furthermore, the oil

levels define the toxic soil in this study and the use of diverse types of oil and water specimens will be useful in ANOVA evaluation.

 Table 2.3 ANOVA data summary with dependent variable pH, the correlation between

pH and EC (Nwankwo, 2014)

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	109.159	49	2.228	45.116	0.000
Intercept	5854.086	1	5854.086	118556.567	0.000
Days	2.52	4	0.630	12.76	0.000
Soil	101.805	9	11.312	229.084	0.000
Days * soil	4.833	36	0.134	2.719	0.001
Error	2.469	50	0.049		
Total	5965.714	100			
Corrected Total	111.628	99			

Dependent variable: pH

Dependent Variable: pH

ANOVA

Model	Sum of Squares	df	Mean Square	F	Sig.
Regression	62.447	1	62.447	124.436	0.000
Residual	49.180	98	0.502		
Total	111.628	99			

Dependent Variable: EC

ANOVA

Model	Sum of Squares	df	Mean Square	F	Sig.
Regression	212817.383	1	212817.383	4.460	0.037
Residual	4676200.052	98	47716.327		
Total	4889017.436	99			

Adam (2001) also used ANOVA analysis of variance using variables such as Minitab package and Tukeys. There are two types of ANOVA analysis the one way Anove and the two-way analysis. In this study, the one way ANOVA, which sets a 95% confidence interval, will be used.

2.13 Impact of oil contamination on plants

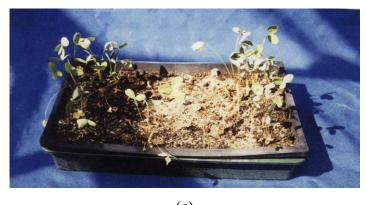
Water and oil do not mix in nature which also applies to soil which uses water for germination of plants. Once diesel spills in the soil, it hinders the growth of plants. Diesel prevents the plants from retaining water adequate for growth. According to Adam (2001) experiments on plants, diesel is harmful to plants as it lowers the rate of water retention in the soil, which is necessary for germination and growth as shown in Figure 2.1. The Figure 2.1 indicates simulated diesel fuel spill on Red clover planted soil, sample of Red clover plants before the spill, directly after the spill and after two months of being cut back .The diesel in the soil kills the moisture in the soil slowly making it difficult for the plant to absorb enough water which is essential for its survival and production of fruits. Therefore, diesel fuel in the land leads to poor plant performance. When the seedlings lack enough water in the soil for growth, they will die which will be evident by the color of their leaves. Healthy plants that receive enough nutrients and moisture from the soil have green leaves or beautiful flowers which are not the same as dying plants which have drying leaves. The dying houseplant eventually dies and can be cut down. Plants can also be revived by removing the harmful components in the soil and giving them enough water and sunlight for photosynthesis before they completely dry up. Using samples of plants the meadow foxtail, and oil-seed to experiment on how diesel affects its growth, the results confirmed that diesel is causes severe harm to the plants. Since the study shows that diesel is harmful to germination of plants, it is evident that it severely kills the control plant, meadow foxtail and the oilseed. Adam (2001) shows the results of the Meadow when exposed to soil contaminated with diesel to be very severe.



(a)



(b)



(c)

Figure 2.1 Simulated diesel fuel spill on Red clover planted soil. (a) sample of Red clover plants before the spill, (b) directly after the spill and (c) after two months of being cut back (Adam, 2001)

The visual circumstance of the plants developed in polluted soil was great, aside from the oil seed rape, whose leaves were very badly change colored. There was no indication of extreme leaf consume, which would demonstrate the plant was happening a portion of the more unstable hydrocarbons. The general state of the plants was great however the extraordinary decrease in plant biomass indicated exactly how severely influenced the plants developed in oil polluted soil truly were. Adam (2001) indicated development in diesel fuel contaminated soil discernibly decreased the generation of top development of each plant screened. Figure 2.2 shows two plant species developed in 0g, 25g and 50g diesel/kg defiled soil for about a month and a half. Oil seed rape was one of the more fruitful plant species picked as its germination rate was 76%, 61% and 48% in 0, 25 and 50g diesel/kg soil individually.

Anyway the germination rate was just reasonably influenced, the pace of development was seriously influenced, as is appeared in Figure 2.2. The Meadow foxtail's germination rate was seriously influenced yet the general plant height was just marginally diminished in the 25g diesel/kg soil treatment contrasted with the control plants. Glade foxtail did not develop well at the larger amount of defilement (50g diesel/kg soil).



(a)



(b)

Figure 2.2 (a) oil seed rape and (b) meadow foxtail plants grown in 0g, 25g and 50g diesel/kg soil for six weeks (Adam, 2001)

Other research by Nwankwo (2014) also explains that diesel and crude oil affects crop production. Studying chemical analysis of the soil is essential as it develops better ways to help farmers on how to recover the contaminated soils to revive it for agricultural use. The investigation by Adam (2001) proved that treating soil polluted by diesel is difficult and it will take more than one year to revive it for growing crops. Crude oil contamination of the soil also affects tomatoes and other plants like onions severely. For further analysis on oil effects on plants, Figures 2.3 and 2.4 will be useful.



Figure 2.3 The controls (no oil) recorded over 80% germination. First tray to the left is soil only and second tray to the right contains 50% compost (Nwankwo, 2014)



Figure 2.4 Test trays containing contaminated soil, the seedlings are struggling. The tray to the left contains 5% oil w/w, the tray to the right contains 7.5% oil w/w and the tray behind contains 10% oil w/w (Nwankwo, 2014)

2.14 Environmental impacts of petroleum refineries

The primary source of environmental pollution in the modern world happens to be oil refineries. This is because they are known for producing a large number of wastes. The wastes are released in water bodies, and by that, petroleum refineries are the primary source of water pollution. Regarding air pollution, petroleum refineries release hazardous carbon dioxide. Apart from polluting water and air, petroleum refineries generate pollutants to the soil, and this may have significant repercussions on the health of living beings. Solids, liquid effluents, and gases are the three states of pollution.

Solid- Petroleum sludge, heavy metals, and toxic organic substances constitute a solid state of pollution. If these substances are released to the environment it leads to the loss of biodiversity.

Gases-many environmental activists have started to set up petroleum refineries. The economic development depends on petroleum refineries. Gases are released to air, water bodies, and soil. Underground aquifer will also be affected negatively when hydrocarbon compounds pass across soil water (Bojes and Pope, 2007). The hydrocarbon compounds in the soil are subjected to the withering process (Lisiecki et al., 2014). Lack of nutrients decreases microbial activities, and unbalanced soil moisture may negatively affect the germination process (Gerhardt et al., 2009). In case of oil spillage during petroleum transportation, it is vital to know that some will float on water bodies and a fraction dissolved into the water bodies such as in lakes, rivers and oceans (Williams et al., 2006).

When discussing about petroleum refineries, it is essential to know that there are many activities that cause the release of petroleum hydrocarbon. Das and Chandran (2011) have marked some of those activities such as oil storage, exploration, production, and transportation. Through the process of biodegradation, petroleum hydrocarbon compounds are attenuated in both sediments and soil (Fathepure, 2014).

2.14.1 Petroleum sludge

It is important to note that petroleum sludge is a generalized term used to define the wastes originating from the storage of petrol. It is a combination of crude oil, solids, and water. Besides, the refining process and processing methods compounds to differentiation of oil sludge chemical composition (Hu et al., 2013). After conducting research, (Tahhan et al., 2011) discovered sludge composition varies from 15 to 50%. Also, petroleum sludge contains metals and petroleum hydrocarbon (Mazlova and Meshcheryakov, 1999). Landfills, Lagoon sludge, and tank bottom sludge are the three classifications of sludge. Since sludge is hazardous to the ecosystem, society has established measures that will protect our environment from degradation. For instance, the 'Environment Protection Act and Hazardous Wastes Handling Rules' advocates for remediation of sludge before it could be released as landfill. The Act cautions against sludge disposal and by that oil companies have a duty of adhering to the requirements of the Act, failure to which they will be subjected to persecution. In 2015, Mansur and his colleagues conducted another research on the composition of petroleum sludge. They found that the disposal of

substances ranges from 5-46%. The percentage of water content ranges from 30-85% (Mansur et al., 2015). In 2003, Ward reported that oil sludge contains up to 75% of compounds. Here, the compounds comprise of Nitrogen, Sulphur, Oxygen, and petroleum hydrocarbon. For the mentioned compounds, there is a chemical formula. However, for compounds such as Asphaltenes, there is lack of compound formula. Asphaltenes, for instance, is formed through a combination of individual compounds- Hydrogen, oxygen, sulphur, and nitrogen. With lack of a compound formula, the physical characteristics differ, and that has been linked to two aspects- density and viscosity (Hu et al., 2013). Petroleum sludge poses a severe threat to our environment. This is because of their poor degradation (Maletic et al., 2013).

2.14.2 Petroleum sludge treatment methods

The principal purpose for incorporating petroleum sludge treatment methods is to separate compounds like Petroleum hydrocarbon from petroleum separate. The treatment methods should connote the requirements of the Environmental Protection Act and Hazardous Wastes Handling Rules. Sludge pyrolysis, ultrasonic radiation, melt treatment, and froth and flotation are some of the crucial methods of treating petroleum sludge (Yan et al., 2012). It is vital to acknowledge the crucial role technology has played in protecting our environment. However, the methods do not solve the problem of disposal of petroleum sludge entirely. They, in turn, minimize the rate at which petroleum sludge is disposed to the environment (Khojasteh et al., 2012).

Establishing safety mechanisms for safe disposal of crude products has remained a crucial challenge the stakeholders in the petroleum sector. Also, pressure from various environmental activists has complicated their quest to integrate safe treatment strategies of petroleum sludge. Safe treatment methods aim to minimize the production of sludge and safe disposal of sludge after manufacture. To promote safety, those in the oil sector have resorted to fitting storage tanks with mixers (Dando and Martin, 2003). Also, consultation is required. Stakeholders in the oil sector, for instance, must resort to doing extensive research regarding sludge treatment. For a specific oil refinery, it is vital to recruit a qualified chemical engineer. The safe treatment and disposal methods can be only be obtained after analyzing the chemical properties of the sludge.

From an economic point of view, understanding the features of petroleum sludge helps an oil company to settle on the appropriate management plan which in turn saves cost suppose an inappropriate waste management plan was integrated initially. Here consultation with other stakeholders such as legislatures and environmental activists is essential. If a petroleum refinery operates in a foreign country, a meeting will help the management to be familiar with the laws of that country as far as ecological conservation is concerned. In that case, the treatment plan will conform to the cleanup standards (Lima et al., 2011). Radhi et al., (2008) asserts the need for management of various oil refineries to consider integrating two safe treatment methods with the chief objective of improvising the result. Also, the strategies will guarantee the recovery of petrol, and from an overall stand, this will bolster the economic state of that particular company. On that front, oil refineries should consider investing more on research that will perfect decisions for selecting petroleum sludge treatment.

2.15 Crude oil spillage onto ground

Since it is a significant pollutant of soil, some institutions in the United States like US-EPA and ASTM have taken the initiative to prevent severe impacts of oil spillage, be it long-term or medium. In recent years, the rate of oil spillage from the negligence of the management of petroleum refineries has been reduced. Still, there has been a prevalence of various diseases like cholera or diarrhea caused by consumption of contaminated. In this regard, several pieces of research have shifted attention to leakages caused by underground storage tanks. Also, Concawe (1979) program has expressed the importance of protecting the vadose zone. The management and maintenance team of a specific oil refinery will not notice a slow leakage and potential dangers can be unknown to them. Besides, to prevent this, the maintenance team needs to resort to doing a frequent checkup on the underground storage tanks. In case of any leakages, the affected tank should be replaced by another which is fault-free.

The models suggested fail short of incorporating early intervention plan after oil spillage on the underground. This is because they lack enough data to echo efforts required in early management planning. In the wake of an oil spillage to the soil, it is vital for the emergency teams to prevent contamination of underground water. In the awareness, the government and private institutions are tasked with the responsibility of avoiding adverse impacts like contamination of underground water, and this can become possible through the implementation of a predictive tool. However, the 2003 survey of Pacific Northwest National Laboratory revealed shocking details. The models were not coupled with a rapid predictive tool (Simmons and Keller, 2003). After an oil spillage, the focus is on specific factors, length of oil retention alongside seepage velocities (Halmemies et al., 2003).

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURES

This chapter present descriptions of the materials used during the experimental study and the procedures followed in performing these experiments. Contaminated and uncontaminated sand mixtures were prepared and used in the experiments. Crude oil was mixed with the sand to get a contaminated soil samples. This study is important to investigate the geotechnical properties of oil contaminated sandy samples with different percentages of crude oil.

3.1 Introduction

This study focuses on the resource of the materials (crude oil, sand and mineral admixtures) as well as the reasons for selecting those materials that were used in this study. Moreover, focuses on the way of preparing test samples as well as methods of different percentages of polluted samples which were mixed and prepared. Furthermore, the reasons for selecting the different percentages of crude oil contamination used in the experiment are also discussed. Besides that, this study defines the various geotechnical characteristics that were tested in this study. Khosravi et al., (2013) stated that directly or indirectly, oil spill pollutions can influence the chemical and physical characteristics of the surrounding sand.

An exploration of sand contaminated with crude oil is significant due to,

- a) Khamehchiyan et al., (2007) have investigated its mechanical characteristics.
- b) It is advantages in ensuring that the soil can be the applied load Khosravi et al., (2013).
- c) Crude oil contamination influence the absorption and permeability properties, and the coefficient of partition of the soil.
- d) In most of the samples, the degree of contamination was different by the soil properties and the general chemical composition of the sampled water, which also varied from place to place.

Nonetheless, there is some extent of inconsistency in most of the findings from different research studies that included the impact of the different factors that is based on the soil properties of the contaminated water and sand including the nature of chemical composition, crude oil, properties of sand, absorption properties and quantity of spillage.

The main objective of this research is to study the influence of oil contamination on the geotechnical properties of sandy soil. Collection and preparation of test samples are also included here.

The following section describes some distinct test programs conducted in this research:

- 1. Compaction test, to study variations of optimum moisture content and dry density of the sand due to oil contamination.
- 2. Direct shear tests to study variations in shear strength parameters (c, ϕ) of the sand due to oil contamination.

3.2 Area of study

In the federal government of Iraq, there are many provinces and districts that have oil production activities such as exploration, drilling of wells, extraction, pumping and transportation of crude oil. Two ways of transportation are used to transfer crude oil from its place to another place. Firstly, a network of pipelines is established from inside country to refineries and industries and to outside of bounder. Secondly, the Tankers are using to transfer crude oils through high ways. Both methods can lead to the pollution of areas closed to the pipeline networks and near to highways.

Oil transportation is the last step preceding the distribution of oil to the market. After oil extraction from below the ground, it needs to be transported to the refinery plant where it will be processed and then later taken to the various market distributors. The refining process produces usable products and they are transported again to the consumer market all over the world. Therefore, oil is transported before and after it is refined.

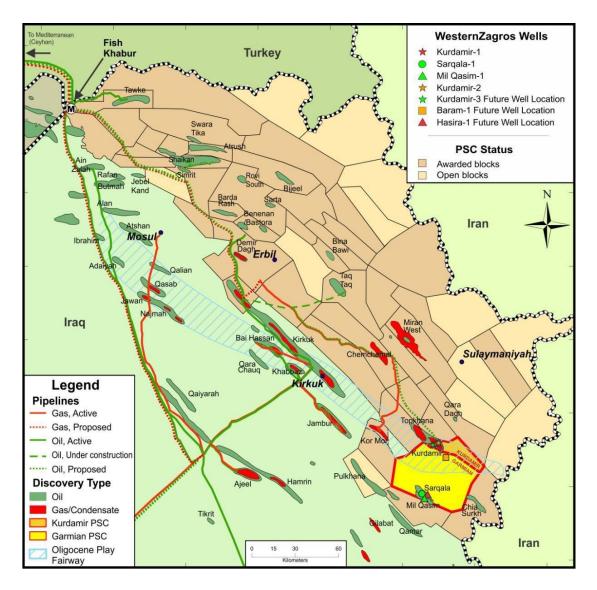
3.2.1 Oilfields

The federal government of Iraq signed a Technical Service Contract (TSC) for the remediation of the country's oil fields. This was done to optimize the production of oil and maximize the revenues obtained from such activities. Figure 3.2 shows the dominance of Iraq in the oil industry with approximately 143 billion barrels of oil which is around 9.5% of the total oil reserves in the world. Moreover, a study done by geologists

revealed that Iraq comes in third place after Saudi Arabia and Iran (Mills, 2016). Table 3.1 shows the various oil fields in the research area.

Field	Oil proved +probable reserves and contingent resources (million bbl)	Gas proved +probable reserves and contingent resources (trillion cubic feet)
Khurmala	2726	3.6
Shaikan	1001	1.3
Atrush	854	0.1
Tawke	731	0.1
TaqTaq	579	0.1
Kurdamir	541	2.3
Sheikh Adi	531	0.4
Pulkhana	409	NA
Topkhana	55	1.7
Chemchemal	110	3.4
Khor Mor	138	4.4
Miran	34	3.5
Bina Bawi	45	4.9
Summail	0	1.4

 Table 3.1 The oil and gas reserves of major fields in KRG (Mills, 2016).



There are many oil and gas fields like underground lakes as shown in Figure 3.1

Figure 3.1 Oil and gas fields and oil pipe lines in Iraq (URL 1)

3.2.2 Transportation of crude oil

3.2.2.1 Transportation of crude oil by pipe line

Unrefined petroleum transportation from the extraction sites to the refinery has caused a lot of environmental and economic concern. Pipelines are used in the transportation of gases, liquids, and any other chemically stable materials that can be moved through a pipeline. Oil in its crude and refined state is transported through a pipeline and the pipelines can be extended so that they are able to carry the substances over a longer distance. They are huge transportation pipes that are underground with a large distribution

network. Their diameter varies depending on their use. Turkey is an oil transit country that deals with the transportation of oil through a pipeline. The Khurmala-Ceyhan pipeline is shown in Figure 3.2.

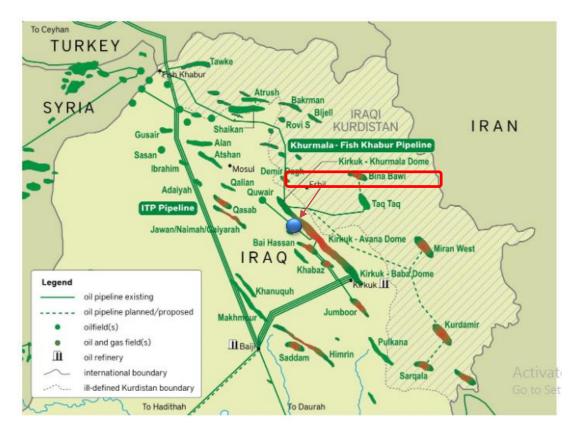


Figure 3.2 Iraq's oil and gas infrastructure (Butt, 2017).

3.2.2.2 Transportation crude oil by oil tankers

Transportations of crude oil by tankers are widely used. Oil transportation in this way includes local transportation and international transportation using high ways. During oil transportation by tanker tracks, several accidents may occur which may result in seepage of oils to the surrounding soils. Today, oil tankers divided into two basic categories, crude oil tankers and oil product tankers. Crude oil tankers are highly used. They transport raw oil from oil wells to the refineries where it's processed into fuel and other products. Oil tankers provide an easy and inexpensive way to transport oil over long distances. In the last ten years, petroleum production processes have been started in Erbil province due to having many activities related to exploration, extraction and producing of crude oil and its derivatives. After that, contamination would take place in land, water and air by crude oil as shown in Figure 3.3.



Figure 3.3 Contaminated soil in study area near refiners.

In this research soil samples were collected in Erbil-Gwer main road. There are many activities of petroleum products across this area. Several refineries are located in western-south of Erbil close to Lajan area as shown in Figure 3.4. There are several storage oil tank, refineries and local industrial available.

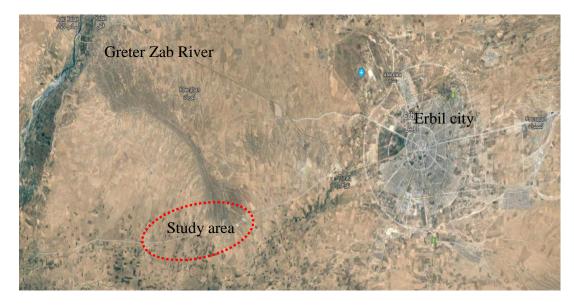


Figure 3.4 Study area in Erbil province (URL 2)

3.3 Materials

3.3.1 Sand

Sand is a granular substance that is made up of finely divided rock and inorganic substances. Soil constitution differs depending on the rocks they were formed from and the climatic conditions of the region. It is a non-renewable resource. The size of sand grains differs in diameter from 0.074mm to 4.75mm. His specification of the particles has never changed for over a century but the Atterberg standard recognizes sand particles with as little as 0.02mm in diameter.

Sand samples were taken from Erbil Province and used in this study. Sand occurs naturally and its components are made up of finely divided mineral and rock particles. It is coarser than silt and finer than gravel and its composition is dependent on conditions surrounding it and the rocks that they came from. The most popular type of sand in the tropical and non-tropical settings is silica in quartz form. The second most common type is Calcium Carbonate (aragonite), which was formed approximately half a billion years ago by organisms such as shellfish and coral.

The particle size distribution analysis of sand were done using a hydrometer and sieve analysis according to (ASTM D422-63 and ASTM D421-58). The grain size distribution curve of the sand is presented in Figure 3.5. The specific gravity (Gs) of the sand sample was 2.619.

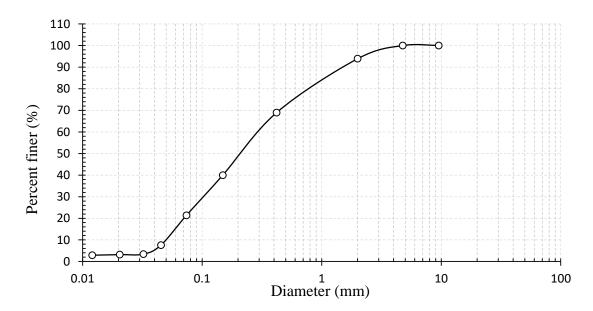


Figure 3.5 Grain size distribution curves of the material used in this study.

3.3.2 Crude oil

Crude oil is naturally occurring liquid phase of petroleum, composed principally of hydrocarbon compounds and is extracted from the earth in the liquid state. Crude oil can be described as paraffin base, naphthenes base or mixed base, depending on the most abundant group of hydrocarbons contained.

The hydrocarbon for this research is a crude oil was brought from Kar refinery in Khurmala oilfield in Erbil province. The properties of the crude oil like flash point, density and API (American Petroleum Institute) at 25 °C and viscosity are shown in Table 3.2.

 Table 3.2 Properties of crude oil.

Sample	Flash Point ^o C	Density @ 25°C(g/cm ³)	⁰ API	Viscosity (Cp)
Kar Refinery	53	0.849	23.261	18.2

Flash Point is the most reduced temperature at which a fluid will shape a vapor noticeable all around close to its surface that will "flash," or briefly ignite, on exposure to an open flame. The flash point is a general sign of the combustibility or flammability of a fluid. Underneath the flash point, deficient vapor is accessible to help ignition. At some temperature over the flash point, the fluid will deliver enough vapor to help ignition. Viscosity is the measure of resistance to flow in crude oils due to internal friction. It is expressed in 'centipoise'.

3.3.3 Fly ash

In thermal power plants, Electrostatic precipitators or other particle filtration are useful in capturing the fly ash during the boiling process. It expelled from the base of the boiler, it is known as coal ash. The fly ash comprises of silicon dioxide (SiO₂), calcium dioxide (CaO), as well as aluminum oxide (Al₂O₃). Fly ash is also significant in cement making industries as it is useful in making cement, concrete blocks, among other building materials. Fly ash mixed with other mineral admixture in different percentage. The developed mixture must possess durability and adequate strength, should be easily compacted, and most importantly should be economical and environmentally friendly. The chemical properties of fly ash used in this study are shown in Table 3.3.

Elements	Concentration
SiO ₂	38.81
Al ₂ O ₃	6.07
CaO	30.17
Fe ₂ O ₃	1.98
MgO	2.66
SO ₃	2.21

Table 3.3 Chemical composition of fly ash.

3.3.4 Ground granulated blast furnace slag (GGBFS)

Ground granulated blast furnace slag (GGBFS) produced by pulverizing granulated blast furnace slag is mixed with flay ash (FA) to improve contaminated soil by crude oil. Slag, which is a residue of different metals, differs according to the elements used in the production procedure. To come up with the best slag product, the company has to use the ore and core residues in the flux to lower the thickness of the metal residue. Granulation process ensures that the slag cools before its temperature rises to 800 degrees. To cool and fragment the slag a granulation process can be applied in which molten slag is subjected to jet streams of water or air under pressure.

The main components of blast furnace slag are SiO_2 , CaO, Al_2O_3 and MgO. In general increasing the CaO content of the slag results in raised slag basicity and an increase in compressive strength. Several compositional ratios or so-called hydraulic indices have been used to correlate slag composition with hydraulic activity; the latter being mostly expressed as the binder compressive strength. The chemical properties of slag are shown in Table 3.4.

Elements	Concentration
SiO ₂	60.69
Al ₂ O ₃	3.01
CaO	5.8
Fe ₂ O ₃	23.94
MgO	0.76
SO ₃	1.56

Table 3.4 Chemical composition of slag.

3.4 Sample preparation

The soil specimens used in this research were collected from the Lajan area, Erbil governorate, Iraq. Sandy soils were taken at a depth of 50cm below the earth surface in a bid to prevent the upper layers from mixing with the samples. Before the laboratory tests were conducted, soil specimens were collected and passed through sieve number four with 4.75 mm diameter. The samples then dried in the oven. After that, crude oil was added to the sample with the following percentages of their dry weight: 2%, 4%, 6%, 8%, 10%, 12%, 14% and 16%. All polluted and non-polluted soil samples are illustrated in Figure 3.6.



(a) Photos show soil sample with 0%, 2% and 4% of crude oil content.



(b) Photos show soil sample with 6%, 8% and 10% of crude oil content.



(c) Photos show soil sample with 12%, 14% and 16% of crude oil content. **Figure 3.6** Sand soil samples with different percentage of crude oil content.

A careful planning of the testing program was divided into several steps as follows.

- a. Collection of disturbed soil samples from the fields and the crude oil from the oilfields.
- b. Preparation of artificially contaminated soil samples at eight different levels by dry weight with crude oil.
- c. Determination of the physical and some chemical properties of soil.
- d. Determination of the physical properties of crude oil.
- e. Determination of the physical and some chemical properties of contaminated soil by different laboratory tests.
- f. Determination of the geotechnical properties of the soil samples.

In this experimental study two groups of specimens were prepared. The first group consists of polluted samples. They were prepared by measuring eight different parts and then mixed with varying percentages of petroleum 2%, 4%, 6%, 8%, 10%, 12%, 14% and 16% by the dry weight of the soil samples (Figure 3.6). Only one part of the sample was left unpolluted and this would act as a control experiment where the impact of oil pollution will be compared and contrasted. The soil samples and oil were mixed by hand and then stored for two weeks in order to be homogenous mixture. The bag helped in preventing evaporation during this period (Figure 3.7).



Figure 3.7 Soil samples in closed containers.

The second group in this investigate consist of a set of mixtures which were prepared by mixing fly ash with ground granulated blast furnace slag and crude oil in unary, binary and ternary conditions with sandy soil to observe the influence of binders at different proportions. The amount of binders and soil replacement conditions illustrated in Table 3.5. It is consist of four percentage of crude oil 0%, 4%, 6% and 8% for each percentage of crude oil three percentage of slag are available 0%, 10% and 15% finally found total binder were mixed with sandy soil to conduct geotechnical test like compaction and Direct shear test.

Mix. No.	Mix Name	Crude oil%	Slag (GGBFS)	Fly ash (FA)	Total binder
Mix 1	C0S0F0	0	0	0	0
Mix 2	C0S0F10	0	0	10	10
Mix 3	C0S0F15	0	0	15	15
Mix 4	C0S10F0	0	10	0	10
Mix 5	C0S10F10	0	10	10	20
Mix 6	C0S10F15	0	10	15	25
Mix 7	C0S15F0	0	15	0	15
Mix 8	C0S15F10	0	15	10	25
Mix 9	C0S15F15	0	15	15	30
Mix 10	C4S0F0	4	0	0	4
Mix 11	C4S0F10	4	0	10	14
Mix 12	C4S0F15	4	0	15	19
Mix 13	C4S10F0	4	10	0	14
Mix 14	C4S10F10	4	10	10	24
Mix 15	C4S10F15	4	10	15	29

Table 3.5 Design of mixtures for all mixes with total binder.

Mix 16	C4S15F0	4	15	0	19
Mix 17	C4S15F10	4	15	10	29
Mix 18	C4S15F15	4	15	15	34
Mix 19	C6S0F0	6	0	0	6
Mix 20	C6S0F10	6	0	10	16
Mix 21	C6S0F15	6	0	15	21
Mix 22	C6S10F0	6	10	0	16
Mix 23	C6S10F10	6	10	10	26
Mix 24	C6S10F15	6	10	15	31
Mix 25	C6S15F0	6	15	0	21
Mix 26	C6S15F10	6	15	10	31
Mix 27	C6S15F15	6	15	15	36
Mix 28	C8S0F0	8	0	0	8
Mix 29	C8S0F10	8	0	10	18
Mix 30	C8S0F15	8	0	15	23
Mix 31	C8S10F0	8	10	0	18
Mix 32	C8S10F10	8	10	10	28
Mix 33	C8S10F15	8	10	15	33
Mix 34	C8S15F0	8	15	0	23
Mix 35	C8S15F10	8	15	10	33
Mix 36	C8S15F15	8	15	15	38

3.5 Some parameters considerable in the study

3.5.1 Utilized crude oil in the study

Different variations of bench mark petroleum are thought to be crude oil. Petroleum has high fluidity, clear and they quickly adhere to surfaces that they come in contact with. This makes it easier for the oil to move into water and soil. Soil pollution by petroleum is one of the most common problems that the ecosystem faces. Petroleum is considered as the most common soil contaminant in Iraq.

3.5.2 The different percentages of crude oil used with small increasing

The given pollution percentages represent points close and away from the pollution source because the concentration of pollution reduces as the horizontal distance increases i.e. 2% is a point away from the source while 16% is closer to the source of the pollutant.

The method of using small increments of crude oil to the sample is to enable us to assess the changes in the geotechnical characteristics as the crude oil contamination differs. The small increments were done so that we can evaluate how small pollutions affect the geotechnical properties of soil. In the event that petroleum pollution is up to 100%, then it would attract a lot of criticism that would lead to the immediate rectification of the polluted soil. This is in contrast to areas where the pollution percentage is small. Nothing will be done to rectify the soil.

Percentages of pollution that were more than 25% were not chosen because this would make the soil too wet for any test to be done on them. The maximum value in the compaction tests of soil specimens with more than 20% of petroleum pollution could not be attained because the sample was too wet. The wetness poses a challenge because the petroleum that is in excess will ooze out of the specimen during the testing period.

Aside from the reasons given for restricting the percentages of the petroleum pollution to 20%, Shroff (1997) argued that the highest percentage of petroleum present in the undisturbed and disturbed polluted soil specimens is within 10% post-pollution. This reason justified the percentage limit of pollution for this study. The primary reason behind the selection of the small increment is that in numerous instances, petroleum pollution within the 16% range will be overlooked. In most cases, petroleum that remains after rectification fall within this range.

3.6 Determination of some physical and chemical properties of soil

The aim of the test program is to determine the effect of different percentages of crude oil contamination on various engineering and chemical properties of soil. Therefore, two series of laboratory tests were conducted.

In the first series of tests, different properties such as specific gravity (Gs), grain size distribution, compaction properties (maximum dry density, optimum moisture content), Direct Shear test parameters such as cohesion (c), angle of friction (ϕ) and chemical properties (pH value) of selected uncontaminated soil samples were determined. The procedures followed the relevant ASTM Standard Codes of practice.

The second series of tests were carried out for contaminated soil. The laboratory tests performed to determine physical and chemical properties of soil samples at 0% contamination and contaminated soils as shown in tables in chapter 6.

3.7 Test program for basic properties of soil

3.7.1 Grain size distribution

Grain size and shape are the most fundamental physical properties of soil from permeability stand point. Information on grain size is utilized by civil engineers, hydrologists, petroleum geologist, and engineering geologist to estimate important physical properties. Information on sediment grain size can be used to study trends in surface processes related to the dynamic conditions of transportation and deposition; engineers use grain size for engineering classification of soil, and estimating its permeability, compressibility and strength; hydrologists use it to study the movement of subsurface fluids.

The percentages of various sizes of particles in a given dry soil sample are obtained by dry sieve analysis and sedimentation analysis or wet analysis. samples of sand that were collected from representative zones were air dried to a constant weight and adequate quantities, performing grain size analysis by using the standard procedure of the American Society for Testing and Materials (ASTM), D421–85 and (ASTM), D 422-02. In dry sieve analysis, particle sizes up to 0.075 mm can be determined by arranging sieves of different sizes in descending order of magnitude and shaking the sieve set for at least 10 minutes in a sieve shaker. For determination of particle sizes smaller than 0.075 mm, wet analysis i.e. hydrometer method was used. Combining the results of dry and wet analysis, particle size distribution curve is plotted on a semi-log graph paper and percentages of different sized particles are determined. On the basis of the test result for uncontaminated (0% contamination) soil have been classified as silty sand.

3.7.2 Specific gravity

This is the ratio of a unit weight of a specified volume of soil solids at a certain temperature to the weight of the same volume of pure water at the same temperature and both weights being measured in air. Soil's specific gravity is often required for several calculations in soil mechanics. This can be done in the laboratory. Specific gravity affects the consolidation and compaction characteristics of soil. According to ASTM D854 the first step for measuring the specific gravity of soil is to offload it into a pycnometer that is filled with water and air bubbles have been thoroughly removed from it. The next step is to evaluate the mass of the apparatus when it has water in it and then the temperature of the mixture is measured. Knowledge of the mixture's temperature and the filled pycnometer's mass can be observed from the register on the apparatus. The assessment of the mentioned samples gives us the specific gravity of all of the soil samples collected.

3.7.3 pH value

The pH value of soil is an important chemical property. pH is used to ascertain the acidic or basic character of soils. The engineering properties of soil are sensitive to the nature and amount of dissolved electrolyte in the pore fluid. The pH value was determined by taking 1: 1 soil and distilled water mixture with the help of Systronics digital pH meter - 335.

3.8 Test program for geotechnical properties of soil

3.8.1 Compaction test

Compaction is a process where soil is made dense by air removal or a process where stress is applied to soil and increases the soil's density since the air between its pores will be displaced. The main purpose for this test is to enhance the geotechnical properties of soil. The level of compaction is calculated in terms of a soil's dry weight. Upon the addition of water to the soil during the compaction process, the soil particles become softer. They overlap each other and maintain a densely packed position. Post-compaction, the dry unit weight initially increases as the moisture content is increased. The maximum dry density (y_d max) and maximum moisture content are well known compaction properties of soil. Compaction characteristics are decided by a Proctor test. This test was developed in 1993 by Proctor and it was associated with the building of the earth fill dams in California (Shaheen, 2011). It evaluates and decides the maximum amount of water to be added to the soil in order to achieve optimum compaction for any soil sample. The accepted sizes of the apparatus utilized in this test were based on ASTM D-1557 using Method-A. The water content was combined with the soil and thereafter, the mixture was placed in a compaction mold with a volume of 0.0009438 m³. It was compacted in five layers and each layer received 25 blows with a 44.5N hammer dropped from a height of 457mm which is illustrated in Figure 3.8. The wet unit weight of compaction was calculated as weight of the compacted soil over volume of the mold.

The dry unit weight gotten from this test was achieved by taking a portion of the compacted sand and heating it in the oven for a day. Since the moisture content was already standardized, the dry unit weight of the soil that was measured by the process was redone for different water content. The resulting data was plotted on a graph and the compaction curve determined the maximum water content and optimum dry unit weight. This was done for the polluted and non-polluted samples of sandy soil.



Figure 3.8 Compaction machine used in the study MATEST type.

3.8.2 Direct shear test

The best method to measure the shear strength of soil is the direct shear test. The shear strength of land is an essential property since it controls the bearing capacity of the foundation system of a structure. Study shows that shear strength of the soil sample can be determined by applying the direct shear apparatus mostly done in engineering laboratories. The ShearTrac-II Direct Shear apparatus machine utilized to measure the horizontal and vertical displacements, as well as the strength of the shear force in the Hawler construction laboratory as shown in Figure 3.9. The experiment was carried according to ASTM D-3080 standard specifications.

The specimens were prepared by compaction in the direct shear mold. The sandy soil samples were added in 3 layers and each layer was compressed using a compaction tool. The compaction was conducted in circular mold with 63mm in diameter and 25.4mm in

height. The sandy soil samples were sieved on a no. 4 sieve (4.75mm). The specimens were prepared at the particular maximum dry density and optimum moisture content obtained from the compaction curves of each ratio of crude oil content for the soil samples. After the compaction, the specimens were transformed into direct shear cells in the constant rate 0.2mm/min.

Direct shear tests were performed to determine the drained shear strength parameters apparent cohesion and angle of internal friction on uncontaminated and contaminated mixtures using three matching samples for each test. The normal stresses used in the three samples were $100kN/m^2$, $200kN/m^2$ and $300kN/m^2$ for three samples in each test. The relations between the normal stress and shear stress were drawn for soil samples mixtures by passing the best-fit line among the three points for each test. The slope of the fit line gives the effective angle of internal friction (φ), whereas its intersection with the y-axis gives the effective apparent cohesion for this mixture.

This test was repeated for the nine soil samples separately with different percentages of crude oil of 0%, 2% 4%, 6% 8%, 10%, 12%, 14% and 16% by the dry weight of the soil samples.

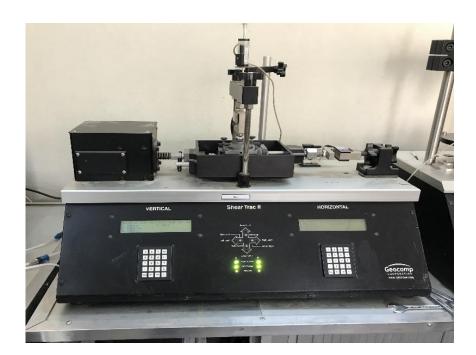


Figure 3.9 Direct shear apparatus system (ShearTrac-II from Geocomp Corporation).

3.9 Environmental pollution in Erbil province

The Erbil province is 414 meters above the sea level with coordinates on longitude 43° 15' E and latitude 35° 11' N to 37° 24 N' (WFP, 2002). Erbil soils are high in magnesium and calcium, which are components that eliminate acidity in the ground. The soil originates from dolomite and has excessive amounts of lime in different proportions. Erbil's has calcareous topsoil with a 1-2% organic matter, which can either be silt, sand, or clay (FAO, 2001). Erbil's climate is characterized by cold winters, mild-growing periods in spring and hot summers (Khudhur and Khudhur, 2015). Erbil's population is over two million people. The region experiences different types of weather, including high-pressure belts, southerly winds, and hot summers, among others. The winds in the Erbil province are strong enough to carry sand which result in high temperatures of over 40 °C during the summer season. The changes in weather patterns imply that the region can grow plants. See Figure 3.10.

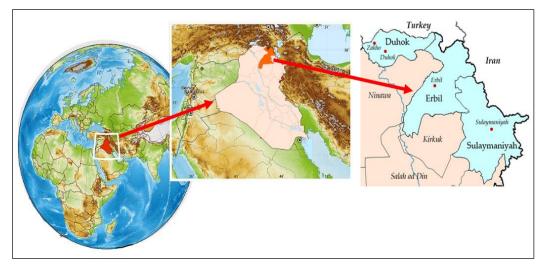


Figure 3.10 Erbil's map with respect to Iraq and world's map.

The site location has a significant effect on the amount of rainfall, precipitation increase from the southwest to the northeast. The climatic condition is important for polluted site, because the wind direction and wind speed have a considerable role to generate storms at these sites. Also the rate of the rainfall is one of the most important factor that runoff on the surface of waste disposal sites which seeping as a leachate through it according to the rate of precipitation, finally contact with the groundwater as a contaminant material.

No.	Sample location	Latitude	Longitude	Notes
1	Soil sample 1	36.196049	43.892063	pit 1
2	Soil sample 2	36.195699	43.895470	pit 2
3	Soil sample 3	36.192185	43.893736	Surface soil
4	Soil sample 4	36.190066	43.891925	Surface soil
5	Soil sample 5	36.189046	43.891448	Surface soil
6	Soil sample 6	36.187100	43.888232	Surface soil
7	Soil sample 7	36.187796	43.883723	Surface soil
8	Soil sample 8	36.316394	43.746598	Kawrgosk soil
9	Soil sample 9	36.319018	43.735377	Kawrgosk soil
10	Soil sample 10	36.180895	43.885962	Control sample

Table 3.6 The coordinates of the locations for soil samples.

In present study, ten sites were selected for soil polluted samples on the basis of the availability of crude oil, oil derivatives and refiner's wastes there as shown in Figures 3.11 and 3.12. The coordinates of the locations were taken by GPS (GARMIN) with accuracy of 5m (see Table 3.6). Two soil samples were taken in pits (soil samples 1 and 2) and one sample as control was taken in unpolluted area.



Figure 3.11 Oil storage tanks in study area, Erbil Provence.



Figure 3.12 refiners and oil storage tanks in study area, Erbil Provence.

3.10 Experimental work and sample preparation

3.10.1 Soil sampling

Since soil contamination is the main topic of discussion, soil sampling sites in Erbil are chosen in line with the how densely polluted the region is toxified by human activities. Using samples of 1kg soil from a sampling point ranging between diverse lengths of the specimen,

by used stainless steel analyst to determine the level of chemical and physical pollutants the ground. The collection of soil samples along the road was carried out at almost five-meter distance around the location of collecting the soil samples. In this research, three samples were collected from three different points. The three soil samples were then mixed in one container, dried, sieved, and later labeled for further analysis and identification.

3.10.2 Soil laboratory analysis

i. Soil pH and electrical conductivity (EC)

The pH and EC were determined for soil samples at the laboratory in Erbil city. To measure the pH exactly, 5g of 2 mm sieved air-dry soil was put in centrifuge tubes and suspended in 12.5 ml of distilled water (suspensions 1:2.5 ratio). The suspension was shaken on orbital shaker model SLM-INC-OS-16 at 40 rpm for 30 minutes to equilibrate and the pH was measured on the resulting slurry. The pH and EC were measured using a Hanna pH-209 portable pH meter and a combined glass electrode (Ag/AgCl; PHE 1004), allowing 5 minutes for the reading to stabilize.

ii. Soil organic matter

The standard method for measuring organic matter was used to measure the percentage of organic carbon in the samples. A known weight of <2mm oven-dried soil in a weighted silica crucible was placed in muffle furnace (Gallenkamp size 3, Weiss-Gallenkamp, UK) for overnight at 550oC to ignite organic matter. The crucibles and soil were then placed in desiccators to cool without gaining moisture from the atmosphere.

iii. Available phosphorous

Available phosphorous was determined using Olsen procedure.

iv. Soil analysis for total elemental (Sodium, Potassium, Calcium, Magnesium) concentrations:

Approximately, 250 mg of finely ground soil was digested using 70 % hydrofluoric acid, nitric acid and perchloric acid (Trace Element Grade (TEG); Fisher Scientific, UK) in a tefloncoated graphite block digestor (Analysco, UK) containing places for 48 PFA digestion vessels.

The digested samples were diluted to 50 m.l⁻¹ using Milli-Q water (18.3 M Ω cm) and stored unrefrigerated in universal sample bottles (5% HNO₃) pending elemental analysis. All digests

were diluted to 1 in 10 with Milli-Q water using a compudil–D auto diluter (Hook and Tucker Instruments) immediately prior to analysis.

Multi-element analysis was undertaken by ICP-MS (Inductive Coupled Plasma Mass Spectrophotometer) (Model X-SeriesII, Thermo-Fisher Scientific, Bremen, Germany) in 'collision cell mode'(7% hydrogen in helium) to reduce polyatomic interferences. Samples were introduced from an autosampler (Cetac ASX-520 with 4 x 60-place sample racks) through a concentric glass venturi nebuliser (Thermo-Fisher Scientific; 1 ml.min⁻¹).

3.10.3 Water sampling

Nine sites of polluted water samples were taken on the basis of the availability of crude oil, oil derivatives and refiners wastes there as shown in Figure 3.13. The coordinates of the locations were taken by GPS (GARMIN) with accuracy of 5m. See Table 3.7.



Figure 3.13 Polluted surface water and soil with petroleum in study area.

No.	Sample location	Latitude	Longitude	Note
1	Water sample 1	36.190074	43.881214	pond
2	Water sample 2	36.189222	43.881250	pond
3	Water sample 3	36.190308	43.892289	flow water
4	Water sample 4	36.187549	43.889497	flow water
5	Water sample 5	36.181768	43.886511	flow water
6	Water sample 6	36.178786	43.884931	flow water
7	Water sample 7	36.192323	43.893896	flow water
8	Water sample 8	36.319059	43.732511	Kawrgosk water
9	Water sample 9	36.312468	43.725177	Kawrgosk water

Table 3.7 The coordinates of the locations for water samples.

Water samples were taken with a polythene bucket, all sample containers and laboratory glasses used in analytical processes were washed with hot water and soaked with 10% HCl solution followed by twice rinsing with distilled water, samples were transferred in a cool box when the temperature was more than 25 0 C and transferred to the laboratory as soon as possible (Smith, 1997). Water samples were transported to the laboratory for analysis of some parameters. The samples were acidified with 1:1HNO₃/D.W for heavy metals detection to minimize the precipitation and adsorption to the container wall were acidified with concentration HNO₃ to bring pH < 2, and stored in refrigerators for later determination (APHA, 2005). Figure 4.7 show water samples location and Figures 3.14 and 3.15 show some of water sampling sites.



Figure 3.14 Water sampling site from polluted area by oil in pond.



Figure 3.15 Water sampling from flow surface polluted water.

3.10.4 Field measurements for water sample

Measuring different levels of water samples after collecting the specimens is the first step in this study. Field investigating is essential to test temperature of water, electrical conductivity through metals, turbidity, as well as concentration of ion pH. Measuring the above components will be done in accordance to the specimen collection process described above. Using the GPS and the personal navigator, the researcher in the study will find the locations of getting the soil samples (GARMIN eTrex H model). Given the fact that most studies examine their samples in laboratories, it is evident that most accurate results from experiments are from field work immediately after sampling (Bartram and Balance, 1996).

i. Coordinates for each sample

The coordinates of the locations were taken by using Geographical Position System (GPS) model (GARMIN) eTrex 10 GPS 2.2-inch TFT according to (APHA, 2005).

ii. Water temperature (°C)

Water temperature were measured by using a clean mercury thermometer with scale marked from (0 to 100 °C) graduated up to 0.1 °C. Water temperature was measured by immersing the thermometer in the water for a few minutes to obtain a constant reading. The thermometer was rinsed with distilled water after every use (APHA, 2005).

iii. Turbidity

Clean water is very transparent due to its colorless color as one can see through to the other side. Dirty or contaminated water reduces the transparency of the water as it changes the color from colorless another color. Turbidity is the using of a turbidity meter to measure the clarity of the water. HANNA instrument model labeled HI 93703 explains that the dirtier the water, the higher its turbidity. The turbidity of water in this study was measured in the ground which was the plan for the experiment. The meter that measures transparency of water uses a standard buffer solution to determine the results which are expressed as NTU.

iv. pH

The hydrogen ion (pH) potential of the water samples was measured directly in the field by using portable pH-meter (HANNA instrument-209 pH meter) which has been calibrated before use by standard buffers as describe by (APHA, 2005).

v. Electrical conductivity (EC)

Electrical Conductivity (EC) of water was recorded by using a portable EC-meter (HANNA instrument model HI 8733) directly in the field as mentioned in (APHA, 2005). Before each sampling, the calibration of the instrument was done by specific standard solutions (0.1N KCl) given by the manufacturing company. Final results corrected at $(25C^{\circ})$ and expressed in (μ S.cm-1).

3.10.5 Laboratory measurements for water sample

From the time of collecting samples to the time of analyzing them, the samples can be infected through chemicals, physical, and biological procedures. The challenge of preservation must be addressed as the scientist must use the appropriate method of conservation to preserve the samples in this case. The utilization of suitable additive techniques will minimize or prevent the impact of physical, chemical and biological processes (EPA, 2000). Before transporting the samples to the lab, it must be filtered and added drops of HNO₃ to the specimens which will be in bottles. The water samples in the bottles are then to be stored in the dark as well as cold place, especially a freezer of about 4°C in temperature ready for transportation to the laboratory for the test and evaluation. The addition of HNO₃ to the water samples was to ensure that metal concentrations do not change before the experiment. Storing the specimens in high temperature containers was risky as it would destroy the samples metal concentrations through precipitation or absorption of water from container walls. Keeping the sample in the same temperature it was found is imperative during testing to get the reliable results. Furthermore, acidification helps in maintaining the specimens in the same manner without degrading or altering the bacterial contents.

Determination of biochemical oxygen demand concentration (BOD₅) in mg.l⁻¹:

The main principle underlying the determination of (BOD₅) is the measurement of oxygen content before and after incubation for five days (20 °C) as described in (APHA, 2005).

i. Total hardness (TH) in (mg. CaCO₃.l⁻¹⁾

EDTA– titrimetric method was used for the determination of total hardness as described by (APHA, 2005). The titration was carried out against 0.01M EDTA (di-sodium salt) solution using buffer solution of pH 10 and Eriochrom Black –T indicator.

ii. Nitrate nitrogen (NO₃⁻) in mg at N-NO₃.l⁻¹:

The concentration of nitrate nitrogen was determined on the bases of ultraviolet spectrophotometer screening method as described by (APHA, 2005).

iii. Chloride (Cl-)

In the present work, argentometric method (Mohor Method) was used for the determination of chloride content in the water samples. Silver nitrate solution (AgNO₃) as a titrant and potassium chromate (K_2CrO_4) as an indicator were used.

CHAPTER 4

ENVIRONMENTAL IMPACT FOR POLLUTED AREA

4.1 Introduction of soil pollution

The contamination of soil can be defined as the existence of granules and toxic chemicals (contaminants) in the soil, in high quantities, which can create a threat to the human health and ecosystem. In some cases, there are cases of contaminants naturally occurring in the soil, and may not be large amounts of hazardous, soil pollution is still occurring when the amount and amount of pollution in the soil exceeds the normal proportion where it should be present naturally.

Pollution of our environment results from harmful substances, chemicals and impurities. Environmental pollution is a serious recent problem that encounters our world. Pollution is increasing over time because of the industrial revolution of the universe, which causes serious damage and significant loss of land (Gray, 2008). Soil contains a variety of naturally occurring compounds, it could be polluted by anthropogenic activity or natural resources. Soil pollutants include inorganic materials, minerals and salts (e.g. nitrates, phosphates, carbonates and sulphate) as well as several organic compounds.

4.1.1 Soil contamination by crude oil

Soil contamination by crude oil or distillate oil products in oil plant areas, such as petrol, diesel fuel, jet fuel, kerosene, hydraulic and lubricating oils. In the industrial pollution, which leads to contamination of soil, air, and water sources. Oil pollution may involve a variety of quantities, ranging from one or more gallons of oil to millions or even hundreds of millions of gallons that seep out of facilities and networks and when transported by oil-loaded vehicles.

Hence, Odewumi (1987) defined pollution as the presence of foreign substances in large quantities. This can be in solid, liquid or gaseous forms. Therefore, pollution of the environment was by crude oil as a source of oil polluted area. Studies estimate that 80% of the oil pollution was caused by spills (Odu, 1977). Science depends mainly and daily

on oil and its derivatives in order to meet the needs of humanity. The science and modern technology depends on the exploration, distribution, and the use of crude oil with hundreds of products derived from them. Oil is used as one of the most important energy resources for the economy of countries in the world.

Because of the technological and industrial development in recent years, the amount of crude oil used has increased dramatically. Accordingly, ecosystem pollution has been increased substantially. Oil refineries and oilfield plays an important role on environmental pollution. Air pollution is often caused by the burning of petroleum products. Other factors such as leaks, spills and the spin-offs of crude oil have severely affected on land and water resources.

Oilfield areas are always exposed to a large number of liquid wastes rich in crude oil and this leads to land degradation is a common phenomenon as well as the health of the people of the region and the environment. During various uses of petroleum (benzene, diesel, kerosene, etc.), the area may be affected where spills, industrial areas, garages and other places cannot be avoided. On the other hand, much of it may flow into neighboring areas. In this regard, preserving the environment is the main objective of society, especially as a result of dealing with crude oil and its derivatives (Rodriguez et al., 2009). As a result, there are significant and negative impacts on soil as a result of oil production, driving, transport, storage and treatment. The properties of all types of oil are very high in dispersion. Once a leak occurs, the oil may spread horizontally, vertically and in all directions depending on the conditions, soil type, humidity and temperature as shown in Figure 4.1. The process of removing the volatile light fraction is easily demonstrated by evaporation and other physical processes, but heavy components such as aromatics - simple, polygonal, human etc. remain in the soil and co-ordinate the particles and pores of the soil for a very long time unless the soil decomposes microorganisms.

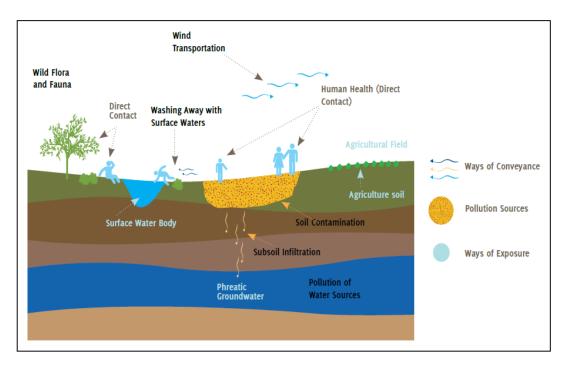


Figure 4.1 Oil pollution by vertical and horizontal spread (Calle, 2013)

There are global environmental guidelines and regulations on oil pollution and their treatment, although these standards have exceeded acceptable limits of the amount of hydrocarbons. However, according to the current sustainable development requirements, it is necessary to introduce the basis and environmental controls for oil exploitation, whose main objective is to analyze and minimize the effects of traditional activities associated with oil and its derivatives. The main objective is to establish the foundations and environmental determinants for the purpose of establishing modern and sophisticated technology to contribute to the active, sustainable and responsible development of the country. The polluting oil causes its harmful effects at first and even before it decomposes into harmless simple compounds. Its effects will increase over time as well as with the type of decomposition mechanism, which can accelerate biological treatment and how soil parameters are affected by oil pollutants and their degradation. This study aims to achieve the current and then to acquire some factual information on this issue based on the experimental results.

4.1.2 Crude oil

Crude oil is a complicated mixture of hydrocarbons corresponding with other organic substances in small, minute and non-hydrocarbon quantities, which contain compounds containing sulfur, oxygen, nitrogen and less amounts of minerals, which is about 5% (Haidari and Al-Muslih, 1989). The crude oil consist of hydrocarbons and hydrocarbon

means organic compounds, which contain only carbon and hydrogen (Patel and Shah, 2012). To better understanding of composition of crude oil and its components by using this definition, four classes of hydrocarbon are included:

- Alkanes are chemical compounds, composed exclusively of hydrogen and carbon atoms and are only linked to single bonds (i.e. saturated compounds) without any cycles. The alkanes include a homogeneous series of organic compounds, see Figure 4.2.
- Alkene is an unsaturated chemical compound containing at least one carbon-carbon bond. One of the simplest types of ring alkenes, with only one double bond and no other functional groups can also be defined as olefin, the main formula C_nH_{2n}. The simplest alkene is ethylene (C₂H₄).
- Alkynes are hydrocarbons and consist of a triple bond between two carbon atoms, acetylenes are known name of Alkynes, in addition, and the name acetylene also refers to with the formula CnH₂n-₂.
- 4) Aromatic Hydrocarbon with alternating double and single bonds between carbon atoms are known as Aromatic hydrocarbon. The arrangement of six carbon atoms in aromatic compounds is recognized as a benzene ring, after the simplest possible such hydrocarbon, benzene.

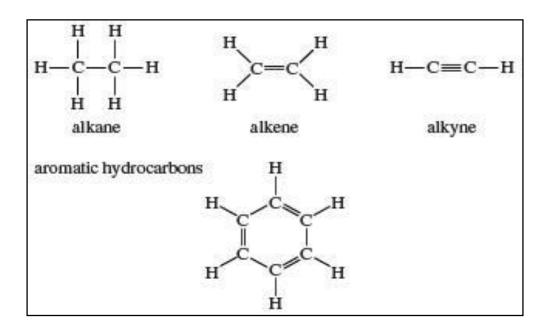


Figure 4.2 Structures of representative hydrocarbons in crude oil (Patel and Shah, 2012)

Oil spills can be considered as a major threat to the environment as they significantly harm the surrounding ecosystems. Since the weight of the oil is lighter than the weight of the water, it floats on the water surface and results in a swift-spreading fire. As a result of leakage from terrestrial pipelines oil spills can also happen. Oil spills on land pose a three threats (Patel and Shah, 2012).

- i. Fire impact hazards
- ii. Groundwater impact by pollution due to percolation
- iii. Air pollution due to evaporation and firing

More often, oil leaks into the ecosystem through leaks in oil refinery accessories. This fact has increased the concerns of scientists to investigate the better distribution of oil and its effects and its fate in the environment.

4.1.3 Sources of soil pollution

Soil pollution by crude oil is a complex process and is generally reflected in the pH of the porous liquid, the soil temperature and the ionic characteristics of solution. According to Eze (2010) the major pollution sources which cause ground or soil pollution of petroleum in the environment include:

- 1. Oil fields
- 2. Pipeline spills
- 3. Natural oil seep
- 4. Refiners and storage tankers
- 5. Industry, power generation
- 6. Accident by oil tankers
- 7. Petroleum exploration and development, Eze, (2010).

Pollutions have indirect and direct impacts on the different soil characteristics, because of the exchange processes between inorganic and organic substances. Interactions between soil and contaminants lead to modify soil behaviors and can also lead to partial or total freezing of contaminants. The effective particle size, specific gravity, index properties (e.g. shrinkage limit, liquid limit and plastic limit) compaction characteristics, hydraulic conductivity, consolidation, and shear strength parameters of soil are modified or influenced by the above interaction. Many engineering problems could be caused by modification of different soil properties. Example of problems are ground subsidence, landslides, erosion and progressive failure, and settlement, structural stability of sub structures, corrosion and durability of foundation problems. Due to the mentioned problems, it is substantial to study the mechanisms that control the soil behavior as well as the effect of soil – pollutant reactions on the different engineering properties of soil.

The pollutant parameters which could affect the soil – pollutant interactions are:

a.characteristics of pollutants

b.pH

c.temperature

d. retention of pollutants

e. Viscosity of solution

Characterization and determination of the ground and surface soil at the site is considered one of the prerequisites for more complete understanding of the soil – pollutant interaction, in the environment. Fang and Kim (2006) has proposed (a) Visual identification of contaminated soils, wherein, emphasis is on observing special items such as: characteristics of site, ground soil or water characteristics, river and stream condition; (b) Colour of the ground soil and the color of the water and linking the soil colour with soil characteristics; (c) Odours in the environment; (d) Cracking patterns of ground soil. The size of soil particles is one of the primary elements for grouping of polluted soil. The kind and strength of connection among soil and pore liquid rely upon the compound arrangement and physico – chemical properties of the molecule surfaces. The soil sensitivity to the environment relies upon the nearby condition, yet in addition, is impacted by a normally mineral structure, for example, bonding patterns between particles, ion exchange capacity.

4.2 Soil – water interaction

Soil can be impacted by water in two different ways: (i) the manner by which soil particles combine in order to construct mineral skeleton – exchange of chemical and (ii) influencing the size of powers transmitting through mineral skeleton – physical interaction. Surface tension is particularly impacts the behaviour. Water is characterized by high surface tension, contrasted with that of different fluids. Water moves and held in soil is determined by surface tension, which again can create changes in soil properties. Moreover, the existence of ions and solutes can adjust the surface tension relying upon relative sizes of proclivity of solutes to water atoms, as on account of natural solutes and cleansers. Likewise, soil – water exchange and the behaviour of the soil need the connate

change from physical to changed state to be clarified. The transport and transformation phases in the saturated and unsaturated state are principally attribute to the changes in soil characteristics. The transformation and transport of toxins in soil are basically due to the physico – substance components, to be specific, scattering and bio – change.

4.3 Environmental impacts of crude oil on the soil

Oil spillage can cause pollution in soil and water in which it has significant effects on ecosystem. It has been remarkably spread all around the spilt land. As per (Wentz, 1995; Kiely, 1996) a portion of the crude oil composition can be considered as a dangerous substances to nature. Therefore, some materials that produce from the oil production can be considered as unsafe waste on the environment and human health. In any case, the classification of the impact of crude oil on the soil:

- (a) Biological impact
- (b) Impact of agricultural production and
- (c) The impact of oil on soil geotechnical properties.

(a) Biological impact

The main risk of oil generally indicates to its toxicity and compounds that do not break up or degrade steadily. Some of them are moved in the natural food chain order and accumulates in living organisms while others are very complicated and not easily moved and have low toxicity. While, the existence of oil on the surface influences the water absorption and germination by plant. Many chemical compounds utilized in the oil industry like the additives in the drilling procedure, improvement the oil and that utilized in the evacuation of fat and dangerous lichens, growths, etc. The direction of oil compound movement must be traced because most of their compound have hurtful impacts and negative effect on the ecosystem, essentially on agricultural production.

Crude oil and the going with materials contain a lot of salt, for example, calcium chloride and sodium chloride also with added to the materials that are included during drilling activities. These salts can pollute the soils because of spillage or pipelines broken. The soil waste coming about because of drilling activities may pollute the ecosystem while contain heavy metals. The heavy metals are not soluble by nature and can transport to a long place by water. The heavy metals are unsafe to people through drinking water or food, and their impact can be a combined and dangerous (Al-Khafaji, 1994; Al-Omar, 2001; Kiely, 1996).

(b) Effect on the soil properties related to agricultural production

The impacts of the hydrocarbons on soil properties and plant growth can be recognized as (Al-Khafaji et al., 1985).

- i. High rates of hydrocarbon gases and CO₂ resulting in absence of oxygen in soil.ii. Heavy hydrocarbon can block soil pores. Consequently, it causes reduce the water hydraulics and permeability.
- iii. Depredating soil structure and reducing water holding capacity.
- iv. Reduction of nutrients that should be used by plants because of pH variation and element competition.

Al-Azaawi (2000) conducted an experiment on soil in Iraq that polluted by gas oil and kerosene (5% contamination). The outcomes demonstrated that these two materials have adversely influenced the production of yellow corn. It was discovered that the expanding of the production is identified with the decomposition rate of the oil products, and reduce of the infiltration rate to reduce of the contamination fixation. In the interim, there were no variety in the pH and electrical conductivity of polluted soils. Many researchers deals with impact of crude oil and hydrocarbon petroleum contamination on oil pollution. (Patel and Shah, 2012) showed that hydrocarbon petroleum contamination effects on soil pollution:

- Reduced soil fertility
- Reduced nitrogen fixation
- Increased edibility
- larger loss of soil and nutrients
- Deposition of silt in tanks and reservoirs
- Reduced crop yield
- Imbalance in soil fauna and flora
- Pollution of drinking water sources due to underground water pollution due to hydrocarbon contamination

- Soil that has been contaminated should no longer be used to grow food, because the chemicals can leech into the food and harm people who eat it.
- Pollution runs off into rivers and kills the fish, plants and other aquatic life
- May create toxic dusts

Natural cleaning of petroleum in water, particularly light oils, occurs through evaporation, photo-oxidation and microbial degradation. The cost implication of cleaning oil spills is enormous and all levels of society should work together in the fight against petroleum pollution. Government can enact more stringent regulations with respect to oil production and transportation and enforce them more rigorously. This they can do by working together with industries to ensure the integrity of the pipeline system as well as that of transportation vessels. Table 4.1 shows twelve worst oil spills since modern compilation began in 1967.

No.	Name	Location	Quantity Spilled (in millions of Gallons)	Date
1	Arabian Gulf	Persian Gulf, Kuwait	520	January 19, 1991
2	Mexican Gulf	Mexico	177	2001
3	Ixtoc 1	Bay of Campeche, Maxico	140	June 3, 1979
4	Atlantic Empress	Off Tobago	90	July 19, 1979
5	Kolva River	Kolva River tributary, Russia	84	September 8, 1994
6	Nowruz Oil Field	Persian Gulf, Iran	80	February 10, 1983
7	Castillo de Bellver	Off Saldanha Bay, South Africa	79	August 6, 1983
8	Amoco Cadiz	Portsall, France	69	March 1, 1978
9	ABT Summer	Off Angola	51-81	May 28, 1991
10	Haven	Genoa, Italy	45	April 11, 1991
11	Odyssey	OffNova Scotia, Canada	41	November 10, 1988
12	Prestige	OffSpain	20	November 13, 2002

Table 4.1 Twelve worst oil spills by volume (Eze, 2010)

4.4 Introduction of water pollution

Oil spills, dumping and oil runoffs are directly effect on water contamination. A severe issue of oil spill comes from a tanker in light of the fact that there is such an enormous amount of oil being spilt into surface water and rivers. Oil can't break up in water and structures a thick muck in the water. For different purposes, water is utilized in oil refineries (Anze et al., 2010).

Recently, one of the most environmental problem is water pollution. Water can be contaminated when it gets changed in its quality either by human and natural actions. Goel (2009) studied that polluted water less appropriate for domestic, drinking, residential, agriculture, mechanical, recreational, untamed life and different uses for which it would have been generally reasonable in its regular or unmodified state. Net contamination of water has its birthplace fundamentally in urbanization, industrialization, agribusiness and increment in human populace being watched (Calhoun, 2005; Goel, 2009). The contamination of water threatens our life and environment and therefore all need to use an expanding array of techniques for its prevention, assessment, and remediation (Calhoun, 2005).

Harmfulness of unrefined or crude oil to a great extent relies upon the concentration of oil in water, scattered into the water at low rate, it is almost no issue and will rapidly get separated. At higher concentration, it is poisonous to most living things and gliding on the outside of water, it will physically smoother on all that it contacts. Most of most kinds of oil will drift on water surface when spilled, however some will break down into water and with the assistance of wave activity, some will be scattered into little beads.

4.5 Soil pollution impact on human health and planting

Soils are presently perceived as affecting human health in various ways. This incorporates positive impacts, for example, the supply of fundamental supplements to create nutritious sustenance items for the human eating routine, purification services of water, and a wellspring of prescriptions, particularly anti-infection agents or antibiotics. In any case, soil can likewise adversely impact human wellbeing because of introduction to dangerous substances and pathogens inside the soil. Soils are not regularly perceived in the writing as impacting human wellbeing through their creation of items, for example, wood (for timber or lumber) and clay (utilized for brick) that are essential in the development of building construction that give shelter from severe climate, fibers, like, cotton that give

garments to body temperature guideline, and fuel sources, such as, wood that give heat. Soil degradation reduce the capacity of a soil to help human health and endeavors to end or turn around debasement improve that capacity (Lal, 2015; Kemper et al., 2017). Ecologically, there is sufficient proof that pipeline spills and ruptures of toxic, polluting has serious implications for the surrounding land and water. In the human healthy point of view, there is growing proof to demonstrate that exposure to oil pollutant causes mild to serious adverse events.

4.5.1 Pollution impact on human health

Pollution has inevitably become undesirable phenomenon of global concern. It is a known fact that industrial revolution gave birth to environmental pollution as it is today. The continuous degradation of an impending damage to our valued environment by pollution is a thing of concern and should not be overlooked. Environmental Pollution affects soil, water and air, presenting health danger to humans, aquatic life, ecosystem and harmful threat to the natural environment (Kusic et al., 2006; Marianna, 2002). The conduit of this Environmental pollution is through the soils/sediments, water and air. Most environmental pollution effects appear initially latent with imminent harmful effect at long exposure. Two major sources of pollution contributions are through human (anthropogenic) and nature (biogenic) activities.

There exist diverse definitions of pollution applicable to diverse topics. Toxification is the disposing of harmful chemicals, bodily wastes, as well as other pollutants which will harm the human health in one way or the other. Polluting the air, soil, and water makes it hard for people to drink the water, plant in the land, as well as to inhale the chemicals that can lead to death. Micro-organisms, human-waste, water-waste, chemicals, are among the toxic materials that contaminate the soil, air, and water. Pollution can also result from man activity, surface objects, agricultural products, and household products. Most authors define pollution as the introducing substances which can cause harm to human health, ecological systems, interfere with processes, as well as damage living resources (Okop, 2010).

Words like contamination and toxification are synonyms of the word pollution. There is a slight difference between pollutants and contaminants. Contaminants are small particles in the location caused by human actions that do not directly harm the people and the environment. The harm from the substance is long-term as people will not consider them as dangerous because they exist in the background. Though they may seem harmless, the substances are silently damaging environment and killing people like factor chemicals that if inhaled in small amounts may cause death in the end. Pollutants, on the other hand, are human activities which cause negative damage directly to the environment (Manahan and Stanley, 2000). The pollutants can either be Primary impurities or secondary toxins and they are both harmful to people and their environs. Primary pollutants are very severe to people, plants, and the environment while secondary is less harmful on the environment, animals, and humans. For instance, secondary pollutants are the source of diseases like cancer, acidity, slow chemical inhalation, and stomach ulcers.

Volatile Organic Compounds (VOCs) is a group of pollutants which cause severe health hazards. The VOCs lead to severe harm to natural and man-made lives and their surroundings. The organic compounds are leaked to the soil which prevents plants and other agricultural products from growing thus causing famine and hunger in countries which can result to death of animals, plants, and people. The VOCs are rare but dangerous and are found in land, soil, water, and the environment as well as in agricultural, urban, industrial areas. They are also an essential class of environmental pollutants found in the soil, water, and air mostly in urban, agricultural, and industrial areas and come in solid, gaseous, and in liquid forms.

VOCs and some liquid petroleum hydrocarbons exposure may cause short or long term health effects depending on the dose and type of pollutants, exposure time and route, individual's constitution, age and sex. (Okop, 2010). Short term effects on human include:

- Headaches, dizziness, fatigue and nausea
- Sore throat inflammation
- Chest pain and congestion
- Lung and skin tumors
- Eye and skin irritation and rashes from oil spills
- Hemolytic anemia
- Affect enzymes producing red blood cells
- Allergies and immune diseases

Long term exposure may lead to:

- Peripheral neuropathy (numbress in the feet and legs)
- Cancer

- Asthma
- Kidney and liver damage

Long term exposure may finally lead to

- Harm to the brain and nervous system
- Foetal damage and decreasing fertility
- Increased incidence of death

4.5.2 Pollution impact on planting and agricultural

Petroleum-well spillages, pipe line and storage (surface and underground) tank leakages, vapor emissions, gas flares, wastewater and similar discharges associated with petroleum contamination instigates environmental health risk and agricultural defects (Resano et al., 2007; Bosco et al., 2005). In recent decades, petroleum and petroleum products have attained the acme of its usage. Extensive amounts of these products are usually stored underground or on the surface tanks or transported in tanks and underground pipelines. Accidental discharges or spills, during transportation, land disposal facilities, engines, large generating plants and illegal dumping or ''bunkering'' are another source of introduction of petroleum contaminants into the soils, sediments and water.

Brady and Weil (1999) in their epidemiological studies reported that the number of deaths resulting from these contaminants equal to or exceed the number of deaths caused by road accidents. Varying amounts of chemical pollutants and contaminants such as sulphur, mercury, nitrogen oxides, and vanadium is also known to contain Pet-coke- a solid residual carbonaceous product (coal), used as fuel (Hendrik et al., 2006). Accumulation of metal pollutants from the leaves and roots of higher plants have been reported (Brady and Weil, 1999). Elemental deposition on plant materials was studied (Alaimo et al., 2000; Dongarra et al., 2003b). Reports show that some trace elements are likely source of environmental pollution; causing catalytic poisoning and corrosion of refining columns and turbines (Akinlua et al., 2008; Lombardo et al., 2001).

The release of crude oil and its products into the environment is a threat to agricultural land. Petroleum hydrocarbons sterilize the soil and prevent crop growth and yield for varying periods of time. For example, a good percentage of oil spills that occurred on dry land, between 1978 and 1979 in Nigeria affected farms in which crops such as rice, maize, yams, cassava and plantain were cultivated (Oyefolu and Awobajo, 1979). The effect of petroleum on the germination and growth of some plants have been reported (Klokk,

1984). The recovery of soil fertility after an oil spill depends on several factors including quantity spilled (McCown and Deneke, 1992). Restoration of the fertility of agricultural land previously contaminated by oil is of great importance.

4.5.3 Crude oil impact on planting in Erbil

Areas close to or around the refiners and oilfields are polluted by crude oil. Moreover, many activities such as transportation by tankers or pipelines and oil products and can cause soil pollution and consequently affects negatively on localized planting. One of the main oilfield in Erbil city named Khurmala oil field which is located in western part of Erbil city. In Quretan village which is located close to Khurmala oilfield, we investigated the impact of crude oil on Tomatoes, Aubergine and Hot Pepper. Two different ratios 0.5 liter and 0.25 were used for each type of vegetables for the duration of four weeks.

The weekly observed of impacts were carried out on such vegetables. As shown in Figure 4.3, illustrated all staged (four weeks) effect of crude oil. Concerning Tomatoes, it has been observed that the effect of the 0.5 liter had significant compared to the rate of 0.25 liter. Consequently, after adding oil on the root of the tomatoes led to the dead of whole parts from roots, steam, leaves, flowers and fruit.

In terms of Aubergine, when adding crude oil by (0.5 and 0.25) liter for two parts of Aubergine. It has been observed that the Aubergine was dead quickly as shown in Figure 4.4. Also, it affected the taste of fruit.

For Hot Pepper, the effect of crude oil was also significant as shown in Figure 4.5. Moreover, the oily sticks were observed on the leaves remarkably. This also caused the dead of steams, leaves and products of the fruit. Generally, after two weeks, we noticed the change of taste of all fruits. Therefore, the polluted soil by crude oil has negative impact on planting especially those areas close to refineries and oil fields.



(e) (f) Figure 4.3 Tomatoes after added crude oil for four weeks.



Figure 4.4 Aubergine after added crude oil for four weeks.



(a)

(b)



(c)

(d)

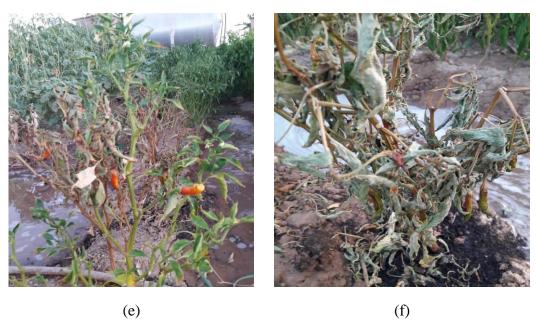


Figure 4.5 Hot pepper after added crude oil for four weeks.

4.6 Remediation of petroleum-polluted environments

Disposing of oil sludge remains to be a significant concern for many petroleum refineries worldwide. Kuriakose and Manjooran, (2001) are admitting that many oil refineries do not have a concrete management plan after the process of petrol recovery has been completed. Physicochemical methods have been incorporated purposely to eliminate the challenge of oil sludge. A physiochemical way is a broad term, and it will be realistic to specify some of the methods oil refineries may consider incorporating. The implementation of oxidative treatment, as well as incineration, is coupled with the technological invention. In this case, it is vital for oil refineries to invest in technology. Bioremediation alongside remediation can also be integrated.

4.6.1 Physicochemical remediation method

There are broad array of physical and chemical techniques that can be used to perform soil clean-up. These methods comprise burning, use of chemical compounds and dispersant, physical removal and performing landfilling procedures. However, these procedures are often expensive to perform, require extensive labor and are not environmentally friendly. This view is supported by an example where use of chemical compounds and dispersants contaminates the environment by introducing harmful chemical materials. Likewise, incineration as physical method of manually cleaning the environment, increase levels of PAHs to the environment since it involve use of high temperatures to decompose and recombine organic molecules. Even though, incineration increases the level of PAHs to the environment, this technique is widely used in refineries. According to Hu et al., (2013), high temperatures of more than 1200°C completely burn oil sludge. Thus, this method is effective in performing clean-ups especially on a large scale.

Several researchers have studied the successful and stable combustion process. For instance, Liu et al., (2009) emphasizes the need to use supplementary fuel sources such as coal-water and petroleum-coke sludge slurry. They further revealed that, using auxiliary fuels leads to increase cleaning performance by more than 90 percent. Sankaran et al., (1998) believed that the performance of oil sludge with high viscosity and high water content need to be first taken through a pre-treatment process before proceeding to incineration. Significantly, Couto et al., (2010); Das and Chandran (2011) demonstrated the major disadvantages of physical and chemical cleaning methods which are associated

with high cost as well as it needs the comprehensive devices to support these procedures. Besides, there are concerns due to adding chemicals such as catalysts or oxidants. These may pose additional troubles to the ecosystem. Calvert and Suib (2007) opposes the idea of using physical and chemical cleaning processes, because to a large extent, these methods do not offer permanent solutions as they cannot completely eliminate contaminants.

4.6.2 Bioremediation techniques

Bioremediation The other method is bioremediation. This technique is preferred because it is cost-effective and provides solutions to the weaknesses of physicochemical treatments (Megharaj et al., 2011). Consequently, this method involves the use of microorganisms to decompose hazardous materials. According to Battikhi (2014), this technique is not complicated to operate, economical and effective justifying why it has been used adversely to treat oily sludge and petroleum that contaminates the soil. In addition, investigations conducted by Das and Chandran (2011); Ubani et al., (2013); Dindar, et al., (2013), reveal that the end products resulting from treatment process such as carbon dioxide, water, and fatty acids are always non harmful to the environment.

Bioremediation has passed through a series of developments in the recent years. The development of microorganisms to support the process and thus aid in the treatment of myriad form of contaminants. Nonetheless, Jain et al., (2011), has highlighted the simplicity and cost-effectiveness of this method of treatment. Based on Jain et al., (2011), the process of biodegradation of petroleum hydrocarbons is complex. Therefore, this requires an approach that considers the amount and type of hydrocarbons involved, especially on a polluted site or sludge. Conversely, Liu et al., (2010) supports this technique based on its ability to comprehensively degrade petroleum wastes apart from polyaromatics available in asphaltenes and resins. The common bioremediation methods according to Powell et al., (2007) were land agriculture, Biopiles and bioreactors.

As outlined by Jordening and winter (2006), bioremediation process is influenced by myriad factors such as the nature of microorganisms involved, remediation time, amount of nutrients, and concentration of hydrocarbon in oily sludge. Studies have established that many bacteria and fungi can successfully deal with petroleum hydrocarbons, a single strain can effectively biodegrade almost all compounds present in petroleum waste (Fan and Krishnamurthy, 1995). The process of biodegrading petroleum hydrocarbons follows

a chronological sequence of reactions, where broad array of bacteria works together to degrade oily waste disposed to the soil.

Equally, duration of the process is important as it affects biodegradation procedures. Therefore, anchored on the views of Sihag et al., (2014), the longer the process goes, the lower the rate of biodegradation due to reduction in biodegradable hydrocarbons and the increase in obstinate materials. According to studies conducted by Boodoosingh et al., (2010), it is imperative to note that the prelude concentration of petroleum hydrocarbons in the soil also affect the rate of biodegradation.

Bioremediation is the use of living organisms or their products to reclaim contaminated soils and waters. When the bioremediation treatment is applied on the site of pollution it is called in situ bioremediation. If the contaminated soil or water is transferred to a different location for treatment it is ex situ.

4.6.3 Land farming remediation

Land farming remediation as a biodegrading process where oil content is separated from solid substances (Hejazi et al., 2003). Here, solid elements include soil and sludge. Through the process of aeration, the separation of mixtures becomes possible, and this is after polluted oil has been spread on a thin layer underground. By the mention of biodegradation, it is vital to reflect on the microbial activities, and this is introduced during the separation process purposely to facilitate the process of aeration. Increasing the rate of microbial activities resonates increasing the number of bacteria in the soil. By increasing microbial activities on the thin layer, there is a possibility of introducing catalysts which will also save time (Ubani et al., 2013). The microbial activities need to be subjected to favorable conditions such as moisture and nutrients (McGenity, 2014).

It is essential to note that the process of oil removal has not been limited to biodegradation. There is the need to pretreat oily sludge since it is nonhomogeneous in nature. As much as the biodegradation incurs extra cost, pretreatment needs to be followed by biodegradation with the aim of removing safe oil. As far as the process of extracting oil is concerned (Sihag et al., 2014) has also acknowledged the impact of integrating photodegradation. As highlighted before, gasoline is one of the components of petroleum sludge. It is a contaminant and is not required after the completion of the oil removal process.

As far as land farming remediation process is concerned, the piles are supplied by moisture and nutrients through pipes and by that, the aeration process is enhanced. How then should the remaining fraction of gasoline be removed? As much as it is a lighter component that can be removed through the process of aeration, the remaining fraction can be removed through the process of degradation, and that is the reason microbial activities need to be increased in the soil so that the contaminants can be broken down entirely. It should be noted that the evaporation of large fractions of the components primarily depends on the climatic conditions (Hejazi and Husain, 2004). For instance, in regions experiencing hot weather, evaporation will be quick compared to regions experiencing chilly climates.

During land farming emission, it is essential to take precaution. It is vital to control the emission of volatile compounds. This should be considered as a risk factor not only to human health but also to the environment. In that case, before discharge (Thibodeaux and Hwang, 1982), it needs to be regulated and controlled so that it curbs serious outcomes like loss of lives and ecological system.

Land farming remediation methods have numerous advantages. For example, the facilitation of microbial activities is cheap, and for a small-sized oil refinery, the management costs will be saved in light of conducting a successful oil removal process. Land farming remediation provides a solution for components that cannot be degraded quickly.

4.6.4 Biopiles or compost piles technology

By this method, scientists can combine microbial activities with technology. When discussing the role of technology on biodegradation, it is crucial to relate it to compost and bio-piles. Here the contaminated soil is piled up purposely to enhance the aeration process, and this reflects the procedures involved in land farming remediation. Biopiles have been deemed as a practical approach to biodegrading all compounds of petroleum sludge (Hazen et al., 2003). For land farming remediation, there is nowhere that has been mentioned on ways of increasing the piles' porosity. In this strategy, the porosity can be enhanced through the following methods- sawdust, bark and wood chips (Marin et al., 2006).

Land farming is combined with bio piles techniques with the aim of increasing the facilitation of nutrients. The adjustment should resonate the ration of C: N: P and this acts

as a catalyst to the process of biodegradation (Ball et al., 2012). It is important to note that the adjustment is attached to the process of bio-stimulation. Sometimes, the bacteria or microbial communities introduced to the process of land farming remediation can be less, and this may be challenging. In this scenario, it is vital to add microbial strains which in turn can be added to the pile and compost systems (Hamdi et al., 2007).

Without the integration of bioreactor technology, it will be difficult to encourage the aspect of solubilization on not only the contaminated soil but also petroleum sludge. During this process, the hydrocarbon can be converted to a less metabolic component, for example, water and carbon dioxide. The aim is to increase the impact of microbial activities on petroleum products like hydrocarbon (Robles-Gonzalez et al., 2008). In this case, it is a clear indication that the incorporation of technology increases the rate at which petroleum components mainly hydrocarbon is going to be removed. The suitable results will be obtained quickly compared to land farming remediation. That said, there is no need to become overwhelmed prior to increasing moisture or nutrients during the aeration process. The process needs to be characterized by regulation attained through keen observation of the progress (Castaldi, 2003). In that case, it is vital to integrate liquid phases while enhancing aeration process.

CHAPTER 5

FLOW AND PENETRATION CRUDE OIL ON SOIL

5.1 Overview

There have been numerous cases of oil spilling on land in the recent years, impacting on management decisions. Most of these accidents have involved crude oil and fuel leak from tankers plying transport and pipeline channels. Thus, it is important to enable accurate estimation on the number of cases in order to understand the evolution of soil contamination through spillage of oil. Also, is important to know the rate of penetration and estimated time for spillage to reach the water table.

In many occasions, the magnitude of spillage may be shorter, and thus it is possible that only basic data will be available to the emergency teams. Early precautionary and appropriate interventions are required to prevent soil and underground water contamination. Of great importance is the ability to estimate the range in regards to area and depth affected by oil spillage. This would be beneficial to emergency teams to make sound decision and formulate necessary preventive strategies. Accordingly, estimation techniques must present users with opportunities to construct accurate representations of land affected, taking into account other environmental factors such as wind, temperature, moisture, and ability of soil to allow penetrations. This will be crucial in formulating and selecting appropriate actions to be taken.

5.2 Simplified method for prediction of the crude oil spills

Oil spillage undergoes several processes. They include evaporation, infiltration and surface flow. The initial step entails measuring the pool area so as to get a picture of the affected region (Grimaz et al., 2008). The idea of establishing a predictive method is borrowed from the gravity theory. A simplified predictive equation can be developed by assessing the process of evaluation. This is where hydrocarbon components are broken down through the aid of ambient temperature. In that case, it is essential to focus on not only climatic factors but also the time factor.

Further research is required purposely to make a valid predictive tool. On that front, it is critical to analyze the distillate data. That aside, through assessing the physical characteristic of petroleum components and comparing that with information from the distillation system, creating a predictive tool becomes easier. Oil spillage should not be allowed. Operations of petroleum refineries have positively impacted the U.S economy. It will be extremely complicated for the United States to survive without these petroleum refineries. Petroleum and gas production are used for commercial and social purposes. Motorists rely on petrol and diesel to fuel their vehicle, and by that, without these products, the transport sector will be paralyzed. In that case, the operation of petroleum refineries needs to be in tandem with the Environmental Act.

5.2.1 Extent of polluted area

Evaluation of the contaminated area is the essential because it helps the leaders to evaluate the damage. Other metrics applicable measure the infected area or the environment. For instance, it will be easier to measure the extent of an accident on the scene after it occurs. Grimaz et al., (2008) propose a formula to use in prediction, which will help in measurement of the extent of pollution. The method by Grimaz applies to accidents and other harms to human beings. Equation (1) is useful in estimating the polluted region, especially by crude oil in the soil. Accidents involving vehicles always have spillage of oil in the ground or soil, which results in pollution of the scene:

$$A_{Pool} \cong 2.3782 \ \frac{Q^{4/5}}{(k_l k_{r,NAPL})^{1/5}} \tag{1}$$

Where:

 A_{pool} is the area of the pool of oil on the surface [m²] Q is the total amount of oil spilt [m³] k_i is the intrinsic permeability of soil [m²] $k_{r,NAPL}$ is the relative permeability of oil (NAPL)

The values of $k_{r, NAPL}$, depending from different grades of water saturation of soil, are shown in Table 5.1.

Table 5.1 Relative permeability $k_{r, NAPL}$ for different scenarios of accidental spillage(Grimaz et al., 2008)

Soil situation	K _{r, NAPL}
Dry - long time without rainfall in warm regions and in hot seasons	1.0
Slightly wet - long time without rainfall in other regions or seasons	0.9
Very wet - from 2 hours to 2 days after strong rainfall	0.3
Completely saturated - during strong rainfall with ponds on surface	0.0

5.2.2 Evaporation

The method of evaporation occurs in a liquid, including oils leakages. To estimate the amount of oil evaporated from the pool it is need to described the time t_{ep} during which the pool stay on the surface. For the case of a pool on a permeable medium it can be considered equal to the time of complete infiltration of the oil into the porous medium. It can be estimated the time t_{ep} by utilizing Eq (2) which considers a theoretical depth of crude oil pool and the crude oil seepage velocity at complete saturation, using Darcy's law.

$$t_{ep} = \frac{h_{tp}}{v_{p.s}} = \frac{V_{spill}}{A_{pool}} \frac{\vartheta_e}{k_{r,NAPL}k} \frac{v_{oil}}{v_w}$$
(2)

Where the symbols not defined earlier are: t_{ep} is the estimated duration of the oil pool on the surface [s] h_{tp} is the depth of the oil pool [m] $v_{p,s}$ is the velocity of penetration of the oil into soil in oil saturated conditions [ms⁻¹] V_{spill} is the volume of oil spilt [m³] K is the hydraulic conductivity [ms⁻¹] ϑ_e is the porosity of soil υ_w is the kinematic viscosity for water [m²s⁻¹]

Then, in order to estimate the percentage of oil evaporated from the pool in tep the simplest equations proposed by Fingas (2004) can be used. In particular, Fingas proposed the following equations, for oils evaporation.

$$\% E = [0.165(\% D_{180}) + 0.045(T - 15)] \ln(t)$$
(3)

Where

%*E* is the percentage (by weight) of oil evaporated

 $%D_{180}$ is the percentage of oil distilled at 180° C

T is the environmental temperature [$^{\circ}$ C]

t is the time of evaporation [minutes]

If it is acceptable to assume that the oil density remains constant during the initial period after the spill, the volume evaporated can be estimated using the following equation:

$$V_E = \% E_{oil, t_{ep}}. V_{spill} \tag{4}$$

Where

 V_E is the volume of oil evaporated [m³] % $E_{oil,tep}$ is the percentage calculated using Eq. (3) at t_{ep} for oil t_{ep} is the time calculated using Eq. (2) V_{spill} is the volume of oil spilt [m³]

5.2.3 Penetration into vadose zone

The spilt crude oil will not only tend to spread out over the surface of the soil and evaporate, but will also penetrate into the ground (unless it is impermeable).

This downward penetration may be arrested in three ways:

- The threshold of residual saturation has not been reached;
- An impermeable layer in the path of the oil is reached;
- The water table is reached.

Residual saturation may be defined as the minimum saturation which a fluid has to attain in order to move in a porous medium (or alternatively the threshold below which it is no longer able to move). It is a non-dimensional parameter and can be expressed as retention capacity, R. Typical values of R for different types of soils are presented in Table 5.2.

The maximum depth of penetration of the NAPL in the unsaturated or vadose zone can be estimated using Eq. (5) (Concawe, 1979):

$$D_{MP} = \frac{V_{spill} - V_E}{A_{pool} R\xi}$$
(5)

Where

 D_{MP} is the maximum depth of penetration of NAPL into the unsaturated zone [m] R is the retention capacity, from Table 5.2.

 ξ is a parameter that depends of the viscosity of the fluid, from Table 5.3.

Soil typology	Retention Capacity – R (m ³ _{NAPL} m ⁻ ³ _{soil})
Stone – Coarse gravel	5 x 10 ⁻³
Gravel – Coarse sand	8 x 10 ⁻³
Coarse sand –Medium sand	15 x 10 ⁻³
Medium sand – Fine sand	25 x 10 ⁻³
Fine sand - Silt	40 x 10 ⁻³

 Table 5.2 Retention capacity coefficient R (Concawe, 1979)

Table 5.3 Parameter ξ for different type of liquids (Concawe, 1979)

Fluid	ξ parameter
Low viscosity (e.g. gasoline, petrol)	0.5
Medium viscosity (e.g. Kerosene, gasoil, paraffin and diesel)	1.0
High viscosity (e.g. light fuel oils)	2.0

In the case, D_{MP} is more than the depth of the groundwater table (more precisely, the depth of the capillary fringe, D_{CF} , which is the groundwater depth, D_{GW} , minus the capillary rise, H_{CR}) then the groundwater may become contaminated. It may be useful to estimate the length of time between the occurrence of the spill and penetration of the oil to the groundwater.

In the case, $D_{MP} < D_{CF}$ then oil does not reach the capillary fringe. In this case, water contamination occurs only indirectly; by dissolution of soluble components of the oil from the contaminated soil layer when water permeates through the upper contaminated zone and subsequently down to the water table. Water velocity and retardation factor must be taken into consideration in the calculation.

5.3 Application to a real case of accidental oil spillage onto ground

In the real case was in which tank truck overturned on main road, due to this accident large quantity of crude oil spilt onto soil beside roadway where the accident occurred. After data collection about the case, it observed an area of the wetted soil beside the road of about 278.2 m^2 . The ground was flat and sandy with a porosity of 0.3 and a permeability of $1 \times 10^{-6} \text{ cm}^2$. The duration of spillage was estimated to be about 328 seconds with an average flow rate of 36.13 l/s for a total of 11850 liters of crude oil spilt. The viscosity of crude oil is 18.1 cP, and the density is 0.84 kg/l. The percentage of distills at 180°C, %D180, is about 18%.

Therefore, evaporation percentage was calculated as 18.66%. As the result maximum depth of penetration (D_{MP}) of this case was 1.38m. Based on the investigation on polluted location groundwater depth was more than 35 m. The oil will cover the surface and will spread in the larger area but the oil will not penetrate deep into the soil. In this case, groundwater pollution could occur by dissolution of soluble compounds and the retardation factor.

CHAPTER 6

RESULTS AND DISCUSSION

6.1 General

A brief note of tests and results of various laboratory tests performed for the purpose of the thesis work are presented in this chapter. Analysis of test results shown by tables and graphs is also added here in. The properties of crude oil and soils (engineering and chemical properties) were determined in laboratory of Erbil construction laboratory (ECL).

In this investigation, the samples were prepared by mixing dry sand with different percentages of crude oil 2%, 4%, 6%, 8%, 10%, 12%, 14% and 16% by the weight of the dry sand. The soil-crude oil mixtures were thoroughly mixed and stored in containers for 2 weeks to allow for homogeneity of the mixtures. Sieve and hydrometer analyses were carried out on the uncontaminated soil sample. Specific gravity, Chemical properties, pH values, compaction and direct shear test were conducted on the contaminated and uncontaminated soil sample. Also, compaction and direct shear test conducted for mixtures which mixed with crude oil in 0%, 4%, 6% and 8% and FA with GGBFS in 0%, 10% and 15% by dry weight.

6.2 Results of index properties of soil sample

6.2.1 Specific gravity

Specific gravity is defined as the ratio of the weight of a given volume of soil solids at a given temperature to the weight of an equal volume of distilled water at that temperature, both weights being taken in air. Specific gravity test is according to ASTM D 854 - 10 Standard Test Methods for Specific Gravity of Soil. The specific gravity influences the compaction and consolidation properties of soil. Specific gravity results of soil depends on their mineralogical composition and the most common primary minerals have specific gravities in the range of 2.55 to 2.75 with a mean value of 2.65. Organic soils have a low and quite variable specific gravity in the range of 2.2 to 2.64.

The results of this investigation for the specific gravity of uncontaminated sand soil is 2.619. A graphical illustration of the results of specific gravity tests on the soil admixed with different percentages of crude oil content is presented in Figure 6.1. The specific gravities of the contaminated soil samples were found in Table 6.1 (in detailed in appendix A) to be decreased in 2% to 16% of crude oil content. This change in specific gravity (decrease) may be due to the presence of organic matter of crude oil in soil.

% Crude oil	Specific gravity
0%	2.619
2%	2.617
4%	2.615
6%	2.607
8%	2.602
10%	2.592
12%	2.584
14%	2.581
16%	2.577

Table 6.1 Specific gravity of contaminated and uncontaminated soils.

Harsh et al., (2016) analyzed effect of rate of crude oil contamination on index properties and engineering properties of clays and sands, the specific gravity decreases by 15.44%, 29.73% and 40.54% for 3%, 6% and 9% of crude oil contamination for sands. Chaudhary (2016) the specific gravity of soil solids decreases due to contamination. The reduction may be due to organic content in the form of hydrocarbon chain present in used engine oil.

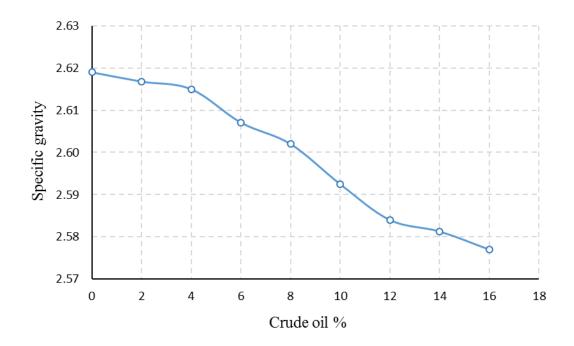


Figure 6.1 Demonstrate the effecting crude oil on specific gravity of soil sample.

6.2.2 Value of pH for contaminated and uncontaminated soil samples.

The pH value of soil is important chemical properties studied in this thesis work. pH is used to ascertain the acidic or basic character of soils. According to Scott (1963), the engineering properties of soil are sensitive to the nature and amount of dissolved electrolyte in the pore fluid. Mitchell et al. (1976) reported that when pore fluid is liquid such as oil and waste chemicals, the dielectric constant of these materials is different from that of normal water. The pH value was determined by taking 1: 1 soil and distilled water mixture with the help of Systronics digital pH meter – 335. As shown in Table 6.2 and Figure 6.2.

Table 6.2 pH value of sand with different ratio of crude oil.

Crude oil %	0%	2%	4%	6%	8%	10%	12%	14%	16%
pH value	7.31	7.58	7.79	7.83	7.93	8.01	8.08	8.15	8.28

Khuraibet and Attar (1998) observed that the presence of oil may lower the pH value of Kuwait soil. Srivastava et al. (1997) studied the "Soil-Industrial Waste Water Interaction Behavior" and observed a marked change in the pH value of contaminated soil from that of uncontaminated soil. Yaji et al. (1997) mentioned that acidic characteristics of highly compressive inorganic soil decreases significantly as the percentage of contamination by crude oil increases.

There was an increase in soil pH after mixing with crude oil, this agrees with a report by Brady and Weil (1999).

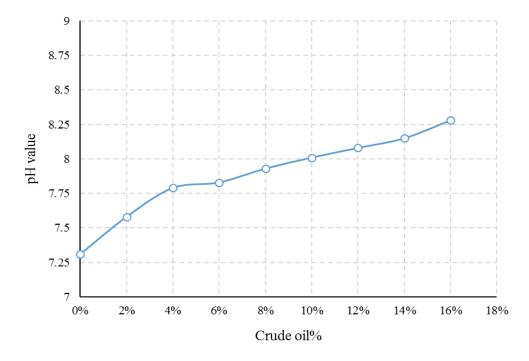


Figure 6.2 pH value of contaminated and uncontaminated sandy soil.

6.2.3 Chemical composition of contaminated and uncontaminated sample.

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high- energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry and forensic science. The test results are given in Table 6.3.

Chemical	0%	2%	4%	6%	8%	10%	12%	14%	16%
component	Oil	Oil	Oil	Oil	Oil	Oil	Oil	Oil	Oil
Na ₂ O	0.021	0.022	0.023	0.025	0.026	0.027	0.028	0.034	0.043
MgO	0.793	0.803	1.222	0.914	0.776	0.713	0.658	0.643	0.612
Al ₂ O ₃	7.804	7.941	8.266	8.026	7.159	6.562	6.241	5.835	5.088

 Table 6.3 Chemical composition of contaminated and uncontaminated soil.

SiO ₂	23.773	24.063	24.415	24.043	23.555	22.073	21.594	20.537	19.049
P ₂ O ₅	0.709	0.697	0.625	0.647	0.681	0.667	0.656	0.671	0.688
SO ₃	0.094	0.109	0.167	0.215	0.251	0.372	0.417	0.562	0.707
K ₂ O	0.366	0.361	0.357	0.343	0.321	0.316	0.261	0.223	0.157
CaO	18.507	17.285	16.625	16.746	16.953	16.184	15.504	15.439	15.308
MnO	0.175	0.155	0.136	0.139	0.145	0.138	0.122	0.117	0.106
Fe ₂ O ₃	4.598	4.557	4.548	4.431	4.279	4.038	3.945	3.824	3.703

6.3 Results for geotechnical tests program of soil mixed with crude oil

6.3.1 Compaction

Compaction is the process of increasing the density of soil by decreasing the air voids by application of mechanical energy, such as, tamping, rolling and vibration. The object of compaction is the improvement of the engineering properties of soil. Maximum dry density (γ_d , $_{max}$) and optimum moisture content are known as main parameters for compaction properties of soil.

Compaction tests were performed on the artificially prepared samples with 0%, 2%, 4%, 6%, 8%, 10%, 12%, 14% and 16% crude oil content. The compaction characteristics were presented in graphical plots as shown in Table 6.4.

Crude oil%	Dry Density (g/cm ³)	Optimum Moisture Content (%)
0%	1.97	10.4
2%	1.966	10
4%	1.958	9.7
6%	1.952	8.6
8%	1.947	6.8
10%	1.933	5.4
12%	1.92	5
14%	1.91	4.3
16%	1.907	4.2

Table 6.4 Dry density and optimum moisture content for soil samples.

Figure 6.3 displays compaction results in the form of dry density versus water content for crude oil–contaminated samples. The compaction curves for contaminated soils clearly moved to the left of the uncontaminated soil's curve as crude oil content increased. The dry unit weight has a general tendency first to decrease as water content increases, and then to increase to a maximum value with the further increase of water content. The effect of oil contamination on the maximum dry density and optimum moisture content can be seen from Figures 6.4 and 6.5.

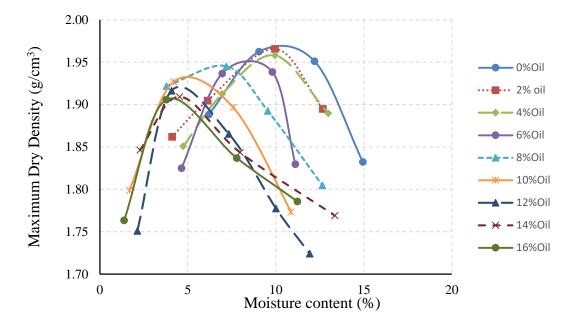


Figure 6.3 Compaction curves for samples with different oil% contents.

Test results in Figure 6.4 show a reduction in maximum dry density with increasing percentage of crude oil content. The reduction of dry density in sand soil samples are low because the pore spaces are larger in these samples and oil can move through the soil particles with the same rate as water and it has the similar lubricating effect. This decrease of dry unit weight with an increase of oil content can be attributed to the capillary tension effect (Khamehchiyan et al., 2007), the capillary tension in the water inhibits the tendency of the soil particles to move around and be densely compacted. Capillary tension is extremely depending on the surface tension of electrolytes and angle of contact. As oil has hydrophobia property, it prevents contact of water with soil particles. As a result, the capillary tension force decreases with increasing crude oil content of soil samples (Soltani et al., 2018). This reflects the lubricating effect caused by the presence of oil, which facilitates compaction and reduces the amount of water needed to reach maximum density. Another reason could be the waste of compaction energy by crude oil. As the

crude oil has a higher viscosity in comparison with water, more compaction energy is consumed for increasing the tension between crude oil molecules. As a result, it absorbs more energy to rise in the soil texture.

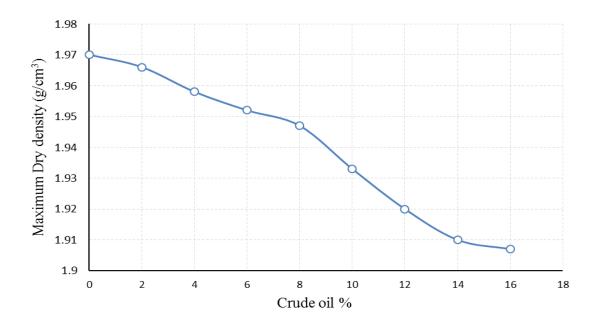


Figure 6.4 Maximum dry density with crude oil.

Figure 6.5 shows the relationship between the moisture content and crude oil content from which it clearly indicated that drawdown trend of optimum moisture content with the increase in crude oil content. It clearly suggests that the moisture content required to achieve maximum dry density has decreased when crude oil content increased in contaminated soil. This is probably due to the fact that oil has partially occupied the interparticles spaces and the occurrence of oil has changed the soil to a state of looser material than an uncontaminated soil. Furthermore, (Puri, 2000) reported the reason of a decrease in optimum water content might be the presence of crude oil instead of water, which has the same effect as the water.

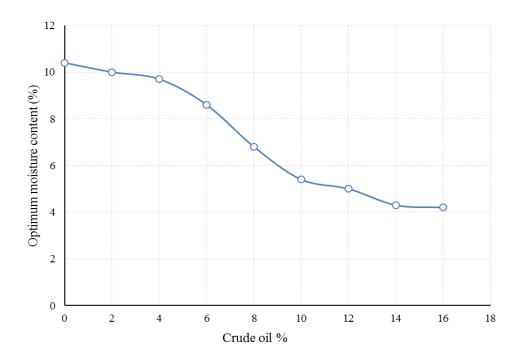


Figure 6.5 Optimum moisture content with crude oil.

Singh et al., (2005) observed that maximum dry density at 3% contamination is more than that of the virgin soil. But after that as the degree of contamination increases, maximum dry density decreases. Also, (Khamehchiyan et al., 2007) and (Soltani et al., 2018) investigated effect of crude oil contamination on geotechnical properties of soil samples in Iran in the results showed decreased maximum dry density and optimum moisture content with increased percentage of oil content. Moreover, Nasehi et al., (2016) conducted influence of gas oil content on sandy soils, which it showed that reduction in optimum moisture content and maximum dry density with increased level of oil contamination. The results in this research are in agreement with those reported by Shah et al., (2003), Khamehchiyan et al., (2007), and Rahman et al., (2010).

6.3.2 Direct shear

The shear resistance of soil is most important parameter because it controls the bearing capacity as well as the slope stability and foundation design of a civil engineering structure. In this research, the samples of direct shear test were compacted to the value of maximum dry density with corresponding optimum water content for each sample. The values of maximum dry density and optimum water content were chosen because the soil particles for each sample have the most particle interaction with each other at their corresponding maximum dry density. Direct shear tests were carried out to find the effect of crude oil contamination on strength parameters of soils. Results indicate generally an

increase in apparent cohesion and a decrease in friction angle of contaminated samples with increase of contamination content.

Crude oil %	Apparent cohesion, (kPa)	Angle of friction , ϕ (degree)
0%	0.266	36.8
2%	16.3	33.5
4%	24	32.9
6%	43.2	29.9
8%	76.1	31.9
10%	67.8	35.5
12%	67.9	35.4
14%	52.6	27.5
16%	48.1	32.1

Table 6.5 Different percentage of crude oil with apparent cohesion and angle of friction.

The present results show a correlation between crude oil content and angle of internal friction (ϕ) in sandy soil samples (Table 6.5 and Figure 6.6). Angle of internal friction (ϕ) shows a slightly decrease – increase trend in these types of soil with the increase in the level of crude oil contamination. This correlation does not have any distinct path in soil samples.

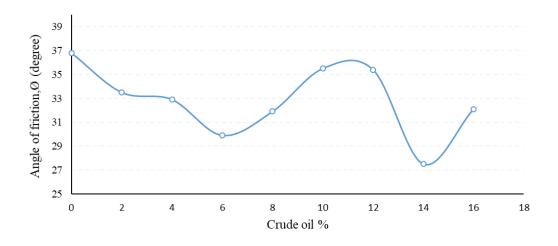


Figure 6.6 Angle of friction with crude oil.

As shown in Figure 6.7, with increasing crude oil content, the apparent cohesion (c) increases to the pick value of 76.1 kPa at 8% of crude oil content. Furthermore, the

apparent cohesion starts to decrease after 8% of crude oil content until it reaches to 16%. The initial increase of the apparent cohesion was due to the oil contamination resulted from the viscosity and inherent cohesion of oil. It may be noted that soil samples show a little apparent cohesion due to the surface tension force of existing water in the soil. However, the shear strength of all soil samples reduces with increasing oil contamination in 2%, 4%, 6%, 8%, 10%, 12%, 14% and 16% of dry weight of sand. Lubrication at particle contact is caused by the viscous nature of the pore fluid. As the viscosity of the pore fluid increases, the shear strength of the granular soil decreases (Ratnaweera and Meegoda, 2005). Ghaly, (2001) used direct shear tests performed on oil-contaminated sands. He showed a reduction in φ with the increase in oil percentage. Shin et al., (2002) reported that a reduction in internal friction angle was observed due to oil contamination in sandy soils. The reason for such behavior could be found in viscosity differences of the crude oil and the water. Moreover, the lubricating effect of the crude oil causes a reduction in the inter-particle friction, decreasing the internal friction angle of the crude oilcontaminated soil (Khosravi et al., 2013). Furthermore, Nasehi et al., (2016) observed impact of gas oil content on shear strength of sandy soil, with in added oil content decreased angle of internal friction and increased apparent cohesion for the soil samples.

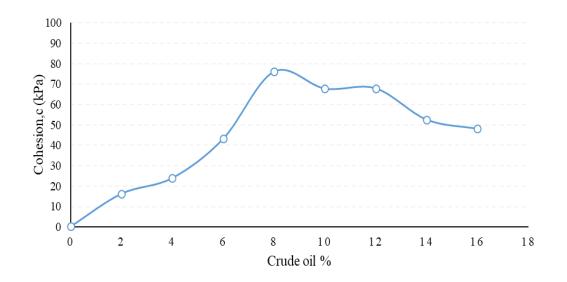


Figure 6.7 Apparent cohesion with crude oil.

Results in this study is agreement with Abousnina et al. (2015) which they investigated effect of light hydrocarbons contamination on shear strength of fine sand. When a contamination enters the earth surface; its chances of being held in the soil are regularly remarkable. Consequently, the contamination doesn't fade as quickly as it may something

else, in air or water. Pollution potential will be high in case of higher the time a contamination stays in contact with soil or air. Higher water dissolvable contaminant is immediately disposed off. Crude oil is not dissolvable in the water. As well as disintegration of crude oil in the soil might not be significant. Accordingly, if spilt crude oil is not immediately eliminated, it enters the soil by percolating through the soil particle pores. During the procedure of permeation it contaminates the soil. The soils which show biggest surface area of all types of soils are fit for complexing different chemicals and particles (Talukdar, 2006).

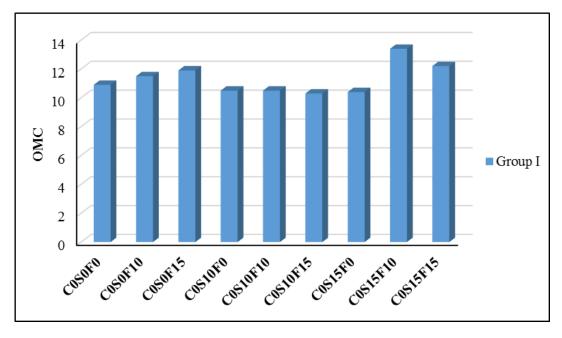
The surface of the adversely charged soil particles could adsorbed water molecules. At the point when replaceable cations are available on the soil surface they tend to be hydrated and may leave the surface. Crude oil is a mixture of hydrocarbons nature of which is non polar. When mixing happen between water saturated soil and crude oil, water molecules will be displaced from the vicinity of the soil particles. Subsequently, charge concentration around the particle surface may increment or diminishes relying on the types of soil minerals. The plasticity behaviour of soil depends on this charge concentration. Liquid limit is additionally depends on the kind of structure of soil. Scott (1963) identified that when soil is not completely saturated, the coefficient of permeability is minimal than that of completely saturated soil. In the event of crude oil mixed soil, crude oil may hamper the soil to saturate totally because of which the coefficient of permeability of crude oil contaminated soil might be diminished.

6.4 Results for geotechnical tests program of soil mixed with crude oil, FA and GGBFS

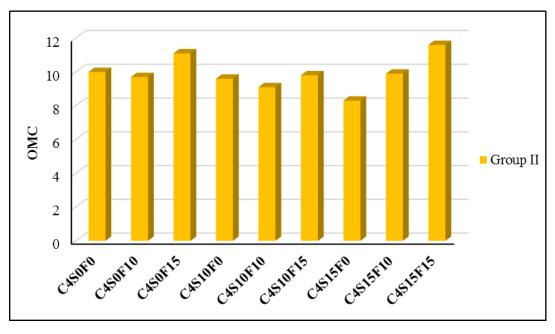
6.4.1 Compaction

Compaction test results revealed optimum moisture content and maximum dry density. In order to show the effect of crude oil contamination and mineral admixture such as ground granulated blast furnace slag and fly ash on both compaction parameters with sandy soil. Soil samples prepared in four groups 0%, 4%, 6% and 8% mixed by dry weight with crude oil. Each group consists of nine mixtures with various percentage of 0%, 10% and 15% from each of GGBFS and FA as shown in Table 3.5 in chapter 3. Figures 6.8 and 6.9 illustrated the effect of optimum moisture content in all groups and in each mixtures. OMC decreased with adding crude oil by 8% to the soil sample, this could be due to the capillary effect in soil. Usually, the spaces between soil particles could be

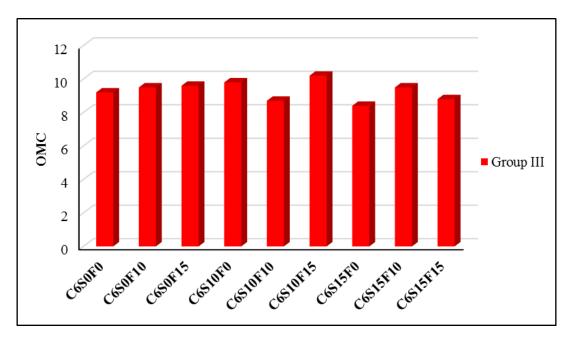
considered as a capillary tube, which causes the rise of the water in it. While the compaction weight is falling on the soil, these spaces became thinner and thinner, which increases the capillary tension. When increased FA in group one, OMC increased in mix.1, 2 and 3. But in other binary mixes significant effect on OMC, the highest value recorded in mix 8 which is contain15% of GGFBFS and 10% of FA. Although, in group1, group2 and group3 optimum moisture content increased with increased fly ash but, decreased with increased ground granulated blast furnace slag. The results supported by work of other researchers such as (Mahvash et al., 2017; Okonta and Govender, 2011; Sabbar et al., 2017).



(a)



(b)



(c)

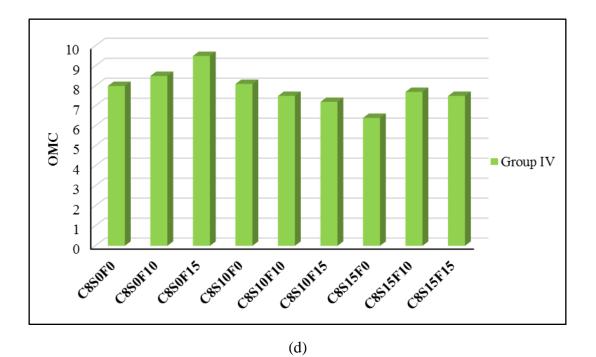


Figure 6.8 Relation between OMC and mixtures in (a) group I, (b) group II, (c) group III, (d) group IV.

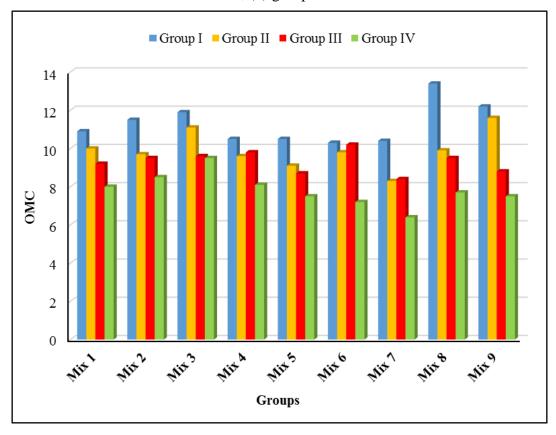
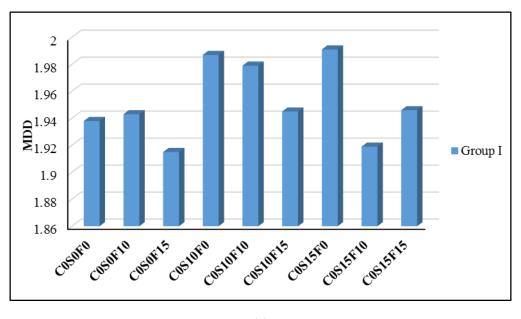


Figure 6.9 Relation between OMC and mixtures in all groups.

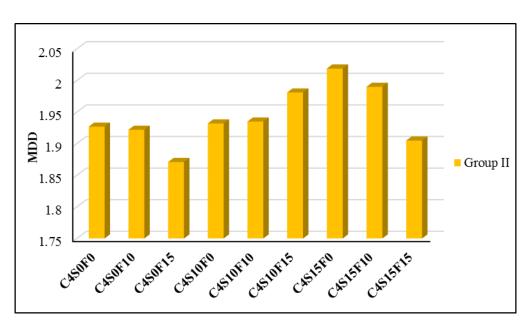
Influence of crude oil contamination and mineral admixtures on maximum dry density of sandy soil samples were showed in Figure 6.10 and Figure 6.11. While increased fly ash

maximum dry density decreased in all groups. After addition of GGBFS increased maximum dry density and in binder mixes demonstrated the effect of both mineral admixtures the peak value of MDD is in mix 7 with contaminated by oil in group 2. Almost always, maximum dry density increased with increased crude oil, the maximum value recorded in 8% contaminated crude oil content. Results for OMC and MDD are supported by results of many researchers such as Mahvash et al. (2017) utilizing FA to improve sandy soil in 5%, 10% and 15% by dry weight with 3% of cement as activator. The results show increasing of OMC with adding FA and MDD reduced by adding FA to mixtures. Okonta and Govender, (2011) found the same results while used FA in different percentage (6%, 12% and 18%) with (4% and 8%) lime in mixtures, decrease MDD and increase OMC with addition of fly ash (FA). Sabbar et al., (2017) display the results, showing how the maximum dry density increased and optimum moisture content decreased with increasing slag content.

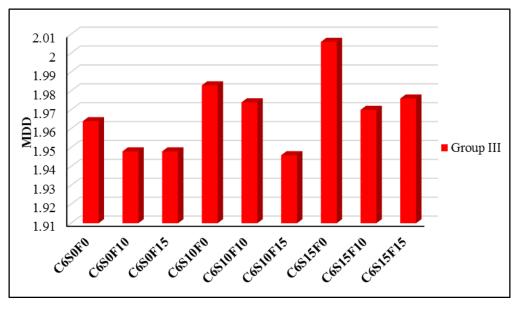
Tyagi and Soni (2019) investigated the effect of GGBFS and FA on sandy soil and utilized 5%, 10%, 15%, 20%, 25% and 30% of GGBFS with 3%, 6%, 9%, 12%, 15% and 18% of FA with the increase in GGBFS and fly ash percentage, optimum moisture content (OMC) goes on increasing while maximum dry density (MDD) first goes on increasing and then decreasing, hence, the maximum compaction of soil is achieved at 15% OMC, 15% GGBFS, and 9% fly ash. Sharma and Trivedi (2016) reported the compaction parameters of sandy silt soil by blending with fly ash in different percentage. Soil is mixed with fly ash at 5%, 10%, 15%, and 20%. The optimum water content increases and dry density decreases with increases in fly ash due to progressive increasing silt particles in soil.







(b)





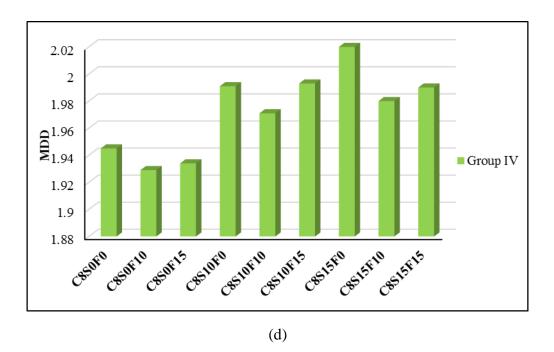


Figure 6.10 Relation between MDD and mixtures in (a) group I, (b) group II, (c) group III, (d) group IV.

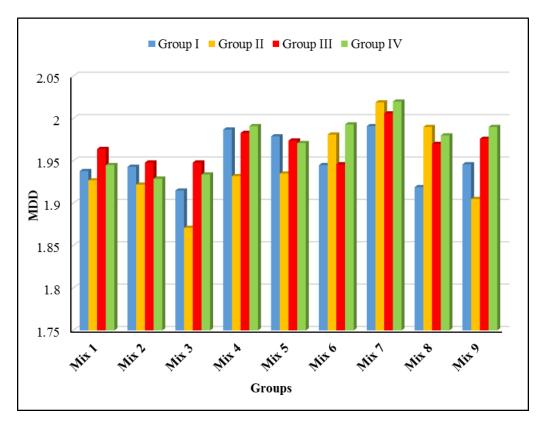
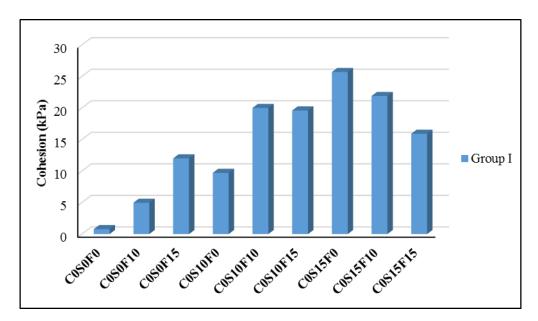


Figure 6.11 Relation between MDD and mixtures in all groups

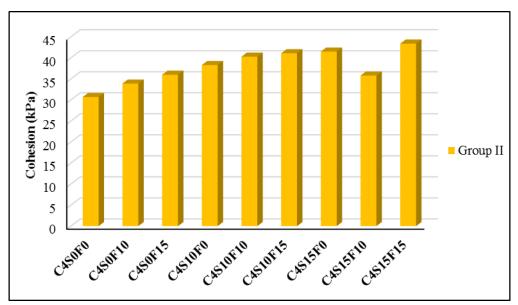
6.4.2 Direct shear

Shear strength parameters are apparent cohesion and angle of internal friction (c and φ). Apparent cohesion results obtained from this study are shown in Figure 6.12 and Figure 6.13. Apparent cohesion increased with increase fly ash in mixes 1, 2 and 3 in contaminated and uncontaminated soil samples. Furthermore, in binary mixes binder significant impact on the result of apparent cohesion, peak value of apparent cohesion is 89.8 kPa at mix 9 in group IV 8% crude oil content. Increased GGBFS also slightly increased apparent cohesion of soil. Although, huge difference value for apparent cohesion between group 1 uncontaminated soil sample with other groups contaminated by crude oil at 4%, 6% and 8% by dry weight of sandy soil due to the effect of crude oil on sandy soil particles. This change of behaviour is attributed to the viscous properties of the contaminants which helps in bringing the individual soil particles more close together hence making it into more compact configuration. Results are in coincident with the outcomes of Sabbar et al., (2017) which they used slag to stabilize sandy soil in 2%, 4% and 6% by dry weight, apparent cohesion increased with increasing slag content up to 6%. The positive impact of slag content on the shear strength of sandy soil may be connected to the role of slag in filling the voids between sand particles. Consequently, it

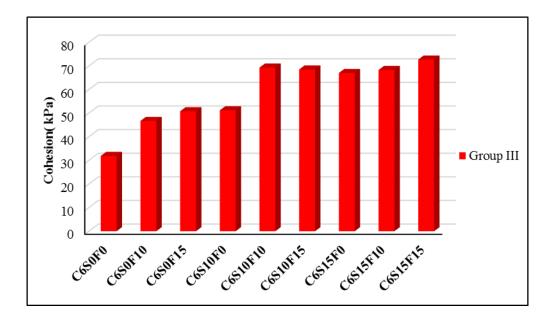


led to increase the internal friction angle and apparent cohesion.





(b)



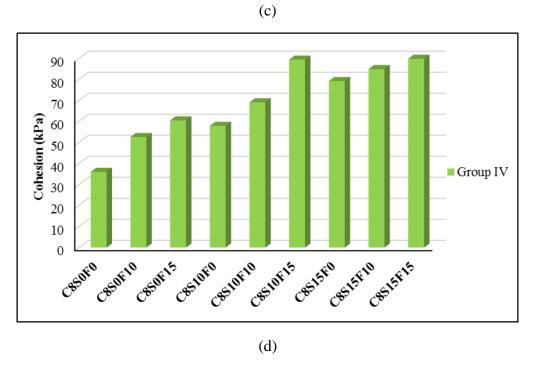


Figure 6.12 Relation between apparent cohesion and mixtures in (a) group I, (b) group II, (c) group III, (d) group IV.

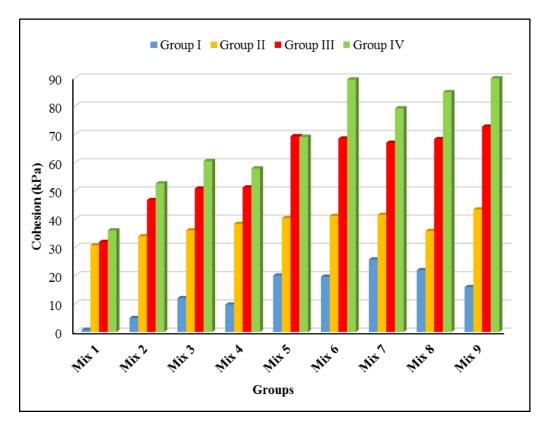


Figure 6.13 Relation between apparent cohesion and mixtures in all groups.

Soil friction angle is a shear strength parameter of soils. Its definition is derived from the Mohr-Coulomb failure criterion and it is used to describe the friction shear resistance of soils together with the normal effective stress. In the stress plane of Shear stress-effective normal stress, the soil friction angle is the angle of inclination with respect to the horizontal axis of the Mohr-Coulomb shear resistance line.

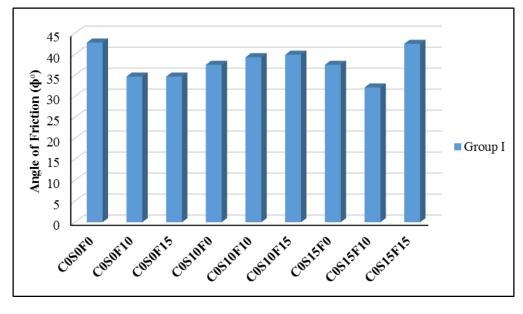
In general, angle of internal friction is decreased by adding crude oil for soil samples. In group one which crude oil content equal to zero, value of angle of internal friction is higher than other groups, furthermore in group one recorded various value for angle of internal friction due to addition different proportions of mineral admixtures FA and GGBFS for nine mixes in this group. Highest value recorded in mix one in group one (C0S0F0) is 42.8° which considerable as a control.

In group II, group III and group IV after addition crude oil by 2%, 6% and 8% respectively angle of internal friction decreased due to increased crude oil as demonstrated in Figures 6.14 and 6.15.

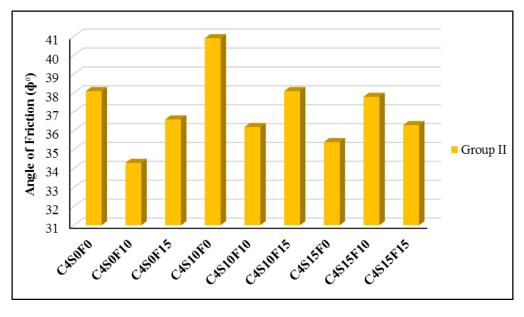
Concerning to addition fly ash and its influence on (ϕ) in all groups decreased (ϕ) with

increased in mixes 1, 2 and 3. However addition GGBFS effected on (φ) increased value but variety in the value depended on the percentage of each mineral in binder as shown in Figure 6.15. the results is confirmed by many researcher such as Kumar et al., (2014) utilized fly ash mixed with sand in different percentage as 100%S, 80%S+20%FA, 60%S+40%FA, 40%S+60%FA, 20%S+80%FA, 100% FA. Shear strength parameter of fly ash and Sand shows a variation in apparent cohesion from 0.01 to 0.021kg/cm² and angle of internal friction (φ) from 23° to 34° in wet condition it can be safely used in construction of embankment.

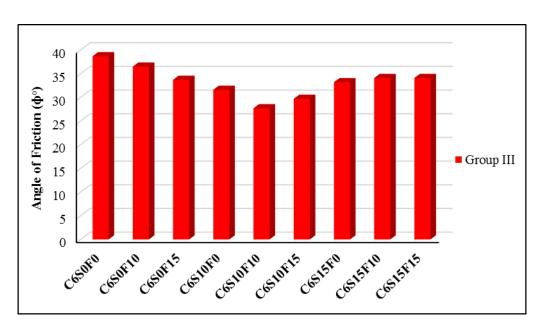
Sharma and Trivedi (2016) reported the shear strength parameters of sandy silt soil by blending with fly ash in different percentage. Soil was mixed with fly ash at 5%, 10%, 15%, and 20%. The shear strength of the soil enhances due to presence of fly ash. So, fly ash has a potential to improve engineering characteristics of sandy silt soil. Hence the main objective of this work is to utilize industrial waste like fly ash to improve the strength of sandy silt soil with its optimum percentage of fly ash.



(a)







(c)

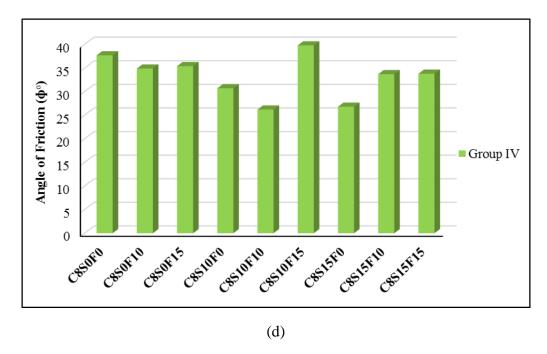


Figure 6.14 Relation between angle of friction and mixtures in (a) group I, (b) group II, (c) group III, (d) group IV.

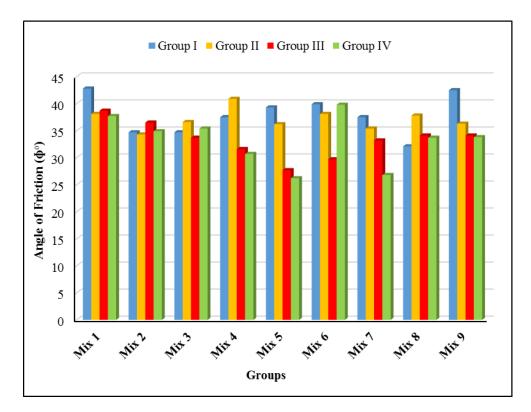


Figure 6.15 Relation between angle of friction and mixtures in all groups.

6.5 Environmental experimental results

6.5.1 Results of soil pollution

The data acquisitions are carried out in laboratory. The data is expressed in tables and graphs for the sake of interpretation. Ten soil samples were collected and used in experimental tests (Table 6.6).

The pH value of soil was 7.4 which is deemed to be within acceptable soil pH values that can sustain growth of plant cover. Other samples collected form an area which had been contaminated as a result of oil spillage and also recorded ideal pH values. This further demonstrated that the spillage of oil had no impact on the soil pH values of the affected areas in Erbil.

However, an increase in Electrical Conductivity (EC) was recorded in the soil from the areas where oil spillage had occurred. The average ratio recorded from soil sample in the affected area was 2.1366 dS/m. This data is relatively high when compared to electrical conductivity from the controlled soil sample which was 0.5 dS/m. The high levels of electrical conductivity Siemens per meter (S/m) in the areas with oil spillage indicate that the soil was containing high levels of cations and anions which are charged ions. In carrying out the EC test, the salinity levels of the tested soil is manifested as high levels of conductivity indicating high salinity levels in the soil.

The study analysed the lead levels in the soil samples. Lead level is the availability of lead elements in a given soil which increases the salinity levels in the affected soil. The data analysed in the study showed an increase in lead concentration levels in the soil samples from areas where the crude oil spillage occurred. The average concentration of lead levels from the crude oil polluted areas was 22.54 ppm. This was higher than the average lead levels recorded from the control soil used (i.e. soil from non-polluted areas) which was recorded at 4.6 ppm. The difference in concentration is remarkably high as crude oil contains high levels of lead.

Para	imeters	рН	EC	Organic Matter	Calcium (Ca)	Sodium (Na)	Potassiu m (K)	Phosphoru s (P)	Magnesiu m (Mg)	Chromium (Cr)	Lead, (Pb)	Sulphate	Chloride
Uni	t	-	ds/m	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
1	Pit 1	7.3	2.71	1.81	76.3	15.6	18.3	8.1	38.4	29.7	26.4	104	250
2	Pit2	6.5	3.03	1.92	82	16.11	16.65	9.85	18.2	24.9	32.3	110	250
3	surface soil	7.1	2.94	1.89	74.33	14.43	15.72	5.03	16.08	20.8	35.2	111	230
4	surface soil	7.1	3.03	1.96	102.5	10.94	19.41	8.1	43.25	27.2	18.2	110	156
5	surface soil	7.3	0.72	1.53	55.2	10.32	13.23	8.38	15.17	14.6	14.5	60	210
6	surface soil	6.7	2.52	1.86	34.7	11.45	11.72	6.8	23.9	19.4	21.1	77	210
7	surface soil	6.6	1.07	1.65	43.1	12.27	17.21	7.5	27.4	13.1	20.6	25	320
8	Kawrgosk Soil	6.7	0.88	1.61	65.3	15.7	16.06	5.3	19.6	12.3	16.2	27	390
9	Kawrgosk Soil	6.0	2.33	1.77	38.2	14.2	18.2	8.2	21	18.6	18.4	74	240
10	control soil	7.4	0.5	0.25	40.3	10.1	20.3	6.1	19.7	11.5	4.6	18	16

 Table 6.6 Soil parameter results for study area.

Moreover, the potassium concentration levels in the soil of study area also affected by the crude oil spillage. The potassium levels in the soil sample from areas contaminated with crude oil had decreased significantly. The average potassium levels from the control soil (collected from non-polluted areas) were 20.3 ppm which was favorable to plant growth. In contrast, the concentration of potassium in soil samples from the crude oil polluted areas were recorded 16.27 ppm. This suggested low value compared to the normal soil potassium concentration range. This can be understood since potassium is sensitive to crude oil and thus its concentration reduced with the presence of the oils. To treat the potassium levels of the soils from the affected areas, it's recommended to use fertilizer with high potassium concentration in the farmlands from some time as this will raise the levels in the soil.

Substance	Target level of soil quality examined through leaching and content tests
cadmium	0.01 mg/l in sample solution and less than 0.4mg/kg in rice for agricultural land
lead	0.01 mg/l or less in sample solution
chromium	0.05 mg/l or less in sample solution
total mercury	0.0005 mg/l or less in sample solution
copper	less than 125 mg/kg in soil agricultural land
dichloromethane	0.02 mg/l or less in sample solution
carbon tetrachloride	0.002 mg/l or less in sample solution
chloroethylene	0.002 mg/l or less in sample solution

Table 6.7 Environmental quality standards for soil pollution (MEJ, 1994)

The environmental quality standards for soil pollution set by the Ministry of Environment (MOE) in Japan evaluate the level of soil pollution and other soil parameters. In accordance with the Basic Environment Law, environmental quality standards for soil have been put in place for eight items to protect human health and conserve the living environment (see Table 6.7); they are reviewed as needed, based on up-to-date scientific findings. These environmental quality standards for soil contamination consist of the elution standards (designed to conserve the soil's capacity to protect foods), each of which

serves as the basis for detecting the presence of contamination and devising relevant pollution control measures.

6.5.2 Results of water pollution

In the Table 6.8 shows the results of Turbidity, pH, electrical conductivity (EC), TH, total suspended solids (TSS), total dissolved solids (TDS), Biochemical Oxygen Demand (BOD)₅, oil and grease, Ca, Cl, NO₃, SO₄ and Mg.

The pH is a unit that states represent the strength of a solution based on its acidic or basic properties. In this study the pH of the test samples ranged from 5.96 to 7.5 showing that the water is acidic. The highest pH value 7.5 was observed in water sample 4. Since the largest variety of aquatic animals prefer 6.5 - 8.5, it thus mean that when the pH is outside this range, diversity within the water body may decrease due to physiological stresses and reduced reproduction. The pH of the water can be attributed to the presence of dissolved salts of some metals in the water. The range for pH of the water was below the range expected for unpolluted water 6.5 - 8.5, hence the water is polluted with regards to pH.

Total suspended solids (TSS) expresses the suspended matter in the river. The results in Table 6.8 revealed that TSS has highest value at the water sample 2 in pond 2 was 380 ppm and decreased in other samples. TSS is highest at pond sample because of the nature of the soil.

No.	Parameters	Unit	WS1	WS2	WS3	WS4	WS5	WS6	WS7	WS8	WS9
1	Turbidity	NTU	35.5	26.8	23.9	18.6	27.3	34.1	26.3	29.2	21.7
2	рН	_	6.83	6.1	7.3	7.5	6.03	6.1	5.96	6.8	7.1
3	EC	dS/m	2.383	2.109	1.192	1.184	0.986	2.174	1.827	2.962	2.719
4	Total Hardness	mg/L	63	55	60	40	132	86	27	91	86
5	Total Suspended solids (TSS)	mg/L	130	380	300	240	270	170	210	316	284

 Table 6.8 Water parameter results for study area.

6	Total Dissolved Solids (TDS)	mg/L	1124	740	592	890	729	861	680	1082	896
7	Biochemical Oxygen Demand (BOD) ₅	mg/L	8.31	7.9	8.04	6.72	11.5	9.16	10.2	13.2	18.7
8	Oil and grease	mg/L	21	18	28	20	19.8	17.6	22	19	22.1
9	Calcium, (Ca)	mg/L	138	153	136	112	148	139	125	164	191
10	Chloride, (Cl)	mg/L	167	398.3	138.2	285.5	106.5	289.3	186.1	297.2	233.4
11	Nitrate, (NO ₃)	mg/L	11.8	13.9	9.32	7.8	23.1	9.6	12.8	10.1	8.9
12	Sulfate (SO ₄)	mg/L	281	326	128	268	184	233	179	218	182
13	Magnesium, (Mg)	mg/L	55.3	135.8	68.12	58.39	86.4	73.8	89.1	158.3	138.1

(WHO, 2000) Observations from the TSS range, indicates the degree of pollution. High level of solids decreases the passage of light through water, thereby slowing photosynthesis of aquatic plants, clogging fish gills and visibility in recreational waters. The measurement of total solids can be useful as an indicator of the effects of runoff from urban and agricultural areas. The observed range for the TSS of water was above the permissible limits of unpolluted water. (WHO, 2000) Observations that TSS has a positive correlation with the ion in the test samples with Mg²⁺ and NH₄⁺. From the results it can be deduced that the high TSS values of the sample are mostly affected by magnesium ion.

Total dissolved solid (TDS) expresses the salinity of the water. The results in table 6.8 show that TDS was highest at pond 1 of pollution water was 1124 ppm and at different levels in other samples. Several results are above the acceptable limits; this indicates that the flowing water at a low rate and the dissolved solids accumulate on the control. This could also depend on the nature of the soil or because the sampling was collected during the rainy season. Samples are taken from source of pollution.

Drinking water with high dissolved solids (dissolved minerals, salts and humic acid) may not taste good and may have a laxative effect. High TDS indicate hardness and cause staining. The high level of TDS is caused by certain metals present, particularly Magnesium, Potassium, Copper and Zinc. Water with a TDS < 1200 mg/l generally has an acceptable taste. For water to be treated for domestic potable supply, a TDS < 650 mg/l is preferred (Belan F, 1988).

The mean concentration of nitrate (NO₃⁻) in the water (11.92 mg/l) was greater than the maximum permissible limit 10.0 mg/l. According to FAO (2017) Irrigation Water Quality Guidelines the results were slight to moderate for degree of restriction. Magnesium is often associated with calcium in all kinds of water. Magnesium is essential for chlorophyll growth and acts as a limiting factor for the growth of phytoplankton. Therefore, depletion of magnesium reduces the number of phytoplankton's population. The quantities of Calcium in natural water depend upon the type of rocks. Small concentration of calcium is beneficial in reducing the corrosion in water pipes. Magnesium hardness particularly associated with sulfate ion has laxative effect on persons unaccustomed to it. In the present study, Calcium and Magnesium contents are with within the recommended standards.

Oil and grease content value greater than acceptable level. Average value for them is 20.83 ppm higher than 10 ppm standard level. In Table 6.9 presented main parameters for irrigation water quality based on FAO guide lines. The salinity, infiltration specific ion toxicity and miscellaneous effects are explained in the table below.

			Degree	Degree of restriction on use			
Potential irrigat	ion problems	Units	None	Slight to moderate	Severe		
Salinity (affects cr availability)	rop water						
ECw		ds.m ⁻¹	< 0.7	0.7 – 3.0	> 3.0		
TDS		mg.l ⁻¹	< 450	450 - 2000	> 2000		
Infiltration (affects infiltration rate of water in to the soil; evaluate using EC _w and SAR together)							
$\mathbf{SAR} = 0 - 3$	and EC _w =		> 0.7	0.7 - 0.2	< 0.2		

Table 6.9 Guidelines for interpretation of water quality for irrigation (FAO irrigationwater quality guidelines, 2017)

SAR = 3 - 6	and EC _w =		> 1.2	1.2 - 0.3	< 0.3
SAR = 6 - 12	and EC _w =		> 1.9	1.9 - 0.5	< 0.5
SAR = 12 - 20	and EC _w =		> 2.9	2.9 - 1.3	< 1.3
SAR = 20 - 40	and EC _w =		> 5.0	5.0 - 2.9	< 2.9
Specific ion toxic sensitive crops)	city (affects				
Sodium (Na)					
Surface irrigation	l	SAR	< 3	3 - 9	>9
Sprinkler irrigation	on	meq.1-1	< 3	> 3	
Chloride (Cl)					
Surface irrigation	l	meq.1 ⁻¹	< 4	4 -10	> 10
Sprinkler irrigation	on	meq.1 ⁻¹	< 3	> 3	
Boron (B)		mg.l ⁻¹	< 0.7	0.7 - 3.0	> 3.0
Miscellaneous eff susceptible crops)	fects (on				
Nitrate (NO3-N)		mg.l ⁻¹	< 5	5 - 30	> 30
Bicarbonate (HC sprinkling only)	O3) (overhead	meq.1 ⁻¹	< 1.5	1.5 - 8.5	> 8.5
рН			Normal	range 6.5 -8.4	

Also, Standard of water quality for agriculture based on Food and Agriculture Organization (FAO, 2013) showed in Table 6.10. To compare and evaluate experimental work results with FAO standard.

Water parameter	Symbol	Unit	Usual range in irrigation water
Electrical Conductivity	EC	ds/m	0 - 3
Total Dissolved Solids	TDS	mg/l	0 - 2000
Calcium	Ca	me/l	0 - 20
Magnesium	Mg	me/l	0 - 5
Sodium	Na	me/l	0 - 40
Carbonate	CO ₃	me/l	0 - 1
Bicarbonate	HCO ₃	me/l	0 - 10
Chloride	Cl	me/l	0 - 30
Sulfate	SO ₄	me/l	0 - 20
Oil and grease	-	mg/l	0 - 10
Nitrate-Nitrogen	NO3-N	mg/l	0 - 10
Ammonium-Nitrogen	NH4-N	mg/l	0 - 5
Phosphate-Phosphorus	PO4-P	mg/l	0 - 2
Potassium	K	mg/l	0 - 2
Boron	В	mg/l	0 - 2
Acid/Basicity	pН		6.0 -8.5

Table 6.10 Standard of water quality for agriculture (FAO, 2013)

• ds/m = deciSiemen/meter in S.I. units (equivalent to 1 mmho/cm = 1 millimmho/ centimeter)

• $mg/l = milligram per liter \simeq parts per million (ppm).$

• me/l = mill equivalent per liter (mg/l ÷ equivalent weight = me/l); in SI units, 1 me/l= 1 millimol/liter adjusted for electron charge.

WHO produces international norms on water quality and human health in the form of guidelines that are used as the basis for regulation and standard setting world-wide. The Guidelines for drinking-water quality (GDWQ) promote the protection of public health by advocating for the development of locally relevant standards (Iraqi Standards) and regulations (health based targets), adoption of preventive risk management approaches covering catchment to consumer (Water Safety Plans) and independent surveillance to ensure that Water Safety Plans are being implemented and effective and that national standards are being met. In Table 6.11 could see WHO and Iraqi drinking standards.

No.	Parameters	Unit	WHO	Iraqi Standards
1	Turbidity	NTU	5	5
2	рН	-	6.5-8.5	6.5-8.5
3	EC	µS/cm	2500	2000
4	Total Hardness	mg/L	500	500
5	Total Suspended solids (TSS)	mg/L	60	60
6	Total Dissolved Solids (TDS)	mg/L	1000	1000
7	Biochemical Oxygen Demand (BOD)5	mg/L	10	10
8	Oil and grease	mg/L	5	5
9	Calcium, (Ca)	mg/L	200	150
10	Chloride, (Cl)	mg/L	250	250
11	Nitrate, (NO ₃)	mg/L	50	50
12	Sulfate (SO ₄)	mg/L	250	250
13	Magnesium, (Mg)	mg/L	150	150

Table 6.11 WHO and Iraqi standards for drinking water (WHO and MOH, 1998)

6.6 Flow and penetration of crude oil

6.6.1 Field investigation for flow and penetration of crude oil

Crude oil spillages are usually an environmental issue that should be subjected to great attention as they contribute greatly to environment and soil pollution. It is recommended that an accurate assessment of the impacts of the spillages on the environment. There are various predictive tools that are used to assess the quantity of the spills and how much has been absorbed by the soil. Identifying the quality helps in coming out with an efficient remedy thus managing the hazards associated with the spill. The study is improving the predictions made on the non-aqueous liquids penetration on the soil in cases of spills using the crude oil spillage case study.

As indicated above, understanding the physical phenomenon of the spill propagation over the surface is key in coming up with remedies. The objective here was on soils that were slightly sloppy thus exhibiting just the fundamental physical mechanisms. The approach was useful as it targeted the gravity controlled, density controlled as well as viscosity controlled mechanism. It was hypothesized that the model tested here to determine the spill propagation could be constituted in a way that could encompass topographical influences. From the spills, it was observed that slight changes such as the spill source geometry could influence the spill spread shape. Such differences make it hard to perfectly simulate an identical spill distribution regardless having all other factors (e.g. spill amount and spill rate) equal. Simmons and Keller (2003) had in their report, which had identified particular soils and non-aqueous liquids for study, indicated such common behaviors on ideal spills on soil surfaces.

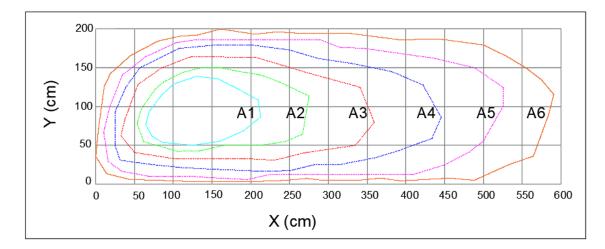


Figure 6.16 Profile of area polluted by crude oil.

In this study, three scenarios were used to observe penetration of crude oil. In each scenario utilized one barrel of crude oil on different locations which has different properties.

First scenario on wet sandy soil, spilt one barrel of crude oil (210 liters) at flow rate 1.926 l/s on the area. Spillage time approximately is 109 second and calculated polluted area is 11meter square. Polluted area divided on six parts based on each 20 seconds in spillage time as shown in Figure 6.16. Penetration of crude oil on sandy soil sample was recorded for five days in each area by special drilling tool. The sand and silt loam always contained a small amount of water to better manage packing them to form a smooth surface. The spread of crude oil on soil surface involves both spreading and infiltration into the subsurface. A modeling challenge is to predict the size of the spill area as a result of the volume of liquid applied. This area is the spill signature that is a visible indicator of the event. Moreover, the spill area dynamically progresses as the spilled volume increases with time.

In the second scenario repeat the same procedure on the dry sand to compare the difference between both types of sandy soil with the same properties of crude oil. In the third scenario also, repeat the same procedure with clay soil which is mixed with a little of loam and sand. Clay soil polluted by one barrel of crude oil with the same properties. Results of crude oil penetration per (cm) in all cases for wet sand, dry sand and clay soils are illustrated in Tables 6.12, 6.13 and 6.14 respectively.

	A1	A2	A3	A4	A5	A6
1 st day	8.5	7	5	4.5	4	3.5
2 nd day	10	9.5	7	7	6	4
3 rd day	12	11.5	9	9	7.5	4
4 th day	13.5	12.5	10	9.5	8	6
5 th day	15	14	11	9.5	8.5	7

Table 6.12 Penetration depth (cm) for each area in wet sandy soil sample.

Table 6.13 Penetration depth (cm) for each area in dry sandy soil sample.

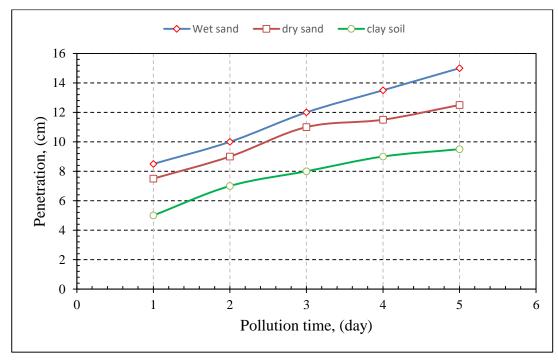
	A1	A2	A3	A4	A5	A6
1 st day	7.5	6.5	5	4	4	3
2 nd day	9	8	6.5	5	4.5	3.5
3 rd day	11	10	7	8	7.5	3.5
4 th day	11.5	12	8	8.5	7.5	6
5 th day	12.5	12	9.5	8.5	8	6.5

Table 6.14 Penetration depth (cm) for each area in clay soil sample.

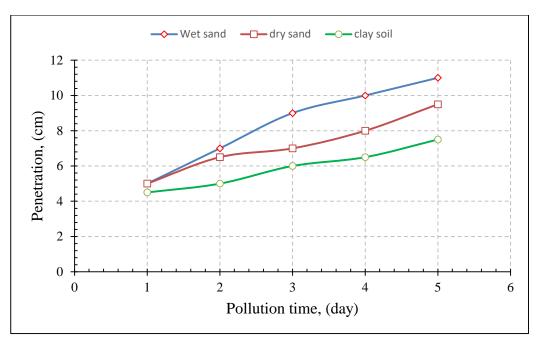
	A1	A2	A3	A4	A5	A6
1 st day	5	4.5	4.5	4	3	2.5
2 nd day	7	6	5	4.5	3	3
3 rd day	8	6.5	6	6	4.5	3
4 th day	9	7	6.5	6.5	5	4.5
5 th day	9.5	8.5	7.5	7	5.5	5

In Figure 6.17 (a) shows the relation between crude oil penetrations in three different soil type with pollution duration in area 1 (A1) at first 20 seconds in spilt oils on soil surfaces. In the results observed that penetration of crude oil as a liquid on wet sand is higher than others and in clay soil is lower due to low permeability properties of clay soil. Figures 6.17 (b) and 6.17 (c) display same results with a decrease in penetration depth in area 3 (A3) and area 6 (A6) respectively.

At all scenarios depth of penetration crude oil in to the soils in root zones and they have negative impact on plants. There are several factors effect on rate of penetration liquids on soil such as properties of liquids, viscosity, density and flow rate. Consequently, duration of pollution, temperature and evaporation considered in influenced factor. Type of soil and porosity and void ratio. Coefficient of permeability of soil has huge influence on infiltration properties of soil.



(a)





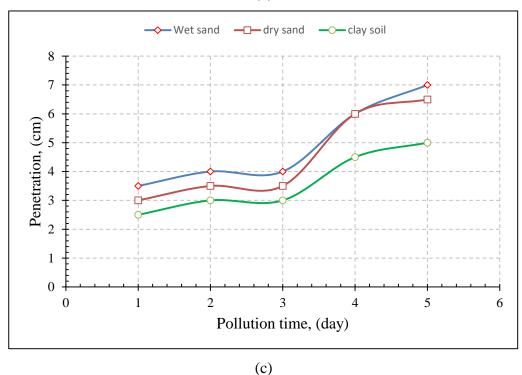


Figure 6.17 (a) penetration depth vs. time in area 1 (A1), (b) penetration depth vs time in area 3 (A3), (c) penetration depth vs. time in area 6 (A6)

6.6.2 Laboratory investigation for flow and penetration of crude oil

Laboratory experiments were carried out to observe the penetration of crude oil into the soil sample. Special mould which has dimensions and weight was utilized in the investigation, as shown in Table 6.15 and Figure 6.18.



Figure 6.18 Sample preparation of soil material.

As shown in Figure 6.18, the height of soil in the side mould was 25 cm, and the remaining space was 10 cm. After that, crude oil was added to the soil sample at the height of 8 cm, and the remaining sample (soil with crude oil) was used to penetrate the crude oil in the soil sample (see Figure 6.19). The penetration depth of the crude oil into the soil was recorded daily until the fifth day. Finally, after the fifth day, the crude oil reached the bottom of the mould, as shown in Table 6.16 and Figure 6.20.



Figure 6.19 Adding crude oil to soil sample.

Many factors can effect on the penetration of crude oil into the soil. The main factors are:

First, type of soil and oil. Second, the density of soil which has a significant influence on penetration of oil. Third, classification of soil and percentage of each class. Clay soil is impermeable material, but if the soil contains clay and sand, the permeability of oil into

soil might be increased. Furthermore, percentage of moisture content and void ratio are very important to indicate the penetration ratio. Type and properties of oil also plays an important roles on penetration.



Figure 6.20 Final step in soil sample.

Parameter	Unit	Value
Mould height (inside)	cm	35
Soil height	cm	25
Crude oil height	cm	8
Mould diameter (inside)	cm	8.6
Mould weight	gram	2055

 Table 6.15 Details of mould soil sample.

Duration (day)	Penetration (cm)	Notes
1 st day	3	Start date
2 nd day	9	
3 rd day	17	
4 th day	21	
5 th day	25	Reach to bottom

Table 6.16 Penetration depth (cm) for each area in clay soil sample.

6.7 Statistical analysis

Statistics science is utilized widely in many areas such as scientific research, business intelligence, financial projects and data analysis and other different areas. Many businesses depend on statistical analysis and it is becoming very important. One of the most important reasons is that statistical data is used to predict future trends and to reduce risks. Moreover, if you look around yourself, you will see a many products that have been improved thanks to the results of the statistical research and analysis.

In the context of business intelligence, statistical analysis involves collecting and scrutinizing every data sample in a set of items from which samples can be drawn. A sample, in statistics, is a representative selection drawn from a data collection.

Statistical analysis can be broken down into five discrete steps, as follows:

- Define and describe the nature of the data to be analyzed.
- Explore the relation of the data to the underlying.
- Create or make a model to summarize understanding of how the data relates to each other.
- Prove (or disprove) the validity of the model.
- Employ predictive analytics to run scenarios that will help guide future actions.

Minitab is a software product that helps us to analyze the data. This is designed essentially for the Six Sigma professionals. It provides a simple, effective way to input the statistical data, manipulate that data, identify trends and patterns, and then extrapolate answers to the current issues. This is most widely used software for the scientific research of all sizes - small, medium and large. Minitab provides a quick, effective solution for the level of analysis required in most of the Six Sigma projects. Analysis of variance (ANOVA) is an analysis tool used in statistics that splits an observed aggregate variability found inside a data set into two parts: systematic factors and random factors. The systematic factors have a statistical influence on the given data set, while the random factors do not. Analysts use the ANOVA test to determine the influence that independent variables have on the dependent variable in a regression study.

6.7.1 General linear model: OMC versus oil, slag, fly ash

The General Linear Model (GLM) is a useful framework for comparing how several variables affect different continuous variables. In its simplest form, GLM is described as:

Data = Model + Error

GLM is the foundation for several statistical tests, including ANOVA and regression analysis. In ANOVA, "data" is the dependent variable scores, the "error" the model is the experimental conditions, and the "error" is the part of the model not explained by the data. In regression analysis, the independent predictors make up the "model" and the residuals are the "error" component.

The general linear model analysis of variance (GLM-ANOVA) is a significant statistical analysis and diagnostic tool describes the statistical connection between responses and factors, and quantifies the dominance of a control factor by decreasing the error variance.

To find the statistical significance of the effective design response parameters at 95% confidence level which are OMC, MDD, c and ϕ on the dependent design factors parameter of oil, slag and FA.

In the resulting p-values shown in Table 6.18 indicate the significance of considered design factors on the design responses obtained from the numerical analyses. When the p-value is less than 0.05, the parameter is accepted as a significant factor on the response at 95% confidence level. Moreover, as illustrated in Table 6.18, the influenced of all

design factors on the responses are found to be statistically significant. In the Tables 6.17, 6.18, 6.19, 6.20 and Figure 6.21 demonstrated information and results in a general linear model for OMC versus oil, slag, fly ash of the factor information, analysis of variance (ANOVA), model summery and coefficients respectively.

• Method

Factor coding (1, 0)

Factor Information

Factor	Туре	Levels	Values
Oil	Fixed	4	0, 4, 6, 8
Slag	Fixed	4	0, 5, 10, 15
Fly ash	Fixed	4	0, 5, 10, 15

Table 6.17. Factor information

Table 6.18 Analysis of variance (ANOVA) results	Table 6.18 Ana	lysis of va	riance (ANC	OVA) results
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Source	DF	Adj SS	Adj MS	F-Value	P-Value
Oil	3	267.726	89.2421	142.38	0.000
Slag	3	8.610	2.8701	4.58	0.004
Fly ash	3	7.538	2.5125	4.01	0.009
Error	182	114.072	0.6268		
Lack-of-Fit	54	112.727	2.0875	198.67	0.000
Pure Error	128	1.345	0.0105		
Total	191	397.946			

 Table 6.19 Model summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.791688	71.33%	69.92%	68.10%

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	11.481	0.181	63.54	0.000	
Oil					
4	-2.139	0.162	-13.23	0.000	1.50
6	-2.220	0.162	-13.74	0.000	1.50
8	-3.245	0.162	-20.08	0.000	1.50
Slag					
5	0.326	0.162	2.02	0.045	1.50
10	0.589	0.162	3.64	0.000	1.50
15	0.391	0.162	2.42	0.017	1.50
Fly ash					
5	-0.130	0.162	-0.81	0.421	1.50
10	-0.319	0.162	-1.97	0.050	1.50
15	-0.525	0.162	-3.25	0.001	1.50

Table 6.20 Coefficients

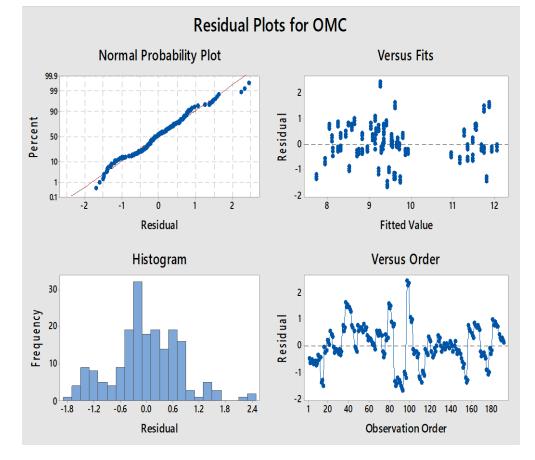


Figure 6.21 Residual plots for OMC.

6.7.2 General linear model: MDD versus oil, slag, fly ash

In the below Tables (6.21, 6.22 and 6.23) and Figure 6.22 show results for the factor information, analysis of variance (ANOVA), model summery and coefficients in general linear model for MDD versus Oil, Slag, Fly ash. The P-Values greater than 0.05 the parameter is not accepted as a significant factor on the response at 95% confidence level.

Method

Factor coding (1, 0) Factor Information

Factor	Туре	Levels	Values
Oil	Fixed	4	0, 4, 6, 8
Slag	Fixed	4	0, 5, 10, 15
Fly ash	Fixed	4	0, 5, 10, 15

Table 6.21 Factor information

Analysis of variance (ANOVA) results

Table 6.22 Analysis of variance (ANOVA) res	ults
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Source	DF	Adj SS	Adj MS	F-Value	P-Value
Oil	3	0.006348	0.002116	0.43	0.729
Slag	3	0.020395	0.006798	1.39	0.246
Fly ash	3	0.002420	0.000807	0.17	0.920
Error	182	0.887799	0.004878		
Lack-of-Fit	54	0.272495	0.005046	1.05	0.404
Pure Error	128	0.615304	0.004807		
Total	191	0.916962			

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	1.9452	0.0159	122.04	0.000	
Oil					
4	0.0134	0.0143	0.94	0.348	1.50
6	0.0095	0.0143	0.67	0.506	1.50
8	0.0147	0.0143	1.03	0.305	1.50
Slag					
5	-0.0289	0.0143	-2.03	0.044	1.50
10	-0.0110	0.0143	-0.77	0.441	1.50
15	-0.0137	0.0143	-0.96	0.338	1.50
Fly ash					
5	-0.0085	0.0143	-0.59	0.554	1.50
10	-0.0028	0.0143	-0.19	0.847	1.50
15	0.0005	0.0143	0.03	0.974	1.50

Table 6.23 Coefficients

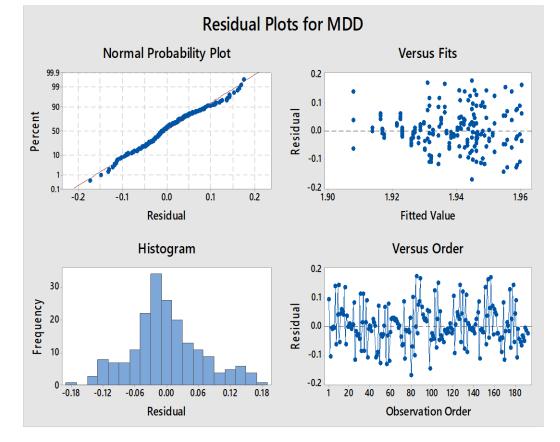


Figure 6.22 Residual plots for MDD

6.7.3 General linear model: Cohesion (c) versus oil, slag, fly ash

In the below Tables (6.24, 6.25 and 6.26) and Figure 6.23 show results for the factor information, analysis of variance (ANOVA), model summery and coefficients in general linear model for Cohesion (c) versus Oil, Slag, Fly ash. The P-Values is accepted as a significant factor on the response at 95% confidence level except for slag is greater than 0.05 the parameter.

Method

Factor coding (1, 0) Factor Information

Factor	Туре	Levels	Values
Oil	Fixed	4	0, 4, 6, 8
Slag	Fixed	4	0, 5, 10, 15
Fly ash	Fixed	4	0, 5, 10, 15

Table 6.24 Factor information.

Analysis of variance (ANOVA) results

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Oil	3	1304.6	434.85	5.31	0.002
Slag	3	554.5	184.84	2.26	0.083
Fly ash	3	1670.9	556.96	6.80	0.000
Error	182	14899.8	81.87		
Lack-of-Fit	54	11560.7	214.09	8.21	0.000
Pure Error	128	3339.1	26.09		
Total	191	18429.7			

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	26.92	2.06	13.04	0.000	
Oil					
4	6.06	1.85	3.28	0.001	1.50
6	3.42	1.85	1.85	0.065	1.50
8	6.57	1.85	3.56	0.000	1.50
Slag					
5	-2.05	1.85	-1.11	0.269	1.50
10	-4.65	1.85	-2.52	0.013	1.50
15	-3.20	1.85	-1.73	0.084	1.50
Fly ash					
5	6.81	1.85	3.69	0.000	1.50
10	4.80	1.85	2.60	0.010	1.50
15	0.16	1.85	0.09	0.931	1.50

Table 6.26 Coefficients

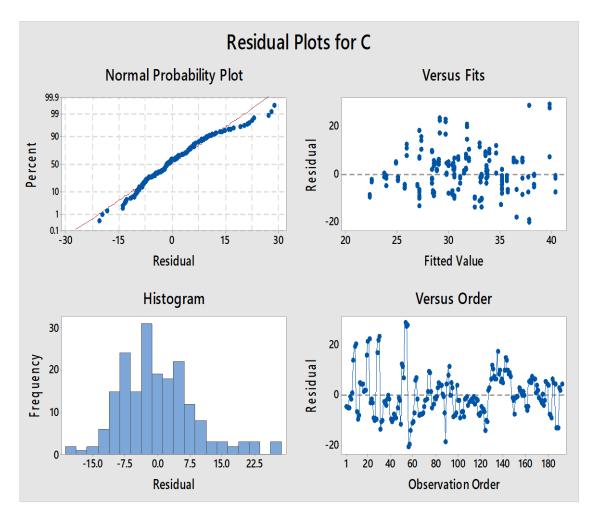


Figure 6.23 Residual plots for c.

6.7.4 General linear model: $\boldsymbol{\phi}$ versus oil, slag, fly ash

In the below Tables (6.27, 6.28 and 6.29) and Figure 6.24 show results for the factor information, analysis of variance (ANOVA), model summery and coefficients in general linear model for angle of internal friction (ϕ) versus oil, slag, fly ash. The P-values is accepted as a significant factor on the response at 95% confidence level except for fly ash is greater than 0.05 the parameter.

Method

Factor coding (1, 0)

Factor Information

Factor	Туре	Levels	Values
Oil	Fixed	4	0, 4, 6, 8
Slag	Fixed	4	0, 5, 10, 15
Fly ash	Fixed	4	0, 5, 10, 15

Table 6.27 Factor information

Analysis of variance (ANOVA) results

Table 6.28	Analysis	of variance	(ANOVA)	results
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Source	DF	Adj SS	Adj MS	F-Value	P-Value
Oil	3	324.41	108.136	4.86	0.003
Slag	3	510.70	170.233	7.65	0.000
Fly ash	3	94.41	31.471	1.41	0.240
Error	182	4048.61	22.245		
Lack-of-Fit	54	3936.84	72.904	83.49	0.000
Pure Error	128	111.77	0.873		
Total	191	4978.13			

Coefficients

Table	6.29	Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	35.35	1.08	32.84	0.000	
Oil					
4	-2.363	0.963	-2.45	0.015	1.50
6	-0.356	0.963	-0.37	0.712	1.50
8	1.258	0.963	1.31	0.193	1.50
Slag					
5	-4.077	0.963	-4.23	0.000	1.50
10	-2.738	0.963	-2.84	0.005	1.50
15	-0.638	0.963	-0.66	0.509	1.50
Fly ash					
5	-1.012	0.963	-1.05	0.294	1.50
10	-0.958	0.963	-1.00	0.321	1.50
15	0.669	0.963	0.69	0.488	1.50

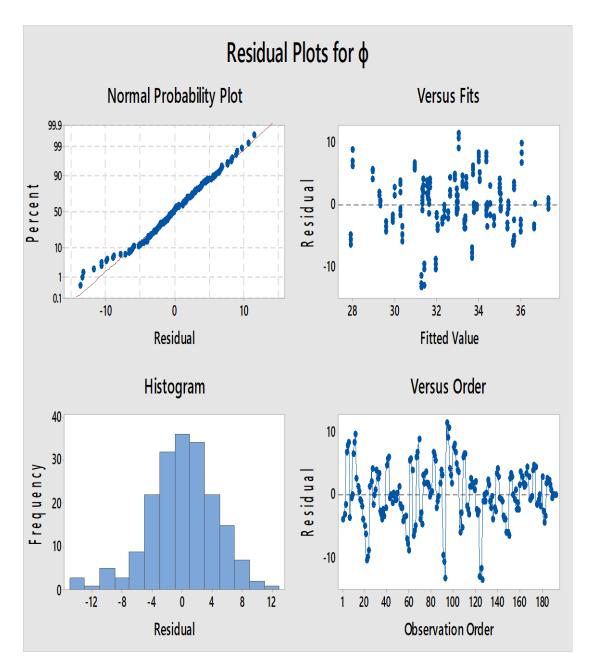


Figure 6.24 Residual plots for φ .

6.7.5 Nonlinear regression equation

A regression equation is used in stats to determine what relationship, if any, exists between sets of data. Regression equations can help you figure out if your data can be fit to an equation. This is extremely useful if you want to make predictions from your data– either future predictions or indications of past behavior. For example, you might want to know what your savings are going to be worth in the future. Or, you might want to predict how long it can take to recover from an illness.

There are several types of regression equations. Some of the more common include exponential and simple linear Regression (to fit the data to an exponential equation or a linear equation). In elementary statistics, the regression equation you are most likely to come across is the linear form

Nonlinear regression is a form of regression analysis in which data is fit to a model and then expressed as a mathematical function. Simple linear regression relates two variables (X and Y) with a straight line (y = mx + b), while nonlinear regression must generate a line (typically a curve) as if every value of Y was a random variable. The goal of the model is to make the sum of the squares as small as possible. The sum of squares is a measure that tracks how much observations vary from the mean of the data set. It is computed by first finding the difference between the mean and every point of data in the set. Then, each of those differences is squared. Finally, all of the squared figures are added together. The smaller the sum of these squared figures, the better the function fits the data points in the set. Nonlinear regression uses logarithmic functions, trigonometric functions, exponential functions, and other fitting methods.

Nonlinear regression modeling is similar to linear regression modeling in that both seek to track a particular response from a set of variables graphically. Nonlinear models are more complicated than linear models to develop because the function is created through a series of approximations (iterations) that may stem from trial-and-error.

By utilizing Matlab software program to determine nonlinear regression equation for each response as OMC, MDD, apparent cohesion (c) and angle of internal friction (ϕ) from experimental laboratory results. The response has been based on three factors oil, fly ash and slag to demonstrate fit relationship between response and factors, in another hand the follow equation going to utilize for prediction OMC, MDD, cohesion (c) and angle of internal friction (ϕ) in any percentage of oil, fly ash and slag.

The nonlinear regression equations for all response shown below and correlation between predicted and actual data illustrated in Figures (6.25 to 6.28).

$$(OMC)^{1.31} = 22.33924 - 0.40556*Oil - 0.74071*Slag - 0.00270581*Fly ash - 0.25441*Oil*Slag - 0.10558*Oil*Flay ash + 0.057939*Slag*Flay ash + 0.21355*Oil^2 + 0.17305*Slag^2 + 0.016804*Oil*Slag*Fly ash + 0.077847*Oil^2*Slag + 0.00771415*Oil^2*Fly ash - 0.032989*Oil*Slag^2 - 0.00558124*Slag^2*Fly ash - 0.030557*Oil^3 - 0.00602431*Slag^3 + 0.00131663*Oil^2*Slag^2 - 0.00161733*Oil^2*Slag*Fly ash - 0.00467490*Oil^3*Slag + 0.00100351*Oil*Slag^3$$

Std. Dev.	1.41	R-Squared	0.8799
Mean	19.61	Adj R-Squared	0.8667
C.V. %	7.17	Pred R-Square	0.8546
PRESS	412.06	Adeq Precisior	39.696
-2 Log Likeliho	654.74	BIC	759.89
		AICc	699.66

Table 6.30 Program results for OMC.

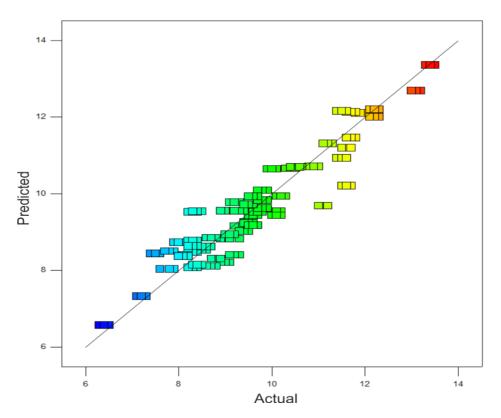


Figure 6.25 Correlation between predicted and actual data for OMC.

 $(MDD)^{-3} = 0.13911 + 0.00482703 * Oil - 0.00386566 * Slag - 0.000864067 * Fly ash - 0.000748595 * Oil * Slag + 0.000961818 * Slag * Fly ash - 0.000640532 * Oil^2 + 0.000961818 * Slag * Oil^2 + 0.000961818 * Slag * Oil^2 + 0.000961818 * Slag * Oil^2 + 0.000961818 * Oil^2 * Oil^2 * Oil^2 + 0.000961818 * Oil^2 *$

 $0.000782776*Slag^2 + 0.0000927973*Oil^{2*}Slag - 0.000157435*Slag^{2*}Fly \\ ash - 0.0000339230*Slag^3 + 0.00000657657*Slag^{3*}Fly \\ ash$

Std. Dev.	0.014	R-Squared	0.1547
Mean	0.14	Adj R-Squared	0.1030
C.V. %	9.90	Pred R-Square	0.0266
PRESS	0.039	Adeq Precisior	7.400
-2 Log Likeliho	-1115.41	BIC	-1052.32
		AICc	-1089.67

Table 6.31 Program results for MDD.

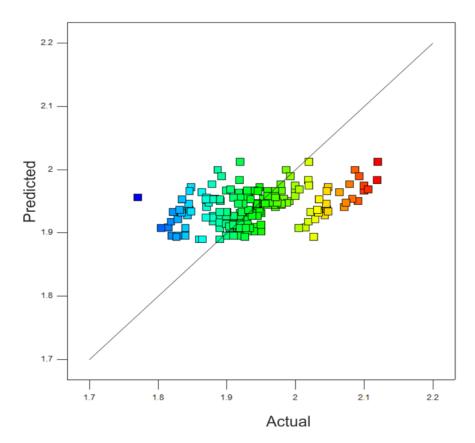


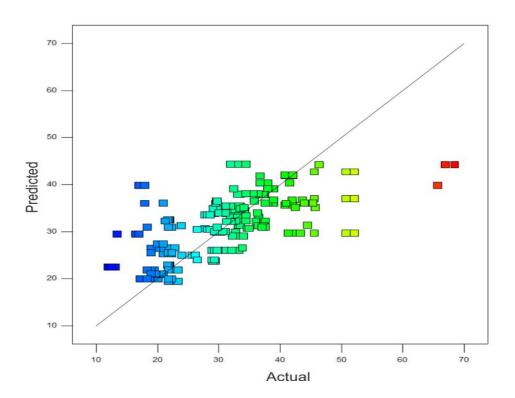
Figure 6.26 Correlation between predicted and actual data for MDD.

(c) ^{0.28} = 2.38414 +0.52207*Oil + 0.010784*Slag + 0.15061*Fly ash - 0.040022*Oil*Slag - 0.043433*Oil*Fly ash - 0.00913960*Slag*Fly ash - 0.16173*Oil² - 0.00120343*Slag² - 0.0010444*Fly ash² + 0.00148939*Oil*Slag*Fly ash + 0.010343*Oil²*Slag + 0.00715567*oil²*Fly

ash + 0.00142207*Oil*Slag² + 0.00138035*Oil*Fly ash² + 0.000641848*Slag*Fly ash² + 0.012934*Oil³ - 0.000156834*Oil²*Slag² - 0.0000930484*Oil*Slag*Fly ash² - 0.000741862*Oil³*Slag - 0.000537780*Oil³*Fly ash

Std. Dev.	0.18	R-Squared	0.4572
Mean	2.60	Adj R-Squared	0.3937
C.V. %	6.87	Pred R-Square	0.3328
PRESS	6.70	Adeq Precisior	10.175
-2 Log Likeliho	-138.88	BIC	-28.47
		AICc	-91.45

Table 6.32 Program results for c



$$\label{eq:product} \begin{split} \mbox{Figure 6.27 Correlation between predicted and actual data for c.} \\ (\phi)^{2.19} &= 2228.17372 - 762.36272*Oil - 378.82157*Slag + 310.87196*Fly ash + 125.91086*Oil*Slag - 181.39064*Oil*Fly ash - 29.12386*Slag*Fly ash + 332.60381*Oil^2 + 69.85210*Slag^2 - 44.87818*Fly ash^2 + 11.01021*Oil*Slag*Fly ash - 35.53429*Oil^2*Slag + 17.39748*Oil^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 12.99396*Oil*Fly ash^2 + 1.67251*Slag^2*Fly ash^2 + 1.67251*Slag^2*Fly ash - 10.34658*Oil*Slag^2 + 10.9558*Oil*Slag^2 +$$

 $\begin{aligned} &30.13546*Oil^3-2.98661*Slag^3+1.96552*Fly\ ash^3-0.87629*Oil^2*Slag*Fly\ ash-0.65062*Oil^2*Fly\ ash^2-0.25787*Oil*Slag^2*Fly\ ash+\\ &3.27653*Oil^3*Slag+0.48326*Oil*Slag^3-0.35395*Oil*Fly\ ash^3 \end{aligned}$

Std. Dev.	528.87	R-Squared	0.4904
Mean	2153.00	Adj R-Squared	0.4172
C.V. %	24.56	Pred R-Square	0.3489
PRESS	5.969E+007	Adeq Precisior	12.500
-2 Log Likeliho	2926.05	BIC	3057.49
		AICc	2983.88

Table 6.33 Program results for φ .

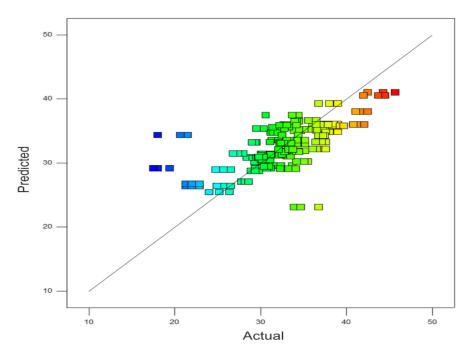


Figure 6.28 Correlation between predicted and actual data for $\boldsymbol{\phi}$

CHAPTER 7

CONCLUSION AND RECOMMENDATION

7.1 Conclusion

7.1.1 Conclusions for geotechnical properties

This study investigates the pollution of soil by crude oil. Mineral admixtures are used to stabilize polluted soil. The compaction and direct shear tests were carried out to samples. In this study, key properties of sandy soils were identified. The conclusion for the properties of the soil are shown as below:

- Apparent cohesion levels went up as oil contamination increased up to 8% but started falling with any increase in oil contamination beyond the 8%. This can be associated with the wetness in soil achieved by the spill.
- As the crude oil abortion to the soil increased, the soil gravity decreased and its change was insignificant at low levels of crude oil penetration to the soil.
- It has been observed that the contaminated soils are not suitable for construction projects unless if make stabilize.
- Both maximum dry density and dry unit weight decreased when crude oil uptake by the soil increased.
- The maximum dry density was showed a remarkable decrease trend when the oil contamination increased. However, the change was recorded as insignificant between soil samples and contamination levels.
- It has been observed that sandy soils strength decreases with an increase in crude oil in the soil.
- A slight reduction in frictional angle was observed for contaminated sand due to the inter-grain lubrication of the sand particles by the crude oil.
- Mineral admixture like GGBFS and FA were used to improve properties of polluted soil.

7.1.2 Conclusions for soil pollution

Environmental pollutions could harm human life, animals and plants growth. In Erbil province, over the past few years, crude oil spills into the ground and caused a devastating effects on human health as well as the ecosystem of the region. The top parts of the soil and underground water have been significantly affected. Also, it causes damage to the social-economic aspect of the region due to petroleum hydrocarbons pollution.

Petroleum exploration activities in the province has generally resulted to a degraded ecosystem; polluted water system, soil contamination and reduced quality of life as they have seen harmful discharges to the environment as well as hydrocarbon chemical wastes released to the environment.

In all oil-producing regions worldwide, crude oil spillage is among the major environmental challenges faced. It threatens the existence of human life by affecting the health system and the agricultural system of the regions affected. In the area of this study-Erbil, there has been little attention paid in researching on the effects of the spillage that occurs from the crude oil and thus minimal efforts have been made done by the authorizes to caution the governorate.

Over the past twenty years, the province has been experienced to heavy crude oil spillage. The elimination of existing farmlands has been observed due to the soil fails to sustain crops and thus any form of vegetation. Oil spillage led to a huge increase in the salinity levels in the soil in a way that the soil can no longer yield any plantation cover. Furthermore, the increased lead concentration in the soil as a result of crude oil spillage poses a significant health hazard to human life, plants and animals. The results showed the decreased levels of potassium in the soils and this may have contributed to the plant cover failure in the region. Also, high Sulphate levels were observed in the soil. Thus, can further hampering vegetation growth.

7.1.3 Conclusions for flow and penetration of crude oil

The study presents a model that can be used to predict the rate of crude oil penetration in to the soil with the aim of improved accuracy. Mathematical computations were carried out using spread sheet and algebraic methods to arrive at the rates. From the model, key information has been derived at that can inform strategies adopted in controlling and managing crude oil spills. The model has shown that the size of the pool has an effect on

the contamination i.e. the larger the pool area, the shallower the zone of soil contamination with the volume spilt being constant.

The model has also shown, to a great extent, the importance of water in oil contamination management. The higher water saturation in the soil, the bigger surface pool of the oil and in turn the shallower the penetration of the oil in to the soil with the amount split constant. Other factors that have been declared as of great importance from the model are time and temperatures as they play a role in the evaporation process of the oil. High temperatures increase the potential of evaporation thus reduced penetration as compared to low temperatures. Also, when evaporation rate is high, there is a risk of vapour concentration in air exceeding the minimum for flammability.

7.2 Recommendation

This study has been performed only on a limited number of soil samples with different level of oil contaminated only up to 16% and utilized two type of mineral admixture. The study recommendations are explaining as below:

- > The study can be made by changing the curing time.
- This observation can also be studied for contamination with various level of crude oil and different type of oil (like kerosene gasoline motorize oil).
- The investigation can also be made by adding crude oil at moisture content other than optimum moisture content.
- The study can be made with different percentage of mineral admixture and use high ratio of them. Furthermore, it could be used various type of mineral admixture such as lignin and silica fume.
- In the study recommends that the province and state authorities must ensure that genuine efforts are made towards addressing the costs of resource extraction in the oil-rich region. The development of the area should not supersede the wellbeing of future generations as well as the health being of the inhabitants of the region.

The property changes of crude oil contaminated soils investigate with respect to mineralogical composition of the soils. The study can also be made on naturally contaminated soil by crude oil and other industrial wastes.

Crude oil spillage on the agricultural land is a big threat to production, and health. It is suggested to deal with the spillage prevention, then fronting the consequences. Crude oil spillage phenomenon in Erbil governorate should be stopped. The government needs to create a modern and professional environmental policy, and should strictly prevent the climatic disturbances. As a result, the study recommends that the government agencies and other environmental conservative bodies should monitor the activities being undertaken in the province by various stakeholders of the petroleum exploration. In collaboration with the academic experts, technologies, like bioremediation strategies, that optimize environmental contamination by the crude oil and other exploration activities can be developed and adopted in the region. The treatment of the contaminated soil with crude oil is a very complex, and costly operation. Contaminated soil excavation, and soil washing are the mechanical technique that are recommended for practicing. The Bioremediation technique is effective for polluted soil treatment. It concerns the addition of fertilizers to the soil. For example, adding chloride potassium to increase potassium content. Adding calcium with water can be used to reduce the salinity of the soil. High sulfate content in the soil can be managed by covering the surface by non-sulfate content soils, and calcium based stabilizer also reduces the sulfate in the soil.

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APPENDIXES

Specific Gravity of the Soil with different ratio of oil crude oil content										
		0% Oil	2% Oil	4% Oil	6% Oil	8% Oil	10% Oil	12% Oil	14% Oil	16% Oil
Can	No.	1	2	3	4	5	6	7	8	9
W 1	Wt of Can gm	43.28	42.87	40.64	41.60	43.39	39.60	40.03	38.90	33.19
W 2	Wt. of (Can + Soil) gm	92.14	90.3	85.50	88.70	90.94	86.20	87.23	82.30	79.02
W s	Wt. of Soil (W2 - W1) gm	48.86	47.43	44.86	47.1	47.55	46.6	47.2	43.4	45.83
Руси	Pycnometer No.		11	8	9	14	7	3	5	2
W 3	Wt. of (Pycnometer+Water+ Soil) gm	361.89	362.5	364.17 9	363.18 9	362.29	364.05	361.63	362.21	363.64
W 4	Wt. of Pycnometer +Water) gm	331.58	333.17	336.45	334.13	332.99	335.4	332.67	335.6	335.57
Tem	Temperature (T) °C		19.0°	19.0°	19.0°	19.0°	19.0°	19.0°	19.0°	19.0°
Tem (K)	Temperature Coefficient (K)		1.0002 0	1.0002 0	1.0002 0	1.0002 0	1.0002 0	1.0002 0	1.0002 0	1.0002 0
-	Specific Gravity of Liquid (GL)		0.9984 1	0.9984 1	0.9984 1	0.9984 1	0.9984 1	0.9984 1	0.9984 1	0.9984 1
(Ĝs.	Specific Gravity of Soil (Gs.t) Gs.t=(Ws/(Ws+W4- W3))*GL		2.6163	2.6145	2.6066	2.6013	2.5920	2.5836	2.5808	2.5764
	cific Gravity of Soil at C Gs@20°C=K*Gs,t	2.619	2.617	2.615	2.607	2.602	2.592	2.584	2.581	2.577

APPENDIX B Certification of calibration

Directorate of Erbil Construction Laboratory		Verificat	d of Mechanical Rammer M D2168-12						
Verification Form No.			S.W. 06	S.W. 06 Revision 02 Approve da				te 02.01.2018	
Division 5		Soil work	Date		Date		2019-	019-1-22	
Balance No. 2		2			Matest		st		
No.	Division Serial No.		mmer Mass 364±0.01) Kg				at Circular Face 8±0.12) mn		Remarks
1	S199/AC/0043		4.54	45	7.2	50.68		-	3
2	S199/AC/0045		4.54	458.1		50.75		-	
3	S199/AC/0040		4.54	457.3		50.90		+	

Note: - The above parameters need to be checked every 6 months,



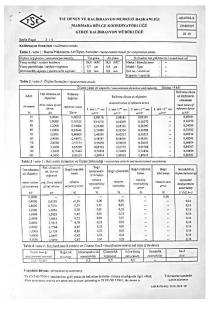
Directorate of Erbil Construction Laboratory			Verificati	Verification Record of Mechanical Ramm ASTM D2168-12				er	
Verification Form No. S.W. 06				Revision 02 Approve of					02.01.2018
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Balance No. 2		2	Manufacturer			r	Matest		
No.	Division Serial No.		ammer Mass 1364±0.01) Kg	Mass Dist		Freely/ Flat Circu tance Face =1.3) mm (50.8±0.12)			Remarks
1	\$199/AC/0043		4.54	45	7.2	50.68			
2	S199/AC/0045		4.54	45	8.1	50.75			
3	S199/AC/0040		4.54	457.3		50.90			

<u>Note:</u> The above parameters need to be checked every $\underline{6}$ months.

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3	Xumpas / caliper	Minister	Dini	11064331	TSE Gebse 11U090 TSE Gebze U01-009
4	Sentil çakışı / sentil menemetre / christeritter	Ormon Scientific	SLEEKT	KM 259	TSE Geber 112E016
	dinigtirde) / fares translater	HBM	Z3H2	D 99370	UME G2KV-0205
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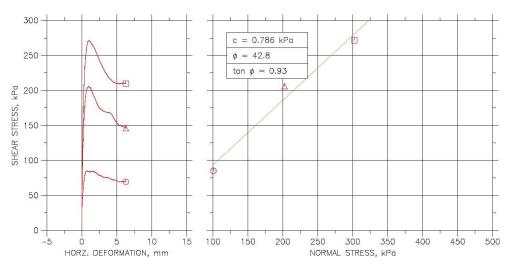


APPENDIX C Raw data for compaction test

Mix.	Crude	Slag	Fly ash	Soil	OMC	MDD
No.	oil%	(GGBFS)	(FA)	100	(%)	(g/cm^3)
Mix 1	0	0	0	100	10.9	1.938
Mix 2	0	0	10	90	11.5	1.943
Mix 3	0	0	15	85	11.9	1.915
Mix 4	0	10	0	90	10.5	1.987
Mix 5	0	10	10	80	10.5	1.979
Mix 6	0	10	15	75	10.3	1.945
Mix 7	0	15	0	85	10.4	1.991
Mix 8	0	15	10	75	13.4	1.919
Mix 9	0	15	15	70	12.2	1.946
Mix 10	4	0	0	96	10	1.927
Mix 11	4	0	10	86	9.7	1.922
Mix 12	4	0	15	81	11.1	1.871
Mix 13	4	10	0	86	9.6	1.932
Mix 14	4	10	10	76	9.1	1.935
Mix 15	4	10	15	71	9.8	1.981
Mix 16	4	15	0	81	8.3	2.019
Mix 17	4	15	10	71	9.9	1.99
Mix 18	4	15	15	66	11.6	1.905
Mix 19	6	0	0	94	9.2	1.964
Mix 20	6	0	10	84	9.5	1.948
Mix 21	6	0	15	79	9.6	1.948
Mix 22	6	10	0	84	9.8	1.983
Mix 23	6	10	10	74	8.7	1.974
Mix 24	6	10	15	69	10.2	1.946
Mix 25	6	15	0	79	8.4	2.006
Mix 26	6	15	10	69	9.5	1.97
Mix 27	6	15	15	64	8.8	1.976
Mix 28	8	0	0	92	8	1.945
Mix 29	8	0	10	82	8.5	1.929
Mix 30	8	0	15	77	9.5	1.934
Mix 31	8	10	0	82	8.1	1.991
Mix 32	8	10	10	72	7.5	1.971
Mix 33	8	10	15	67	7.2	1.993
Mix 34	8	15	0	77	6.4	2.02
Mix 35	8	15	10	67	7.7	1.98
Mix 36	8	15	15	62	7.5	1.99

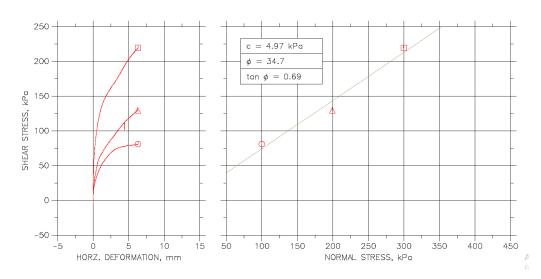
Compaction test results

APPENDIX D Raw data for direct shear test

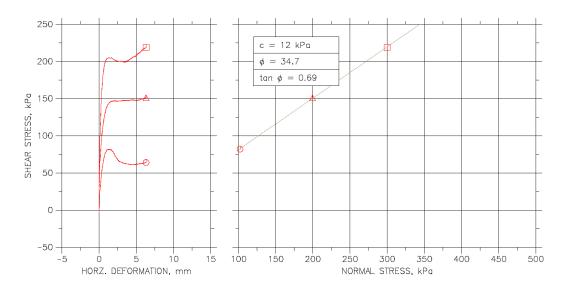


Mix 1

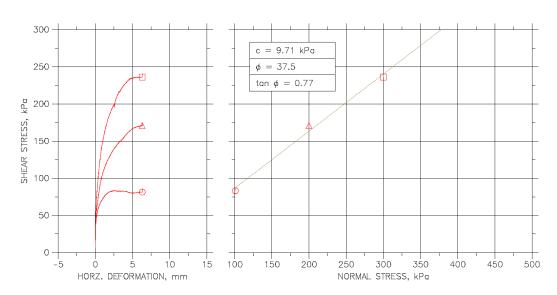




Mix 2



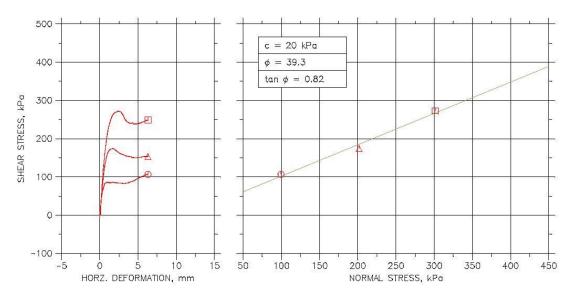
Mix 3



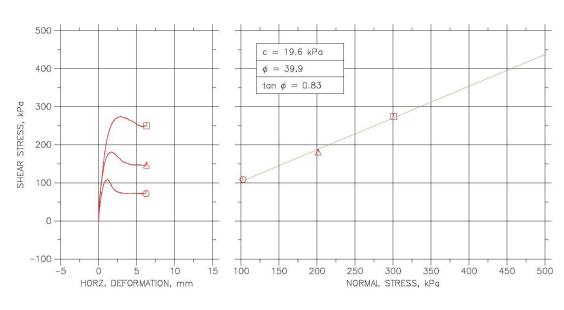
DIRECT SHEAR TEST by ASTM D 3080

Mix 4

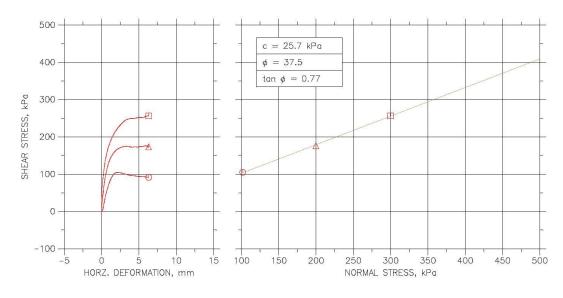




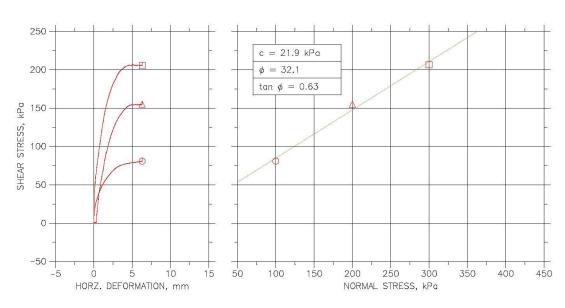
Mix 5



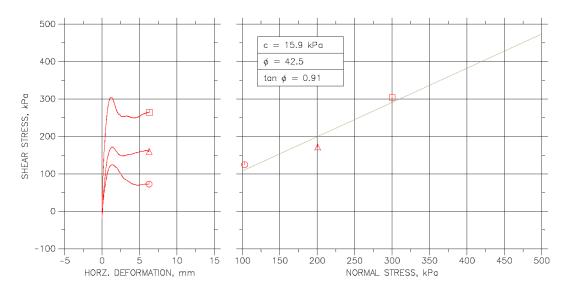
Mix 6



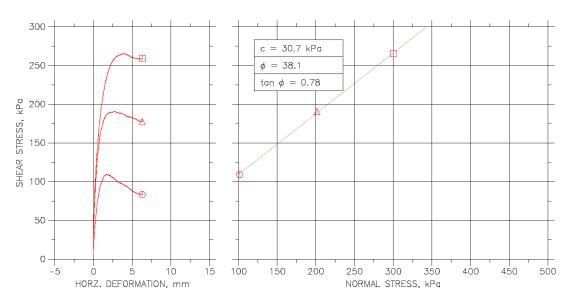




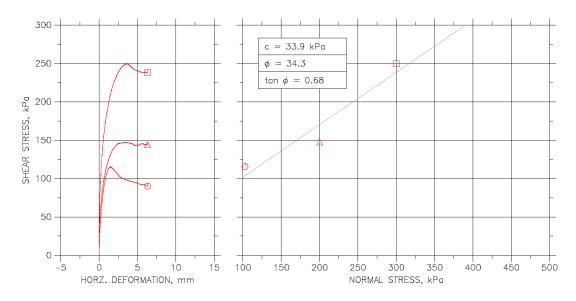
Mix 8



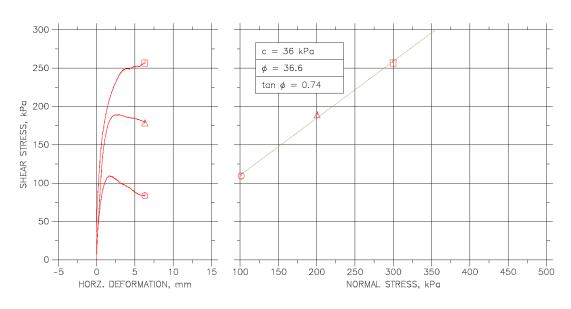
Mix 9



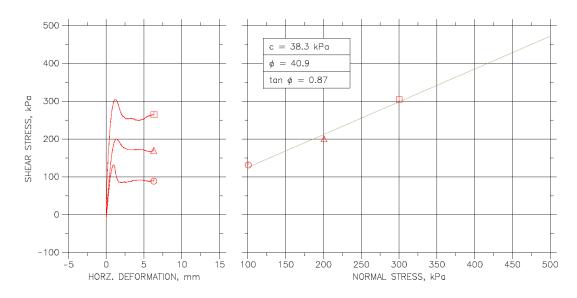
Mix 10



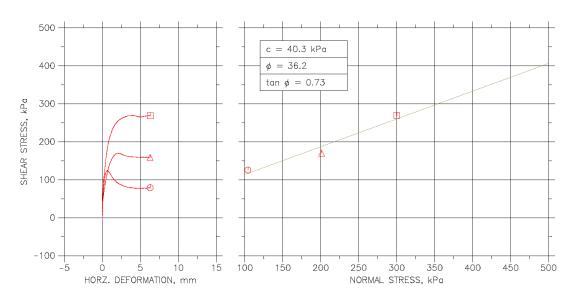
Mix 11



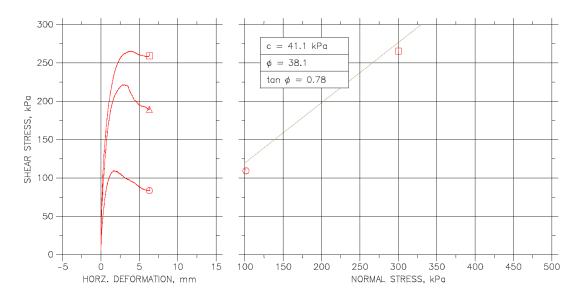
Mix 12



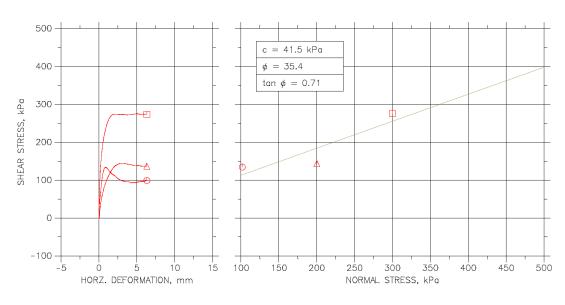
Mix 13



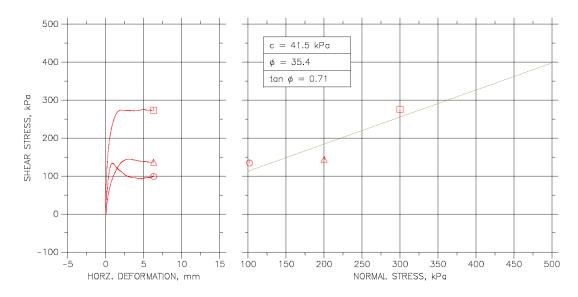
Mix 14



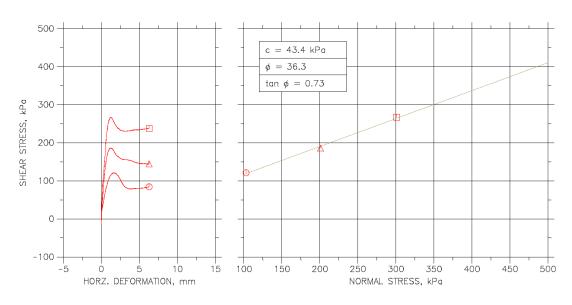
Mix 15



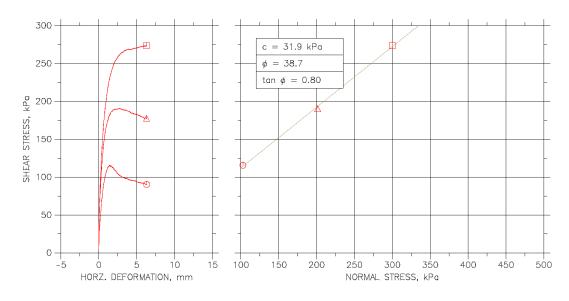
Mix 16



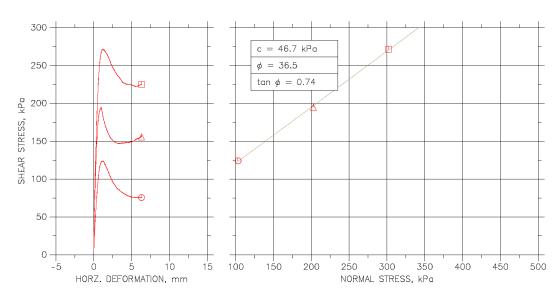
Mix 17



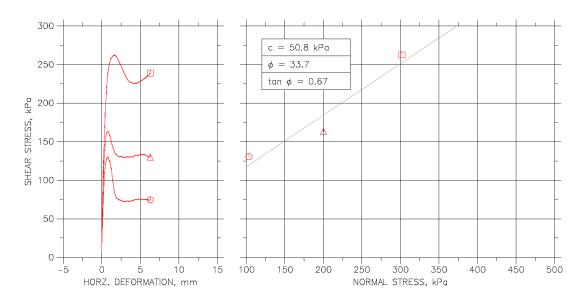
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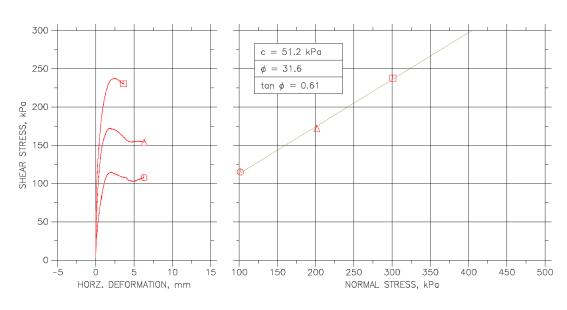
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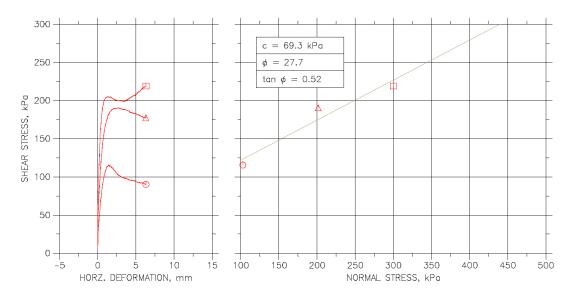
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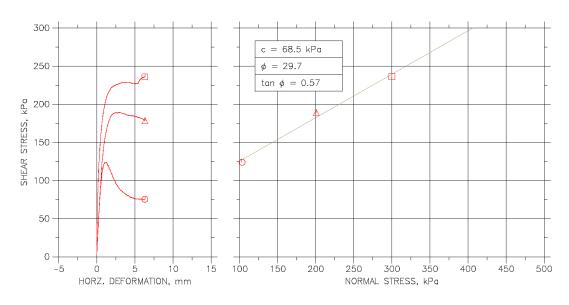
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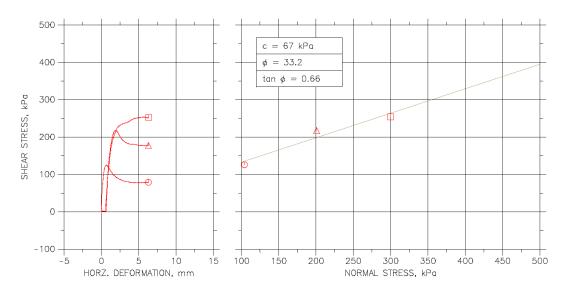
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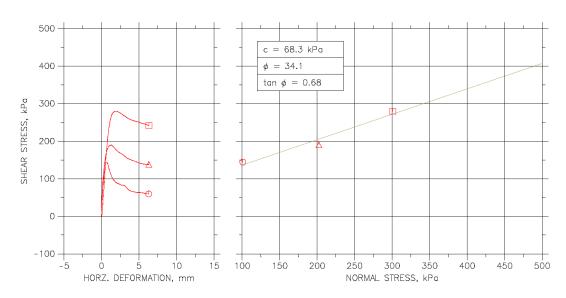
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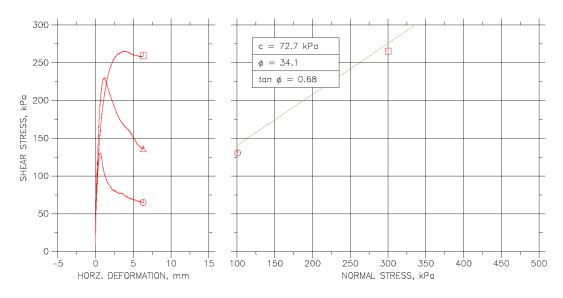
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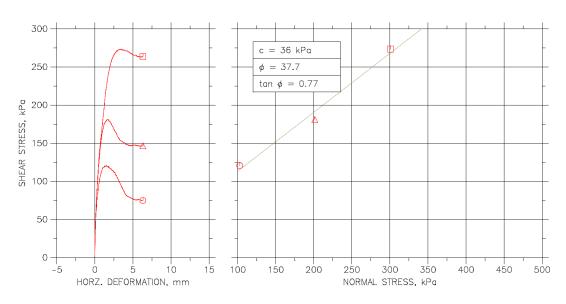
Mix 25



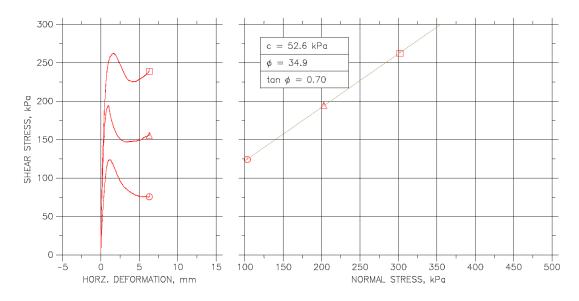
Mix 26



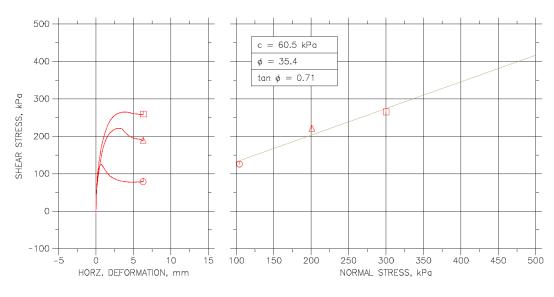
Mix 27



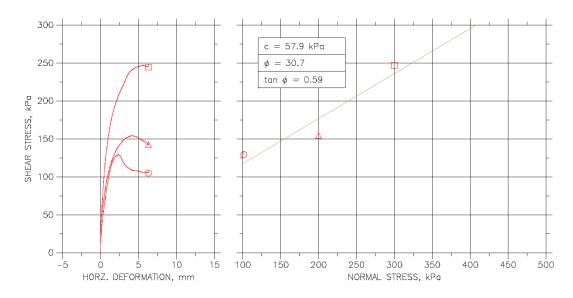
Mix 28



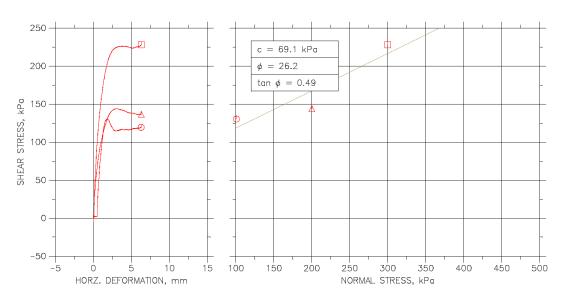
Mix 29



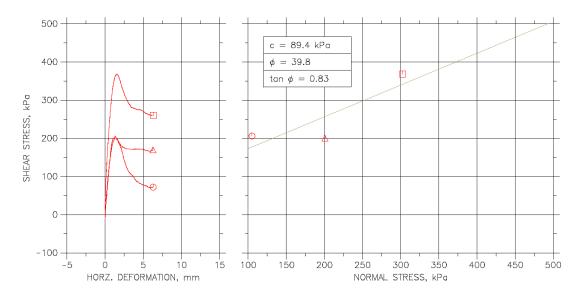
Mix 30



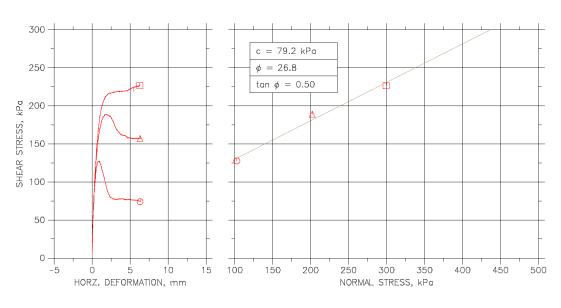
Mix 31



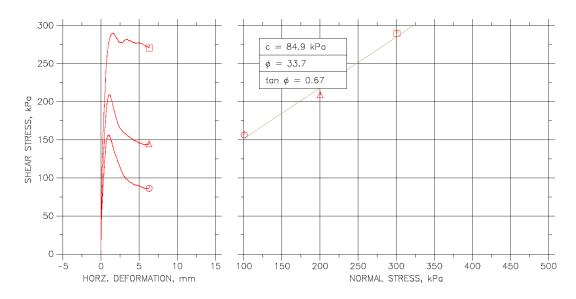
Mix 32



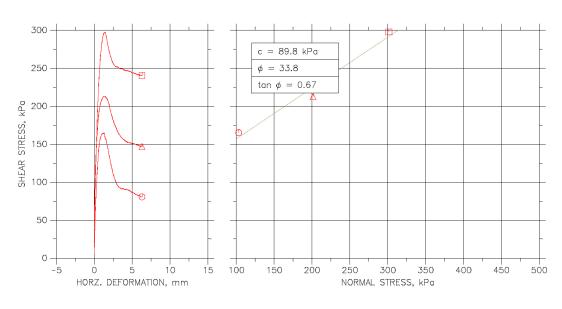
Mix 33



Mix 34



Mix 35



Mix 36

CURRICULUM VITAE

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2015 11050m	1 ministry	or manner	punty u	ia tourism

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- 2005-2006 worked in private sector

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English

Arabic

Turkish