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PROPERTIES OF MORTAR AND CONCRETE CONTAINING FINE SAND CONTAMINATED WITH LIGHT CRUDE OIL

A thesis submitted by

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Abstract

Sand contaminated with crude oil has become a major environmental concern worldwide. This problem poses threats to human health, the ecosystem, and the properties of the surrounding sand. Due to the prohibiting cost of the existing remediation methods, a more cost-effective way of utilizing oil contaminated sand is warranted. Mixing oil contaminated sand with cement and using this mix as alternative construction material is considered an innovative approach to reduce its environmental impact. This study is the first to investigate the effect of light crude oil on the physical and mechanical properties of fine sand, and mortar and concrete where contaminated sand is an ingredient. This approach is a critical step to sufficiently evaluate the suitability of this waste product as a sustainable building and construction material.

In the first stage, an extensive experimental study was conducted on the important geotechnical properties of fine sand contaminated with light crude oil. The results showed that water absorption, permeability, contact angle, frictional angle, and cohesion decreased with high levels of oil contamination. However, these properties of fine sand were enhanced at 1% oil contamination. The highest value of cohesion (10.76 kPa) and 10% enhancement in shear strength was observed at this oil contamination level. More importantly, the results of this stage provided information on the suitability of using this waste material as fine aggregates in mortar and concrete.

The second stage consisted of an evaluation of cement mortar properties containing fine sand contaminated with light crude oil. Mixing cement and water before adding the oil contaminated sand yielded up to 19% higher compressive strength compared to the cement mortar prepared by mixing the sand and cement before adding the water, due to a better reaction of cement particles and water during the hydration process. Similarly, curing in a fog room produced mortar of up to 45.6% higher compressive strength compared to mortars cured under other curing conditions, i.e. in water, in air, and in plastic bags. The scanning microscope observations revealed that cement mortars cured in the fog room had lower total porosity, smaller capillary pores, and denser calcium silicate hydrate compared to those cured under other methods. A w/c ratio of 0.5 was found to produce cement mortar with a higher compressive strength than mortar with a w/c ratio of 0.4 or 0.6. It was also found that the cement mortar with sand having more than 2% oil contamination requires a longer curing period to fully develop its compressive strength. The results of this stage demonstrated that proper mixing and curing methods, w/c ratio, and reasonable curing time are important for a cement mortar containing oil contaminated sand to achieve reasonable physical and mechanical properties for building and construction.

An investigation of the suitability of a geopolymer binder to produce mortar containing oil contaminated sand was investigated during the third stage. It was found that heat curing can increase the compressive strength of geopolymer mortar up to 54% compared to ambient curing situation. The geopolymer mortar with 1% of light crude oil contamination yielded a 20% higher compressive strength to mortar containing sand with a saturated surface dry condition. This was due to the high alkalinity of the solution, leading to the generation of more geopolymeric binder. Similarly, the formation of efflorescence decreased as the level of oil contamination decreased due to light crude oil filling up the pores. From this stage, it was demonstrated that geopolymer mortar containing oil contaminated sand has the potential as a new engineering material which has a positive impact on the environment.

An investigation of the properties of concrete containing oil contaminated sand was implemented as the last stage. The results of the investigation showed that the density of concrete deceased as the amount of crude oil increased due to an increase in the surface voids and total porosity. The highest compressive and splitting tensile strength was obtained for concrete with 1% of light crude oil contamination due to the oil optimising the sand cohesion. Above 1%, the bond between the cement paste and aggregates was affected, resulting in a decrease in strength properties. The developed simplified prediction equations to estimate the compressive strength of mortar and concrete containing fine sand contaminated with light crude oil gave a 98% accuracy between the experimental results and the predicted values.

An enhanced understanding of the behaviour of fine sand contaminated with light crude oil and the properties of mortar and concrete utilising this waste material

is the outcome of this investigation. This outcome will provide a benchmark for future studies and useful information to carefully consider oil contaminated sand for use in building and construction, and as a cost-effective alternative remediation method.

Certification of Dissertation

I certify that the ideas, experimental work, results, analysis and conclusions reported in this dissertation are entirely my own effort, except where otherwise acknowledged. I also certify that the work is original and has not been previously submitted for any award, except where otherwise acknowledged.

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(Dr Jim Shiau) Date

Signature of Supervisors

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Associated publications

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Abousnina, RM, Manalo, A & Lokuge, W 2015, 'Mechanical properties of mortar with oil contaminated sand', in Concrete 2015: *proceedings of the Concrete 2015* Concrete Institute of Australia’s Biennial National Conference Melbourne, Australia.

Rajab M. Abousnina, Jim Shiau, Allan Manalo & Lokuge, W 2014, 'Effect of light hydrocarbons contamination on shear strength of fine sand', in Fourth International Conference on Geotechnique, Construction Materials and Environment: *proceedings of theFourth International Conference on Geotechnique, Construction Materials and Environment* Geomate, Brisbane, Australia, p. 5.

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Acronyms

API	American Petroleum Institute
AD	air-dry
AFt	Ettringite
A	Air
AS	Australian Standard
AC	Ambient
AC	Air curing
AC-USSD	Air-curing- Saturated surface dry condition
AL: FA	Alkaline liquid to fly ash ratio
COIS	COIS Crude Oil-Impacted Sand
CSH	calcium silicate hydrate
CWS	Cement water sand
CSW	Cement sand water
C-S-H	Calcium silicate hydrate
C_2S	Dicalcium silicate
C_3S	Tricalcium silicate
C_3A	Tricalcium aluminate
C_4AF	Tricalcium aluminoferrite
CL	clay
c	Cohesion
CSH	Calcium silicate hydrate
CAH	Calcium aluminium hydrate
DFTD	Direct-Heated Fast-Quenched Thermal Desorption
EPA	Environmental protection agency
F-H	Full hydrated
FA	Fly ash
FR	Fog room
GP	General Purpose
GPC	Geopolymer concrete
HCO	Heavy crude oil

HC	heat curing
HC-SSD	Heat curing-Saturated surface dry condition
HT	Heat transfer
k	permeability
LCO	Light crude oil
MS	silty sand
NaOH	Sodium hydroxide
Na_2SiO_3	Sodium silicate
OPC	OPC Ordinary Portland Cement
OD	oven-dry
OG	Oil and gas
OGP	International association of oil & gas producers
OMC	Optimum Moisture Content
PHC	Petroleum Hydrocarbon
PSD	particle size distribution
P	pore
P-H	partially hydrated
PB	Plastic bag
RH	Relative humidity
SP	poorly graded sand
S/S	Stabilisation/Solidification
SSD	Saturated Surface Dry
SEM	scanning electron microscope
US	United State
US-EPA	US Environmental protection agency
USSD	Unsaturated surface dry condition
UK	United Kingdom
VOC	Volatile organic compound
WTC	Wastewater Technology Centre
w/c	Water cement ratio
W	Water
α	degree of hydration
$ø^{o}$	Frictional angle

Chapter 1

Introduction

1.1 Background

Oil and gas are considered to be the most significant sources of energy worldwide, and as such their importance keeps increasing due to the ever increasing global demand for energy (Hubbert, 1975). One of the main drawbacks of these energy sources is damage to the environment caused by oil leakage (Rahman et al., 2010a). For instance, in the Gulf in 1991, it was reported that about 1.1 billion litres of crude oil were spilled into the Arabian Gulf, the Persian Gulf, and in the Kuwait desert. These are considered to be the largest oil spills in history (Al-Sanad et al., 1995, Mashalah et al., 2006). As a consequence of this intentional leakage, 700 kilometres of coastline between Kuwait and Saudi Arabia were polluted, and approximately 49 square kilometres of the Kuwait desert were affected. Furthermore, the British petroleum BP deep water horizon drilling rig that exploded in the Gulf of Mexico in 2010 caused a spill of around 91 million litres of oil that affected about 110 km of the Louisiana coastline (Aryee, 2013). Moreover, around 71 million litres of crude oil was intentionally discharged from oil storage tanks at the Harouge Oil Operation petrochemical and refining complex at the Ras Lanuf Terminal in Libya in August 2008 (Mees, 2008) to circumvent an explosion in the tank from a fire caused by human error during annual maintenance. In addition, approximately 60 kilometres of beaches were polluted by oil in 2009 at Spitfire Creek and Eagers Creek on Moreton Island in Australia and it is considered the largest section of wetlands affected by crude oil spillage (Natural Resources and Environment Policy Division, 2009). Most of these crude oil spills have been caused unintentionally as a result of ageing facilities, lack of maintenance, and human error. Figure 1.1 shows an example of an oil leakage in Amal field, Libya in 2014.

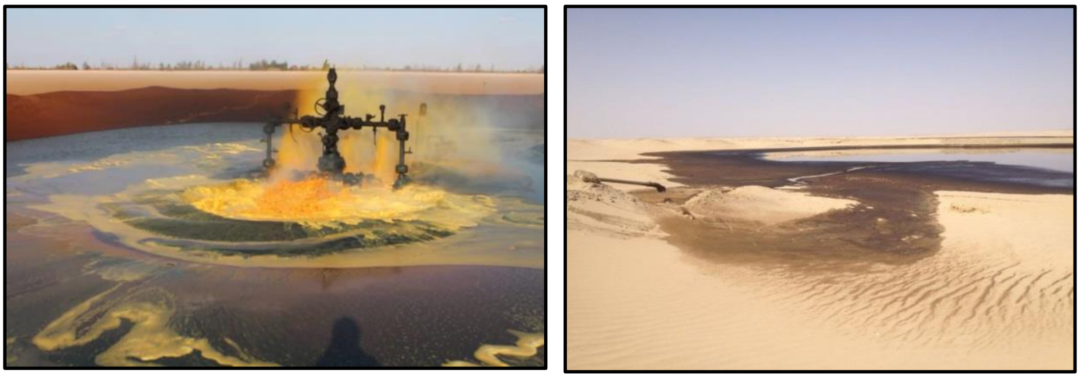


Figure 1.1 Well-head leakage in Amal Field, Libya in 2014

Crude oil contamination has a direct effect on the erosion of sand and water infiltration, and may also cause fire on the ground (Shakesby et al., 2007). Crude oil contamination can also affect the physio-chemical characteristics of the surrounding sand (Osuji and Ezebuiro, 2006). Sharma and Reddy (2004) concluded that the intrinsic permeability (k) of contaminated sand increases when there is an increase in density and a decrease in the viscosity of the fluid filling the voids. When the permeability of the sand increased due to the decreased viscosity of the crude oil, the crude oil spread faster, and hence a larger area was affected. Furthermore, the possibility of the crude oil contamination to reach the underground water was higher. Several studies (Delin et al., 2012, Delin et al., 1998), indicated that ground water contaminated by crude oil, and other petroleum-based liquids, is a widespread problem. In addition, the aggregation of fine particles, and the fusion of minerals due to oil contamination, may reduce the stability of the sand-organic matter aggregate. Rahman et al. (2010b) showed that not only is the ecosystem affected by the spillage of crude oil, so too is the safety of civil engineering structures. The oil contamination in sand causes significant changes in the sand plasticity, causing a loss in its bearing capacity and a differential settlement of the foundations (Rehman et al., 2007, Ukpong and Umoh, 2015). Moreover, oil contamination can adversely affect the plant and ground water resources used for drinking or agricultural purposes, as shown in Figure 1.2, and hence, oil contamination is considered to be a significant worldwide concern.

Figure1.2 Oil impacted site in Ogoniland Nigeria, showing a contaminated river and loss of vegetation cover (Kadafa, 2012).

The extensive seepage and contamination caused by crude oil spills requires major remediation and/or reclamation of the sand to make it suitable for any future use. Research studies have resulted in several technical methods which could remediate these problems. However, the high cost of existing remediation methods is a main concern. For instance, the cost of alternative remediation methods as suggested by USEPA (1997) varies from 50 - 1000 US $ per ton. The most expensive methods are incineration and vitrification, which cost between $280 and $1000, and between $100 and $1000 per ton respectively, while the cheapest methods are soil washing and solvent extraction at between $60 and $230 per ton USEPA (1997).

In every instance a clean-up requires knowledge of the mechanical properties of the contaminated sand and the level of crude oil contamination in order to select the best remediation method in terms of cost and efficiency. Several methods were addressed, as mentioned above, but they were not considered to be cost effective (Riser, 1998). Eagle et al. (1993) presented the capital cost of the cheapest remediation method, i.e. soil washing, where the soil washing plant used attrition, screening, and wet classification, and where remediation took 23 months. This cost would be magnified in developing countries where none of the above mentioned remediation methods are available. On this basis, there is a definite need to find a better and more cost-effective way of utilising oil contaminated sand. A potential alternative would be to use oil-contaminated soil in construction and mix it with cement to solidify and stabilize. The end product can then be used in different engineering applications.

Some studies have been carried out to determine the beneficial use of contaminated sand in construction. Mirza, (1996) investigated the effect of heavy crude oil on the geotechnical properties of soil and he indicated that the direct shear tests show a straight-line relationship between relative density and angle of friction for the uncontaminated sand using 6% heavy crude oil. The direct shear tests give friction angles greater than these obtained in the triaxial test for the same relative density. However, no information is provided on the vertical confining stress (normal loading) used in the direct shear tests. On the other hand, the effect of nutrients, surfactants, and oil-degrading microorganisms of oil-contaminated sand was conducted by (Kim et al., 2005). The results showed that the addition of inorganic nutrients accelerated the rate of CO_2 evolution by a factor of 10.The application of oil-degrading microorganisms in a concentration greater than that of the indigenous population clearly increased biodegradation efficiency. The application of surfactant has slightly enhanced the oil degradation rate in the contaminated sand treated with the higher concentration of oil-degrading microorganisms. Similarly, the feasibility of fuel oil removal from artificially contaminated sand by coal agglomeration using ball milling as a high shear mixer has been investigated by Shin & Shen, (2011). They concluded that sand cleaning efficiencies of 96%, 95%, and 90% can be achieved for the 500, 160 and 90 um oil-contaminated sands, respectively, by this simple one-step process but it’s considered as an expensive remediation option.

A recent study was conducted by Ajagbe et al. (2012) and investigated the effect of crude oil on the compressive strength of concrete. They concluded that 18 to 90% of the compressive strength was lost due to 2.5 to 25% crude oil contamination. Furthermore, (Almabrok et al., 2011) investigated of oil solidification using direct immobilization method. They concluded that although the compressive strength of cement mortar decreased with increasing oil content after 28 days; the results demonstrated that cement based stabilizer/solidification technique can be effective technology. Moreover, the effect of used engine oil on the structural behaviour of reinforcement concrete (Hamad and Rteil, 2003), and the effect of used engine oil on the properties of fresh and hardened concrete were investigated. It was concluded that the oil acted as a chemical plasticiser that improved its fluidity and doubled the slump of the concrete mix while maintaining its compressive strength (Hamad et al., 2003). Furthermore, Hamad et al. (2003) concluded that adding engine oil to a fresh concrete mix could be similar to adding an air-entraining chemical admixture, which enhances some of the durability properties of the concrete. Additionally, when sand contaminated with petroleum was used in highway construction, its potential for use in road construction was considered to be appropriate (Hassan et al., 2005).

As can be deduced from the findings of previous researchers, they fail to agree on the effects of the crude oil and its contaminants on the mechanical properties of the concrete. Some have suggested that the oil contamination has adverse effects on the mechanical properties of the produced concrete but some studies have drawn attention to some positive effects. The lack of agreement stems from several factors such as the type of crude oil, the permeability of sand, sand properties, absorption, chemical composition, quantity of spillage, and the sources of oil contamination (Nudelman et al., 2002, Fine et al., 1997, Tuncan and Pamukcu, 1992). Furthermore, numerous investigations have focused on the effect that crude oil contamination has on the environment in terms of pollution of surfaces, such as ground water, flora, fauna, air pollution, and fire hazards (Manoli and Samara, 1999, Onwurah et al., 2007, Bustamante et al., 1991, Foster, 1998, Aghalino and Eyinla, 2009, Collins, 1971), but very little research has been done on the interaction of sand-crude oil and the effects of crude oil on the geotechnical properties of sand, and the mortar and concrete it produces, in order to provide a better understanding of the potential benefits of its use in building and construction.

To the best of author’s knowledge, this study is the first one to scientifically investigate the physical and mechanical properties of mortar and concrete containing fine sand contaminated with light crude oil. It focuses on understanding the effects of critical parameters such as mixing and curing methods, water-to-cement ratio, curing time, and types of cement binders on the strength and microstructure of the hardened mortar and concrete. The outcomes of this study provide a benchmark for future studies and useful information to carefully consider oil contaminated sand for use in building and construction.

1.2 Research objectives

The overall aim of this research is to investigate the influence of light crude oil contamination on the properties of fine sand, and in turn on the produced mortar and concrete utilising this waste material. The specific objectives are to:

1) Evaluate the effects of different levels of light crude oil contamination on the important physical and mechanical properties of fine sand when applied to construction;
2) Determine appropriate mixing and curing methods for cement mortar containing oil contaminated sand that will provide the optimal mechanical properties;
3) Investigate the effect of water-cement ratio and time of curing on the physical, mechanical and microstructure properties of cement mortar containing oil contaminated sand;
4) Investigate the physical, mechanical and microstructure properties of geopolymer mortar containing oil contaminated sand; and
5) Investigate the effect of light crude oil contamination on the physical, mechanical and microstructure properties of concrete.

1.3 Scope of the Thesis

This study focuses on understanding the behaviour of fine sand contaminated with light crude oil and investigates its potential use in building and construction applications. Light crude oil and fine grained sand are considered in this study as the former is similar to the Libyan oil that is commercially classified as Brent, while the latter closely represents the sand that can be found in the Libyan oil fields. During the course of the study, particular attention is given to the following:

- Review of the environmental impact caused by oil industries, and the existing remediation methods used in terms of the cost and the geotechnical properties of oil contaminated sand;
- Material properties and characterisation related to construction are determined for fine sand contaminated with light crude oil;

- Physical and mechanical characterisation of mortar prepared using different mixing and curing methods, with varying water-to-cement ratios, curing times, and types of cement binders.
- Physical and mechanical properties of geopolymer mortar containing fine sand contaminated with light crude oil;
- Porosity measurements and microstructure observations, and correlation with changes in mechanical properties;
- Physical and mechanical properties of concrete containing fine sand contaminated with light crude oil;
- Development of a simplified mathematical model to correlate the mortar properties with those of concrete, which can then be used to predict the strength at any value of crude oil contamination within the limit used in this study (0-20%).

However, the surface chemistry and measurement of the interfacial bond between cement paste and oil contaminated sand particles are beyond the scope of this study due to the unavailability of facilities and equipment such as X-ray diffraction and others. Nonetheless, the results of this study provided a base knowledge on the fundamental physical and mechanical behaviour of fine sand contaminated with light crude oil and mortar and concrete containing this waste material from which further research could continue. Furthermore, the presence of detergent or any chemical(s) used to remove crude oil contamination is not considered because in developing countries such as Libya none of the remediation methods are used due to the prohibited cost.

1.4 Thesis structure

The structure of this thesis is schematically described in Figure 1.3. It consists of nine Chapters, which contain information that is described below:

- The first chapter is an introduction and outlines the objectives of this study.

- Chapter 2 provides an overview of the main sources of oil contaminated sand, the existing solutions, as well as the main factors affecting the mechanical properties of sand, mortar and concrete due to oil contamination. It also gives specific consideration to problems associated with oil contaminated sand, as well as a justification for undertaking this research.

- Chapter 3 presents the results of the investigations on the important properties related to construction applications of fine sand contaminated with light crude oil, such as particle size distribution (PSD), moisture content, water absorption, permeability, contact angle, and shear strength.

- In Chapter 4, two mixing methods and four commonly used curing conditions are considered and their effects on the mechanical properties of cement mortar with oil contaminated sand (0, 2 and 10% by weight of sand) are investigated. In addition to compressive testing, microscopic observations have been performed to analyse the microstructure of the cement mortar with oil contaminated fine sand.

- Chapter 5 investigates how the water-to-cement (w/c) ratio influences the physical and mechanical properties of mortar containing light crude oil contaminated fine sand. Three w/c ratios were considered (0.4, 0.5, and 0.6) and the properties of cement mortar, produced consisting of fine sand with different levels of light crude oil contamination, were investigated.

- Chapter 6 investigates the physical and mechanical properties of cement mortar containing fine sand contaminated with light crude oil. Compressive strength tests, porosity measurements, and SEM observations were conducted to cement mortar containing sand with different levels of light crude oil contamination, and cured at different times, up to 365 days.

- In Chapter 7, the physical and mechanical properties of geopolymer mortar using fine sand contaminated with light crude oil are investigated and compared with cement mortar. Further investigation was conducted on the main factors affecting the polymerisation process such as curing, surface conditions, pH, the influence of the temperature on the activated fly ash, and heat transfer. Porosity measurements and SEM observations were also conducted to geopolymer mortar containing fine sand contaminated with light crude oil.

- Chapter 8 presents an extensive investigation to evaluate the effects of light crude oil on the compressive and tensile strength properties of concrete. Microscopic observations were also conducted to examine the porosity and microstructure of concrete containing oil contaminated sand. Moreover, data analysis and modelling was implemented to develop simplified equations to describe the mechanical properties of a concrete mix containing fine sand contaminated with light crude oil.

- The main body of the thesis ends with Chapter 9, which presents the main conclusions of the research and the recommendations for future work.

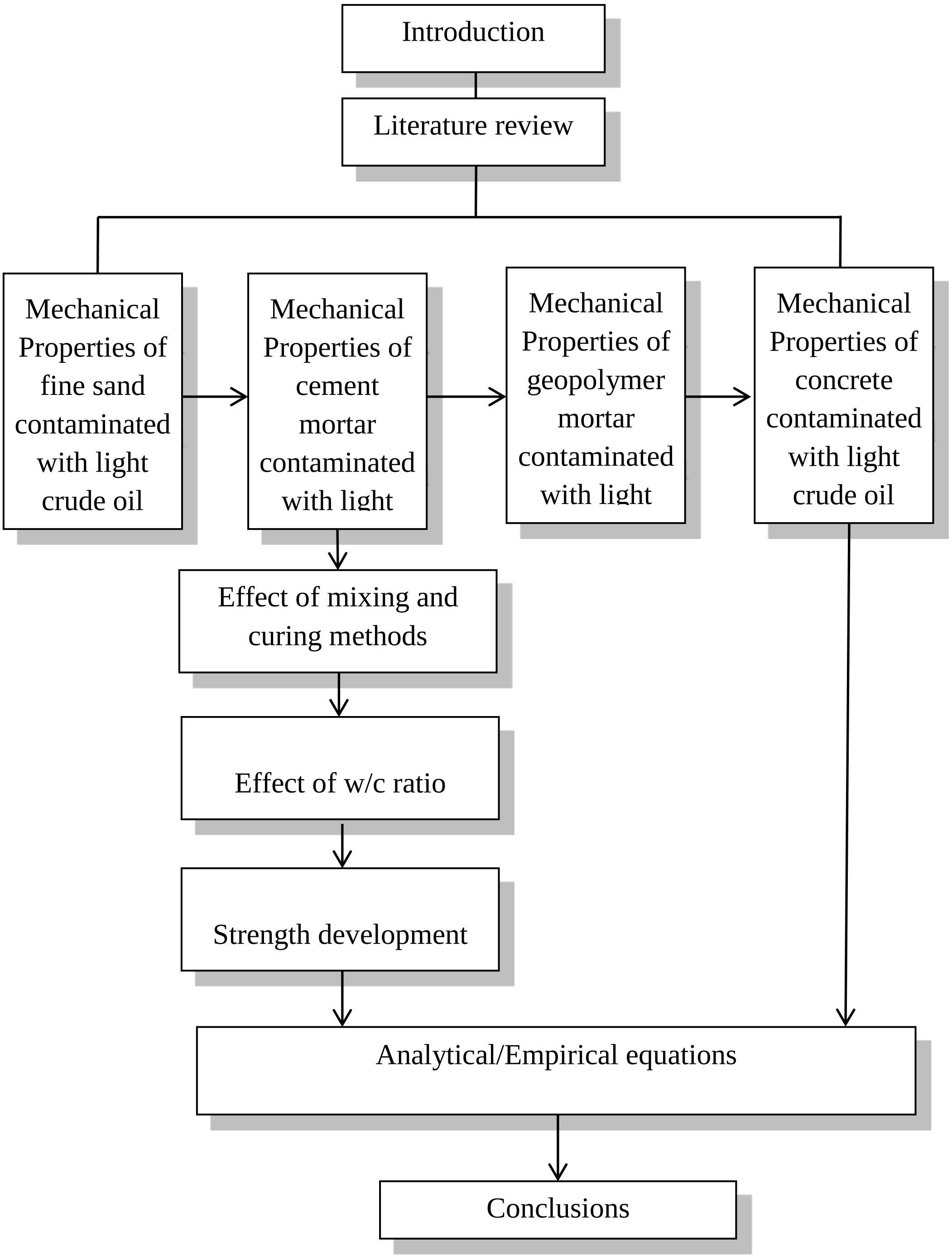


Figure 1-3 Schematic roadmap of the dissertation.

1.5 Summary

A high volume of crude oil is being spilled every year due to ageing facilities, lack of maintenance, and human error in oil production. This problem of oil contamination is significantly affecting ecosystems, posing risks to human health, and changing the mechanical properties of the surrounding sand. As a result, several remediation methods have been trialled and implemented to minimise the adverse effects of oil contaminated sand. However, the cost of the existing remediation methods is prohibitive in most developing, but oil producing, countries. A potential alternative and cheap remediation method is to mix oil contaminated sand with cement and use that in construction. A number of studies have been conducted in this area but have shown conflicting results. Moreover, none have focused on fine sand and light crude oil, which are the types of sand and crude oil in Libya. Understanding mechanical properties of this type of oil contaminated sand, and the behaviour of mortar and concrete containing this waste material, have been the key motivations for this research.

Chapter 2

Current State of Knowledge on Oil Contaminated Sand

2.1 Introduction

There is growing public concern about the wide variety of toxic organic chemicals that are either deliberately or inadvertently being introduced into the environment. Petroleum hydrocarbons are a common example of these chemicals because they enter the environment frequently, in large volumes, and in a variety of ways. Leakage from natural deposits is one of the major ways that crude oil affects the environment (National Academy of Science, 1975) Co-produced water associated with the production of oil and gas is also another source of oil contaminated sand (Khosravi et al., 2013, Ajagbe et al., 2012, Veil et al., 2004). Intentionally or accidentally, oil spill contamination impacts on the properties of the surrounding sand and changes its physical and chemical properties (Khosravi et al., 2013). To minimise its effect on the environment, methods of remediation ranging from sand washing, bio-remediation, electro-kinetic sand remediation, and thermal desorption have been implemented, but are not considered to be cost effective [5]. One alternative method of remediation is using contaminated sand for engineering applications, indeed some researchers have already investigated its use in that area and concluded that sand contaminated with oil can be used for road base materials or topping layers in parking areas [6-8]. This Chapter presented an extensive literature review in a way to show the gap of the study, and hence it is structured in a titles and subtitles to make easy to understand. This chapter provides a general overview of the current state of knowledge on oil contaminated sand. It also gives specific consideration to problems associated with this waste material, as well as justification for undertaking this research. This chapter consists of nine Sections including this brief introduction. Section 2.2 identifies the different kind of crude oil Section 2.3

identifies the petroleum industry in Libya in terms of quantity, locations, and crude oil classifications. Section 2.4 presents the main sources of oil contaminated sand. Section 2.5 discusses the effect of crude oil on the physical and mechanical properties of the sand. Section 2.6 presents the current solutions to oil contaminated sand, such as the existing remediation method, as well as the advantages and disadvantages of each method. Section 2.7 reviews the existing research on mortar and concrete containing oil contaminated sand, and current applications. Section 2.8 discusses the main factors affecting the mechanical properties of mortar and concrete such as mixing and curing methods, water-to-cement ratio, curing time, and the type of cement binder. The research gaps have been identified and the proposed solutions addressing these research needs are presented in Section 2.9.

2.2 Crude Oil

Crude oil is naturally occurring, complex mixtures of hydrocarbons with varying amounts of sulphur, oxygen and nitrogen, as well as trace amounts of metals such as nickel and vanadium. Chemical and physical compositions vary with the origin and age of the crude oil (Speight, 2014). Crude oil can be thought of as a distribution of paraffinic, naphthenic and aromatic species of increasing molecular weight and complexity with the largest and most complex being the asphaltenes. The proportions of the constituents in different crude oils vary and the physical properties also vary accordingly. Crude oil can be classified or characterized in different ways; for example, by its physical properties (e.g., specific gravity, viscosity), recovery methods, elemental composition (amount of carbon, hydrogen, nitrogen, sulphur), carbon distribution, boiling point distillation curve, nature of residue after distillation (e.g., paraffinic, naphthenic, aromatic, asphaltic), or solubility class (e.g., amount of saturates, aromatics, resins, and asphaltenes).

2.2.1 Type of Crude Oil

Crude oil varies widely in appearance which range in colour and properties they contain. Most of crude oil essentially hydrocarbon with difference in properties because the variations in the molecule structure. The variation may influence its suitability and quality of the product. Crude roughly divided in three groups depends on the nature hydrocarbon they contain

- Light crude is liquid petroleum that has a low density and flows freely at room temperature. It has a low viscosity, low specific gravity and high API gravity due to the presence of a high proportion of light hydrocarbon fractions. It generally has low wax content. Light crude oil receives a higher price than heavy crude oil on commodity markets because it produces a higher percentage of gasoline and diesel fuel when converted into products by an oil refinery.

- Medium crude oil have higher viscosity (102 –105 mPa.s) and lower gravity (20o to 10o API) than Light crude. They have lower mobility at reservoir conditions and their primary recovery usually requires thermal stimulation of the reservoir (enhanced oil recovery). In contrast to conventional oils, heavy oils are darker in colour or black.
- Heavy crude oil is extremely viscous hydrocarbon materials which cannot be recovered by either conventional or enhanced oil recovery methods. These heavy asphaltic crude oils occur in near-solid state, are incapable of flow at reservoir conditions and are generally recovered by mining operations and in-situ recovery methods. Their viscosities are higher than 105 mPa.s and their gravity is less than 10o API.

The density of crude oil is reservoir dependent and generally falls between 800 and 1000 kg·m-3. It gives an indirect indication of the crude composition, giving rise to the classification of crude based on density. The density of different crude oil is shown in Table 2.1.

Table 2.1Crude oil classification based on density at 15°C

Classification	*Density range (kg·m^{-3})*
Light crudes	< 825
Medium crudes	825-875
Heavy crudes	875-1000

Whereas light crude oil are rich in low boiling and paraffinic compounds, heavy crude oils have greater amounts of high boiling and asphalt-like molecules, are more aromatic, and contain larger amounts of heteroatoms. The hydrocarbon content of petroleum can be as high as 97% by weight in conventional crude oil or as low as 50% by weight or less in heavy oils and bitumen (Speight, 2014). The non-hydrocarbon constituents tend to concentrate in the higher boiling fractions of the crude oil. This study the only crude oil will be investigated is the light crude oil which can simulate Libyan crude oil.

2.3 Petroleum industry in Libya

2.3.1 General overview

More than 95% of the Libyan economy depends on the production and export of oil and gas. Libya holds about 46.4 billion barrels of oil and it is known to have the largest reserves of oil in Africa (Figure 2.1). In addition, Libya also has 55 trillion cubic feet of natural gas reserves (U.S Energy Information Adminstration., 2011). There are five major onshore sedimentary basins, namely the Sirt basin, the Murzuq basin, the Kufra basin, the Ghadamis basin, the Cyrenaica platform, and one offshore basin, the Tripolitanian basin (Heron and Thusu, 2007). The main production basins in Libya are Sirt, Ghdamis, Murzuq, and the offshore Tripolitanian Basin (Figure 2.2). The Tripolitanian Basin was discovered in 1976 in the Mediterranean Sea, and it forms part of the El Bouri oil field. The proven oil reserves in this field are 2 billion barrels (Hassan, 2009).

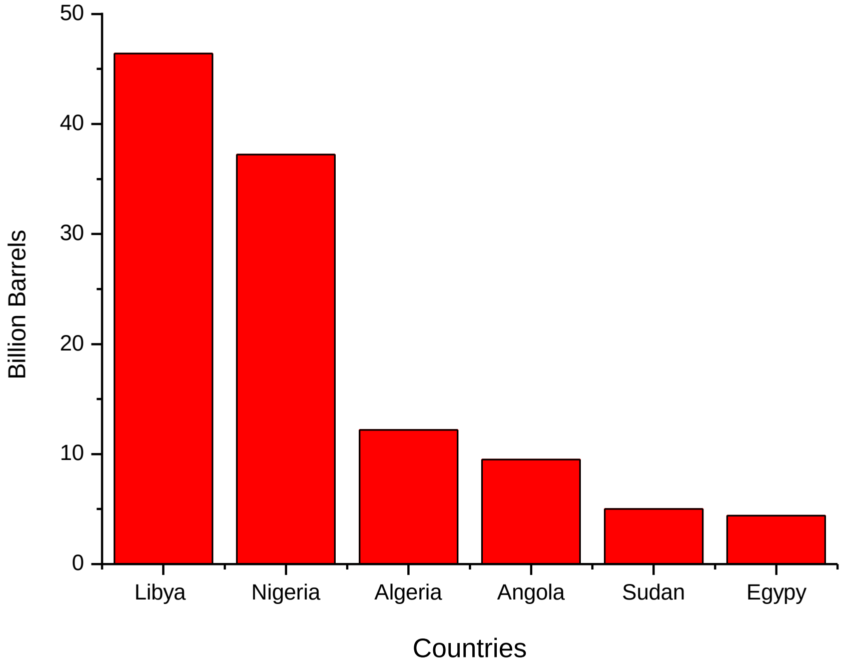


Figure 2.1 African Proven Oil Reserve Holders, 2011 (U.S Energy Information Adminstration., 2011)

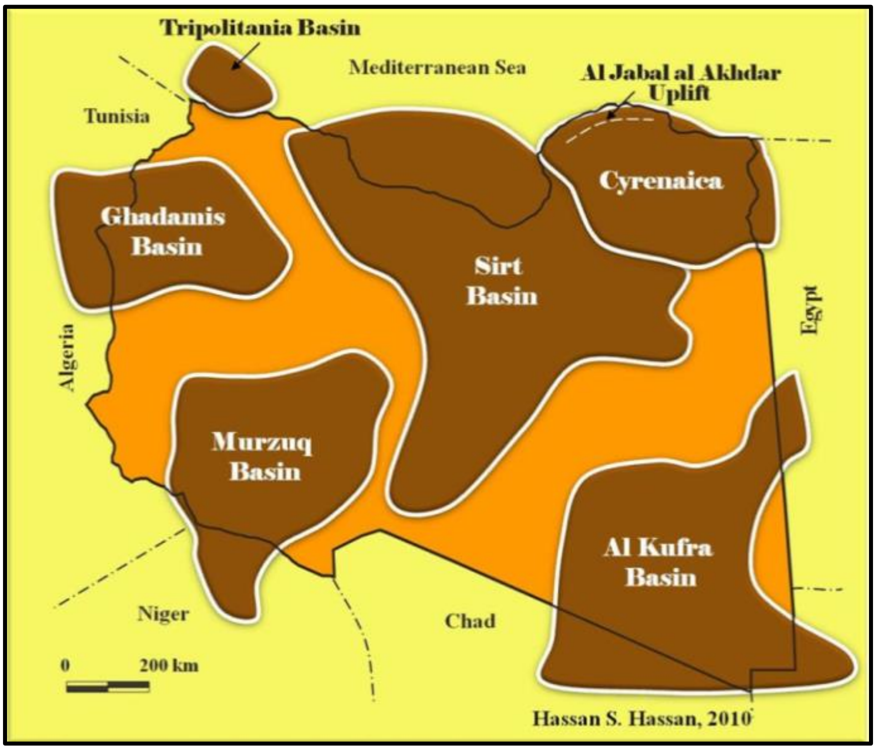
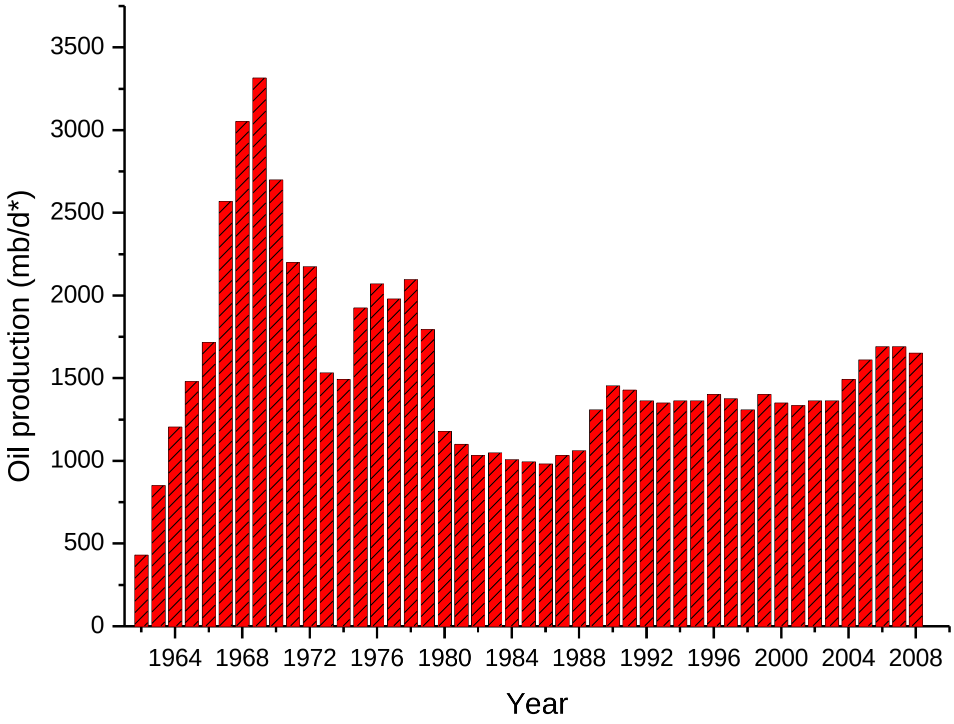


Figure 2.2 Location of major Sedimentary Basins Libya (Hassan, 2013)

The quality of crude oil is measured in terms of its density and sulphur content (sweet or sour). The density is directly related to gravity and is classified by the American Petroleum Institute (API). Crude oil with an API gravity of more than 38 degrees is considered light whereas crude oil with an API gravity of 22 degrees or less is considered heavy. Libyan oil is generally light (with a high API gravity) and sweet (sulphur content of less than 5%) (Heron et al., 2007). Libyan crude contains a high percentage of hydrocarbons and is commercially called “Brent”.

2.3.2 Total oil production in Libya

Libyan oil production peaked at more than 3 million bbl/day in the late 1960s, but since then it has been in decline (Figure 2.3). The National Oil Corporation (NOC) of Libya planned to raise the production to 2.3 million bbl/day by 2013 (Energy, 2010). This data was taken before the revolution and thus far the impact of the regime change is still not clear. In the Libyan Desert, all the oil companies are committed to using alternative solutions to optimise the amount of water resources used, and to eliminate the environmental impact of oil water (produced water) disposal and crude oil contaminations. One solution is to re-inject produced water into onshore oil fields, while contaminated sand is considered to be one of the most significant issues to be solved (Eni-Oil, 2009).



* Million barrels per day

Figure 2.3 Libyan oil production over the past 40 years (National Oil Corporation, 2011)

Figure 2.4 shows the estimated reserves (remaining crude oil potential of the sediments in Libya in 1999). This study shows that the estimation of crude oil in each basin was approximately 107 billion barrels, including the relative proportion of reserves estimated in each basin. The total offshore reserves included prospective areas in the Mediterranean offshore Sabratha basin areas (Misrata Trough, Tripolitianan), the Gulf of Sirt, and Cyrenaica (Gulf of Bomba and offshore Benghazi) areas (Heron and Thusu, 2007).

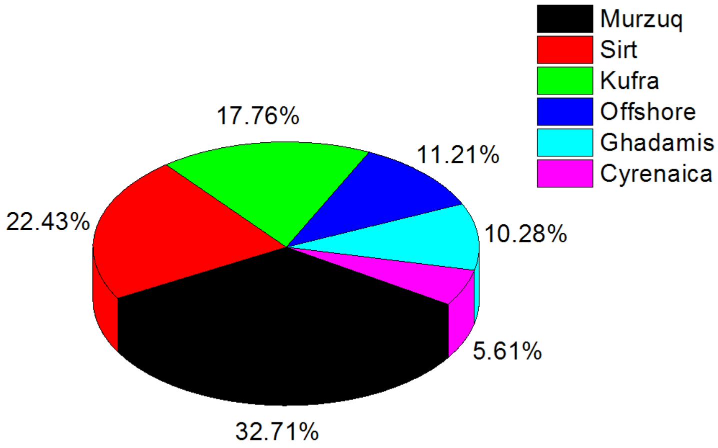


Figure 2.4

Figure 2.4 Hydrocarbon potential of the sediments of Libya (Heron and Thusu, 2007)

2.4 Sources of oil contamination

2.4.1 Oil spillage

Oil leaks either happen accidentally or intentionally during exploration, production operation processes, and transportation of crude oil. However, most crude oil spills have been caused unintentionally due to ageing facilities, lack of maintenance, and human error. Libya is one of the main countries exporting oil (Luciani, 1994), and as such has been effected by the issue of sand contaminated with oil where large areas have been contaminated. Figure 2.5 (a) shows the major oil pipelines, refiners, and major oil fields in Libya, while Figure 2.5 (b) illustrates the final stage of produced water and shows the contaminated sand around the discharge disposal point. Figure 2.6 shows the oil spillage in 2014 at one of the oil fields that belong to the Harouge Oil Operations called Tibisti oil field, Libya.

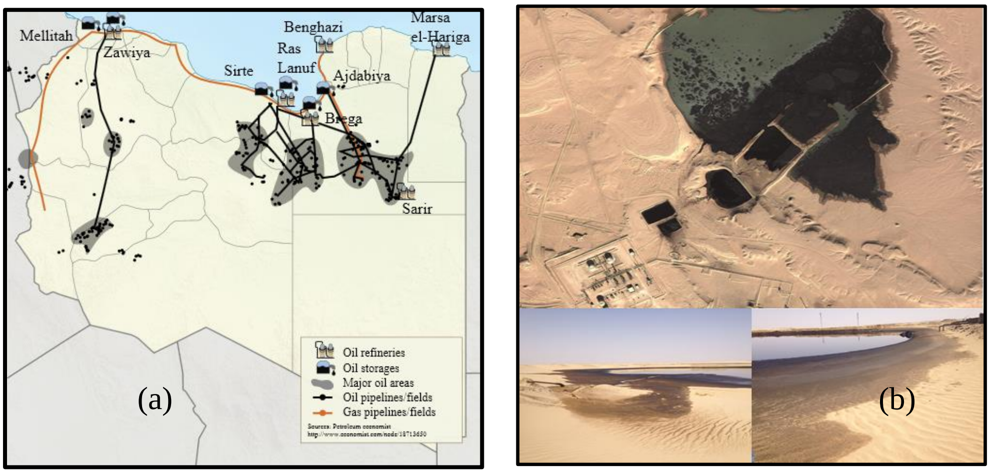


Figure 2.5 Libyan major oil pipelines, refiners and major oil fields (source: National Oil Corporation, Energy Intelligence, Petroleum Economists, (U.S Energy Information Adminstration., 2011)

Figure 2.6 Oil spillage in Tibisti oil field, Libya in 2014

2.4.2 Oily waste water (Produced water)

The second source of contaminated sand is the oily waste water (produced water), which is considered to be the major volume waste stream in the oil production industry - roughly three barrels of water for every barrel of oil (Halliburton, 2010). It exists as a consequence of the production of oil and gas from underground reservoirs, which consist of formation water (Ray and Engelhardt, 1993). The globally estimated average of produced water is 210 million bbl/day, which results in an annual production of 77 billion bbl/year (Khatib and Verbeek, 2003). The estimate of produced water in offshore platforms worldwide is approximately 107 million bbl per day, while the estimated total production of offshore oil is 120 million bbl per day. Figure 2.7 shows the comparison between onshore and offshore produced water over a fifteen-year period. More than 44 million bbl/day of produced water is discharged into the sea (Teodor, 2009). The quantity of produced water by the oil industry has increased dramatically and this does not remain constant during the operational life of an oil well; indeed it has been shown that the amount of produced water increases as the production of oil decreases (Fakhru et al., 2009). In some older oil fields, the water cut exceeds 95% (Khatib and Verbeek, 2003; Halliburton, 2010).

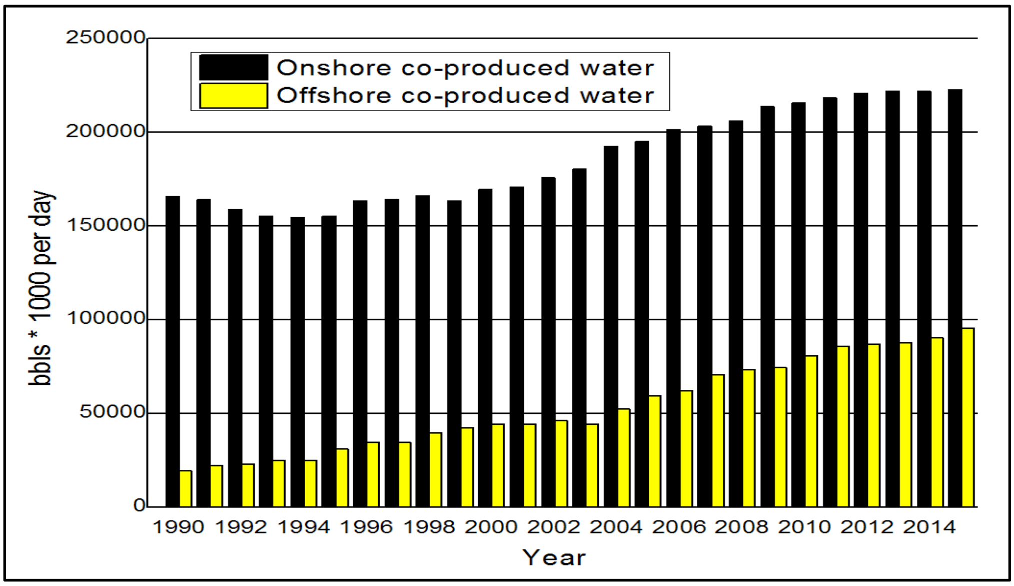


Figure 2.7 Global onshore and offshore water production (Fakhru'l-Razi et al., 2009)

The quantity of produced water is expected to continue to increase into the future, and due to this inevitable worldwide increase of oily wastewater, the effect of discharging oily waste water into the environment has become a significant concern (Gilbert et al., 2002). The issue with produced water is that it contains a high percentage of crude oil; dispersed oil consists of small oil droplets suspended in oily waste water. This concentration of dispersed oil can be affected by several factors such as its density, the efficiency of the separation stages, its chemical treatment, the shear history of the droplet, and interfacial tension between the water and the oil (Ali et al., 1999). Chemical treatment and soluble organics play a large role in decreasing the interfacial tension between oil and water in produced water. The methods of removing oil and gas (OG) depend on the end use of the produced water and the internal composition of the oil. Table 2.2 illustrates the typical treatment and performance of oil removal, expressed by the minimum size particle of oil removed.

Table 2.2 Oil and grease removal technologies based on the size of the particles removed (Arthur et al., 2005).

Oil Removal Technology	Minimum size of particles removed (µm)
API gravity separation	150
Corrugated plate separator	40
Induced gas flotation (no flocculants)	25
Induced gas flotation (with flocculants)	3-5
Hydroclone	10-15
Mesh coalesce	5
Media filter	5
Centrifuge	2
Membrane filter	0.01

Produced water from the separators (an item of production equipment used to separate liquid components of the well stream from gaseous elements), typically contains 40-1200 mg/L oil droplets of less than 20 µm, and 1-50 mg/L solid particles of less than 10 µm. Because the current systems cannot remove particles (oil droplets) that are less than 10 µm, small droplets of oil can interfere with oily waste water (Bansal and Caudle, 1999). Based on EPA regulations, the daily maximum limit for OG is 42 mg/L and the monthly average limit is 29 mg/L (Fakhru et al., 2009). Despite the fact that many countries have implemented more stringent regulations for discharging produced water to reduce the effect of these components on the environment, huge amounts of produced water are still discharged either onshore or offshore, which is considered a second major source of oil contaminated sand worldwide.

2.5 Petroleum contaminants

Over the last few decades there has been an increased public awareness of environmental issues, particularly when the contamination of sand, water, and air is involved. Worldwide, scientists and environmentalists are faced with the challenge of overcoming the detrimental effects of the contamination of sand, air, and water. The spillage of crude oil onto sand, leakages from pipelines, underground and surface fuel storage tanks, indiscriminate spills, and careless disposal and management of waste- and other by-products of society, constitute the major sources of petroleum contamination.

2.5.1 Sand contaminated with oil

One of the most critical environmental impacts of the oil industry is the spillage of crude oil, which severely contaminates the sand. Remediating contaminated sand takes longer and costs much more than it does for water contaminated with oil. Hence, it is very important to investigate the properties of sand contaminated with oil (Jia et al., 2011) because its physical and chemical properties change as soon as the sand comes into contact with crude oil (Tuncan and Pamukcu, 1992). The degree of this change depends on many factors such as the type of sand and the specific composition and quantity of the spilled crude oil. When crude oil is spilled, the liquid hydrocarbon migrates down to the groundwater causing partial saturation of the sand and the pathway of the hydrocarbons. As shown in Figure 2.8, once crude oil reaches the ground

The permeability of contaminated sand is based on the density and water table, the light hydrocarbons start to spread horizontally by migrating within the capillary zone, which causes further saturation of the sand (Tuncan and Pamukcu, 1992). These spreads are much greater with light crude oil than with medium and heavy crude oil, because light crude oil contains a high percentage of light hydrocarbons that can easily penetrate and migrate through the sand particles. This is why sand contaminated with light crude oil is considered to be one of the most adverse environmental issues.

A number of studies have already been carried out on the geotechnical properties of the sands contaminated by petroleum hydrocarbons. Cook et al. (1992) experimentally investigated the compaction, compression, and strength properties of uniformly graded sands contaminated by crude oil. They reported that although oil contamination had no significant effect on the compaction characteristics, it decreases the friction angle and considerably increases the compressibility of the sand. Similar results were obtained by Puri (2000) and Meegoda and Ratnaweera (1994) for sandy and clayey sands, respectively. Studies on the geotechnical characteristics of fine-grained sands have just recently gained momentum. Khosravi et al. (2013) studied the geotechnical properties of the oil-contaminated clayey and sandy sands and found a reduction in strength, permeability, maximum dry density, optimum water content, and Atterberg limits of these sands. Singh et al. (2008) found an increase of 35%–50% in the consolidation settlement of fine-grained sands upon contamination with petroleum hydrocarbons. From the previous studies in can be considered that the uniformly graded sands, clayey sands, fine-grained sands showed similar results however, when clayey and sandy sands was used the strength, permeability, maximum dry density, optimum water content, and Atterberg limits were decreased. Although none of the previous studies were investigated the absorption test of crude oil, it is expected that the type of sands may play a great role properties of oil contaminated sand. Thus conducting the absorption test should be considered when oil contaminated sand is used.

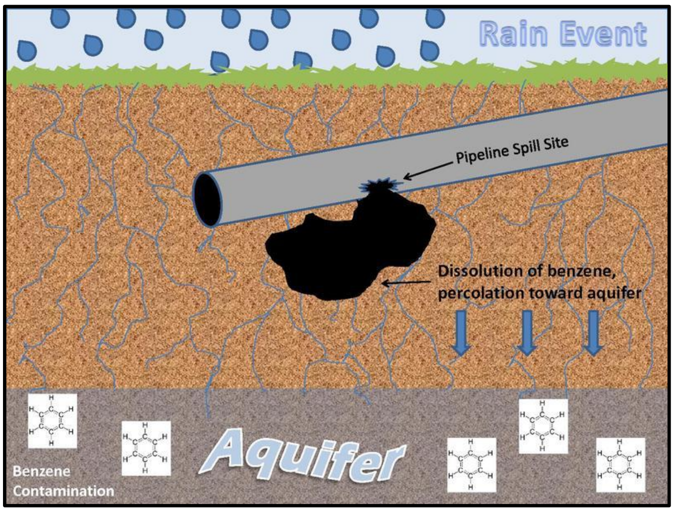


Figure 2.8 Crude oil spillage and the leaching of light hydrocarbons to the aquifer (NTSB, 2010).

The main sources of this kind of leakage are from crude oil pipelines, underground storage tanks at petrol stations, refineries, and production facilities (Aikman et al., 2002). Hydrocarbon contamination has a direct effect on the erodibility of sand and water infiltration, and may also cause fire on the ground. Furthermore, the aggregation of fine particles, and the fusing of minerals, may lead to a reduction in the stability of the sand-organic matter aggregate. Whereas fire-induced or fire-enhanced sand water repellence has often been cited as the major cause of post-fire enhanced runoff and erosion (Shakesby et al., 2007), hydrocarbon contamination can also affect the physio-chemical characteristics of sand (Osuji and Ezebuiro, 2006).

The permeability of contaminated sand is based on the viscosity of the fluid filling the voids, as was concluded in a study by Sharma and Reddy (2004), and there is an increase in intrinsic permeability (*k*) when there is an increase in density and a decrease in viscosity, all of which indicates the significant effect that density and viscosity have on the permeability of sand. It is not safe to construct buildings on contaminated sand because any changes in the engineering properties and behaviour of the layers of sand may affect the bearing capacity and differential settlement of the foundation (Rehman et al., 2007). A previous study by (Rahman et al., 2010) has shown that is not only the ecosystem that can be affected by the spillage of crude oil, but the safety of the civil engineering structures as well. Cleaning up contaminated sand is a complicated job due to the long period of time needed, and the high cost and limitations of disposing the excavated sand. Furthermore, proper environmental regulations are not available due to the lack of proper management in many developing counties such as Libya, which then leads to disused oil and illegal dumping of other hydrocarbon components, which could have helped to tackle the environmental issue, as well as the economy, in the form of construction materials such as sand. Moreover, oil contamination can adversely affect plants as well as contaminate ground water resources for drinking or agricultural purposes (Rahman et al., 2010).

2.5.2 Mechanical properties of oil contaminated sand

Sand is a naturally occurring material, which is considered to be an engineering material. Thus, its physical characteristics can be determined by experiments, which then may enable these properties to be used to predict their expected behaviour under working conditions, which in turn raises the possibility for its potential beneficial use to be determined (Head, 2006). The advantages of examining the mechanical properties of sand is that it permits a greater accuracy of measurements, so that any changes in conditions can be simulated to represent the conditions during and after construction, and the sand parameters can be derived within a reasonable time scale.

Understanding mechanical properties of sand is beneficial to an engineer in terms of reducing the uncertainties in the analysis of foundations and earth work and the creation of structures, and in the use of sand as a construction material. In this application, the mechanical properties such as cohesion, frictional angle, shear strength and contact angle are important. Also, the relevance of physical properties such as Particle size distribution, moisture content, water absorption, permeability and microstructure observation is discussed in the subsections.

2.5.2.1 Moisture content

Moisture content is an important factor when developing the proper ratio of water and cement. The moisture of the aggregates is based on the porosity of the particles and the moisture condition of the storage area. The moisture content can range from less than 1% and up to 40% in very porous sandstone and expanded shale. Aggregates can be found in four different moisture states that include oven-dry (OD), air-dry (AD), saturated-surface dry (SSD), and wet. Of these four states, only OD and SSD correspond to a specific moisture state and can be used as reference states to calculate the moisture content (Mindess et al., 2003; Kosmatka et al., 2002).

2.5.2.2 Water absorption

The water absorption of an aggregate reflects its porosity, which is often related to characteristics such as strength, durability, and in some cases potential shrinkability. Australian Standard 1465-1974 “Dense Natural Aggregate” specifies a minimum dry bulk density of 2300 kg/m^3, a maximum dry density of 3000 kg/m^3, and a maximum water absorption of 5%. This is considered to be an important experiment because this value is used in calculating air voids, while water absorption may also be an indicator of absorption of water from concrete/ mortar mix. A highly absorptive aggregate may result in a mixture with low durability. In Portland cement concrete, the specific gravity of the aggregate is used in calculating the percentage of voids and the volume of sand aggregate in computations of yield. This absorption is important in determining the net water-cement ratio in the concrete mix.

2.5.2.3 Shear strength

The shear strength of sand is one of the most important parameters in civil engineering applications. The safety of any mechanical engineering structure is based on the shear strength of the underlying sand (Budhu, 2008). All constructions, when in or on the land, impose loads on the sand that supports the foundations of that particular construction or building. The load imposed on the sand may cause shear failure of the underlying sand, which occurs when the shear stress imposed on the sand mass exceeds the maximum shear resistance (shear strength) that the sand can offer (Smith, 2013). The shear strength of the sand is considered to be an important aspect in many foundations, such as in the bearing capacity of shallow foundations and piles, the lateral earth pressure on retaining walls, and the stability of slopes of dams (Das, 2008). Hence, understanding the shear strength can play a great role in terms of the entity classification of the sand (Coduto, 2001), which in turn can assist engineers to derive the critical aspects of the overall sand mechanics in a specific environment.

The shear strength of common engineering materials, such as steel, from a continuum mechanics viewpoint, is governed by the molecular bonds that hold the material. The higher the shear strength of a material, the stronger the molecular structure (Das, 2008). Nevertheless, the shear strength of sand operates under a different set of principles. Sand is a particulate material, so shear failure occurs when the stresses between the particles are such that they slide or roll past each other. Due to the particulate nature of sand, unlike that of a continuum, the shear strength depends on the interaction of anti-particles (is it a particle of the opposite charge), rather than the internal strength of the sand particles themselves (Coduto, 2001). Sand derives its shear strength from two sources: cohesion between particles and frictional resistance between particles. Cohesion is the cementation between sand grains or the electrostatic attraction between sand particles (Smith, 2013).

2.5.2.4 Permeability

Sand is considered to be permeable because it consists of solid particles and a network of interconnected pores. The degree of permeability is based on a number of factors such as sand type, water content, grain size distribution, and degree of compaction. The capability of sand to transmit water is characterised by the coefficient of permeability (k). The permeability of sand is a measure of its ability to allow a fluid to flow through it (Head and Epps, 2010), and it is the property of porosity that permits the transmission of fluid through the sand. Permeability is considered to be a major parameter in design and landfill, and thus for example in contaminated ground and in the design of earth dams, etc. In addition, permeability is one of the parameters that play a major role in hardened concrete (Givi et al., 2010), where the workability of the concrete can be affected by the permeability. For these reasons, understanding the characteristics of sand permeability is necessary for many construction projects where drainage is considered to be an important feature. Furthermore, in terms of contaminated sand, the permeability test is important because understanding the permeability properties of sand is necessary in estimating the quantity of underground seepage. Moreover, the permeability test is important in terms of solving problems that involve pumping seepage water from construction excavations, as well as in stability analyses of earth structures and earth retaining walls that are subjected to seepage forces. A permeability test on sand contaminated with crude oil is also required when determining the rate at which the groundwater is contaminated, as well as for ground water remediation.

2.5.3 Effect of oil contamination on sand properties

The engineering properties of sand are subjected to change as soon as they become contaminated with crude oil (Rehman et al., 2007). The stability and permeability of sand in landfill sites can be affected by contamination with crude oil, and sand seepages might cause the sand on which pipelines are laid to expand and contract (Rehman et al., 2007). Most industrial waste is now discharged, after treatment, into land based containments, and has been ever since engineered waste disposal was established. Nevertheless, sand contamination, caused by intentional disposal, or accidental leakages of chemical substances, can change the mechanical properties of sand, resulting in their enhancement or degradation, and sometimes leading to the functional or structural failure of structures.

Any change in the mechanical properties or behaviour of sand may affect the bearing capacity and may cause an increase in the total differential settlement of foundation systems of a structure (Rehman et al., 2007). In addition, polluted water may affect the workability and durability of concrete when used for mixing concrete (Klein and Sarsby, 2000). It has been reported that the present structural damage to industries and residential buildings has been from chemical contamination of sand, which thus emphasizes the importance of the modification of the mechanical properties of sand by chemicals (Rao et al., 2008). The presence of chemicals may affect the mechanical properties of sand and its behaviour, so understanding the different phases of sand is critical when considering any re-use of contaminated sand (Sharma and Reddy, 2004). Several studies have been conducted on the effect of crude oil, and its related contaminants, on the mechanical properties of sand. However, there has been a lack of agreement regarding the effect of oil contamination on mechanical properties as shown in Table 2.3.

Table 1.3 Effect of oil contamination on sand properties

Mechanical properties	Petroleum	Effect	Author
Cohesion	Crude oil	Decrease	Khamehchyan et al., 2006; Rahman et al., 2010; Rahman et al., 2010
	Methanol	Increase	Olgun and Yildiz, 2010
	Ethanol-gasoline	Decrease	Kermani and Ebadi, 2012
Friction angle	Crude oil (motor oil)	Decrease	Evgin and Das, 1992; Cook et al., 1992; Al-Sanad et al., 1995; Shin et

			al., 1997
	Methanol, ethanol-gasoline	Increase	Olgun and Yildiz, 2010; Kermani and Ebadi, 2012
Permeability	Crude oil	Decrease	Al-Sanad et al., 1995; Shin et al., 1997; Khamehchyan et al., 2006; Rahman et al., 2010; Rahman et al., 2010
	Hydrocarbon Methanol	Increase	Bowders et al., 1986; Olgun and Yildiz, 2010
Optimum Moisture content	Crude oil	Decrease	Al-Sanad et al., 1995; Rahman et al., 2010; Rahman et al., 2010b
Strength	Crude oil	Decrease	Ola, 1991; Alsanad et al., 1995
	Hydrocarbon (phenol)	Increase	Chan et al., 1986
	Crude oil	Increase	Al-Sanad and Ismael, 1997
Compaction	Heavy crude oil-light crude oil	Improved up to 4%	Alsanad et al., 1995
	Ethanol-gasoline mixture	Decrease	Kermani and Ebadi, 2012
Compressibility	Heavy crude oil-light crude oil	Increase	Alsanad et al., 1995
	Heavy - Medium crude oil	Increase	Aiban, 1998; Cook et al., 1992

Further investigations into the effect that leakages of crude oil have on the environment in terms of pollution of surfaces such as ground water, flora, fauna, air pollution, and fire hazards, have been undertaken, but very little research has been done on the interaction between sand and crude oil, the effects of crude oil on the mechanical properties of sand, and its ability to be used as a construction material.

2.6 Current remediation methods for oil contaminated sand

The threat posed by contaminated sand to humans and the environment has made the assessment and remediation of contaminated sites become very significant. Over the past decade, the awareness of contaminated sites has increased, especially where the public water supply is relying on ground water. Sand contamination has also become an issue for society due to adverse health and environmental problems. The extensive seepage and contamination caused by the spillage of crude oil is based on the properties of the sand (Fine et al., 1997). Sand contaminated by crude oil needs major remediation and/or reclamation in order to become suitable for any future use. Research and studies have resulted in several technical methods which could remediate these problems, but they do have both advantages and disadvantages (Grande and Barbosa, 2003; Silva and Fiuza, 2005). Table 2.4 compares the most common alternative methods for sites contaminated by hydrocarbons. This table also includes a general brief summary of advantages and disadvantages (USEPA, 1997).

Table 2.4 Advantages and disadvantages of remediation methods (USEPA, 1997)

Remediation Method	Advantages	Disadvantages
Incineration	Destroyed hydrocarbons Organic contaminated (solid & liquid) can be treated. Can be used as stationary and mobile.	System efficiency and achievement not 100%. Unable to destroy inorganic contaminants (heavy materials).
Chemical Dehalogenation or Dechlorination.	Uses chemical reaction to remove hydrocarbons. Can be used as mobile technology. An efficient method for treating hydrocarbons. Inexpensive ($225-$380 per ton).	The performance of this system can be affected by the presence of metal. (It increases the amount of hydrogen). Some of them use

	Hydrocarbons can be treated at any concentration.	polyethylene glycol which is not recommended because it affects the performance.
Solvent Extraction	Has the ability to separate the hazardous contaminants from sand & sediment. Uses organic chemicals.	Organic wastes cannot be destroyed by this method. Incineration is needed for any further treatment.
Sand Washing	Contaminants can be removed by dissolving or concentration. Mobile technology.	Sometimes it needs further treatment due to some of the process’s residuals.
Stabilization / Solidification	Reduces the mobility of hydrocarbons. On site treatment. Inexpensive materials such as Portland cement, cement kiln dust, or fly ash.	This process can be considered as inconclusive due to possible volatilization in some of the hydrocarbons and to being inhibiting with other materials.
Vitrification	Can be used for sand and sediment contaminants. It can be used for organic or inorganic materials. Can be used for radioactive contaminants. Has the ability to destroy the hydrocarbons. This method is recommended by EPA as one of the verification treatment systems for hydrocarbons. Can be used in-situ and ex-situ.	Further treatment might be needed for the scrubber water.
Direct-Heated Fast-Quenched	Can be used in-situ and ex-situ. Rapid cooling system prevents	Involves site disturbance (sand excavation).

Thermal Desorption. (DFTD).	formation of dioxin. Expensive method ($90-$380 per ton). Successful method in terms of destroying hydrocarbons.	Uses high temperatures and a slower process when further treatment is needed.

The cost of the alternative remediation methods, as described by the USEPA (1997) varies from 50 - 1000 (US $ per ton). Figure 2.9 indicates that the cost is dependent on the remediation technique and the concentration of the contaminants.

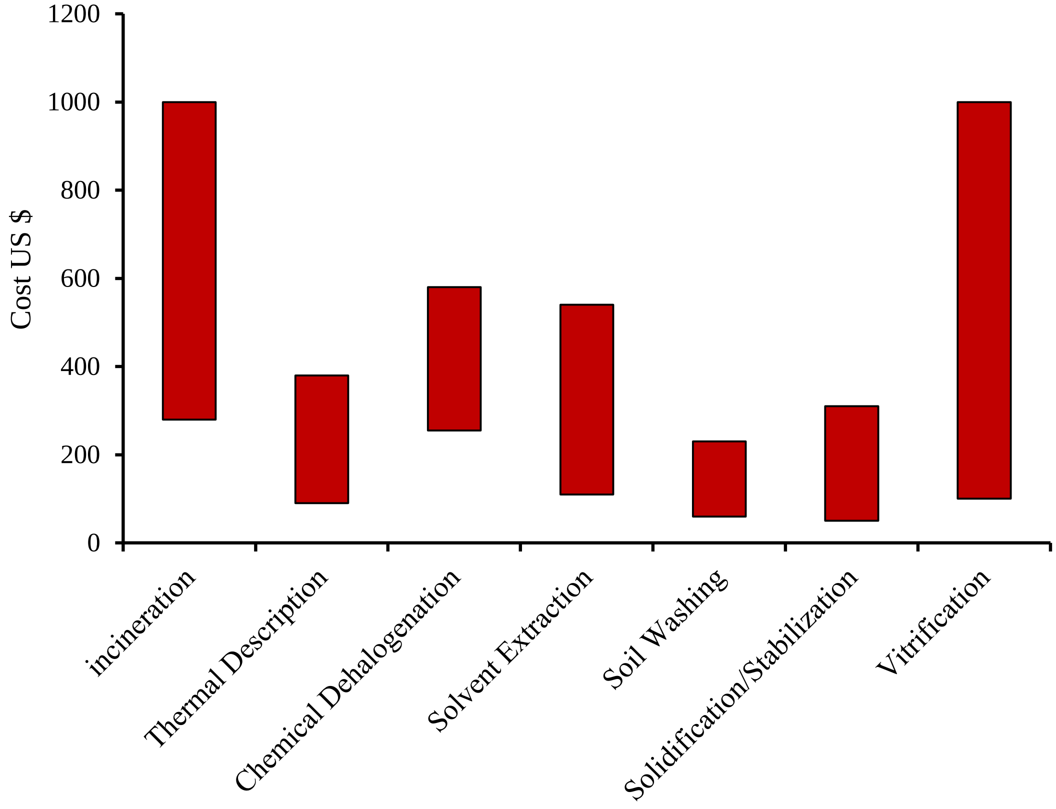


Figure 2.9 Cost of hydrocarbon remediation methods (Adapted from USEPA (1997)

In all cases, the clean-up requires knowledge of the mechanical properties of the sand, but very few studies exist that address the mechanical properties of contaminated sand. Several methods, such as the methods mentioned above, have been considered, but not all are deemed to be cost effective (Riser, 1998). Thus, there is a strong need to find a better alternative and a more cost-effective way to utilize the oil contaminated sand. One possible approach is to mix it with cement and use it in construction.

2.7 Stabilisation of oil contaminated sand by mixing with cement

Several studies have investigated the mechanical properties of concrete utilising oil contaminated sand and have evaluated their potential use in construction. These studies are presented in this section, as well as the current usage of oil contaminated sand in construction.

2.7.1 Effects of oil contamination on the properties of mortar and concrete

Hamad and Rteil (2003) revealed that oil acted like a chemical plasticizer, improved the fluidity, and doubled the slump of the concrete mix, while maintaining its compressive strength. A similar study was conducted by Hamad et al. (2003) who added engine oil to a fresh concrete mix and found that its effect was similar to adding an air-entraining chemical admixture, which enhanced some of the durability properties of concrete. Additionally, the potential use of sand contaminated with petroleum in highway construction was investigated by Hassan et al. (2005), and they concluded that it could be used for this purpose.

In a recent study by Ajagbe et al. (2012) the effect of crude oil on compressive strength of concrete was investigated, and they concluded that 18 to 90% of its compressive strength was lost due to 2.5 to 25% contamination with crude oil. Ahad and Ramzi (2000) indicated that there was a significant reduction in the compressive strength and about an 11% reduction in the splitting-tensile strength of concrete soaked in crude oil. Table 2.5 summarises the effect of oil contamination on the mechanical properties of concrete. Nevertheless, there are still disagreements about the effect of crude oil and its produced content on the properties of produced concrete.

Table 2.5 Effect of oil contamination on the properties of concrete properties

Test	Petroleum Hydrocarbon	Effect	Author
Compressive strength	Engine oil	Maintained	Hamad and Rteil, 2003; Hamad et al.,2003
	Oil, phenol,	Decrease	Cullinane and Bricka, 1987
	Hydrocarbon (phenol)	Maintained	Hebatpuria et al., 1999.
	Low % of mineral oils	Maintained	Hamad and Rteil, 2003
	Crude oil	Decreased (18-90%)	Ajagbe et al., 2012
	Soaked in crude oil	Decreased (11%)	Ahad, 2000
Workability	Engine oil	Increased	Hamad and Rteil, 2003; Hamad et al.,2003

Table 2.5 shows that most of these researchers disagree on the effect of crude oil on the behaviour of concrete. The inconsistency of some of the factors such as type of crude oil, permeability of sand, sand properties, absorption, chemical composition, and spillage quantity (Nudelman et al., 2002; Fine et al., 1997; Tuncan and Pamukcu, 1992) were considered as the main reason beyond this lack of agreement. Thus, there is a need to further investigate the properties of oil contaminated sand and its effect on produced mortar and concrete.

2.7.2 Beneficial use of mortar and concrete containing oil contaminated sand

As was addressed in the previous section 2.5, a range of remediation methods for sand contaminated with oil have been recommended but they are not cost effective

(Riser, 1998). The possibility of an end-use scenario of treated material or contaminated sand was addressed, based on the results of the compressive strength. For instance, less strength is required for landfill but a higher compressive strength is required to make bricks or for some other structural objectives. Based on the United States Environmental Protection Agency (USEPA) guidelines, the recommended compressive strength, at 28 days, for landfill disposal material is 0.35 MPa, while it is 1.0 MPa in France and the Netherlands (Spence and Shi, 2004). A higher compressive strength of 3.5 MPa in a sanitary landfill is required according to the Wastewater Technology Centre (WTC) in Canada (Stegemann and Cote, 1996). Based on the British standard for precast concrete masonry units (BSI, 1981) a higher compressive strength is required for blocks and bricks, of 2.8 and 7 MPa respectively. Additionally, a minimum of 7 days cube compressive strength, which should vary between 4.5 and 15 MPa, is required for sub base and base materials, as regulated under the department of transport in the UK. This shows that there is high potential in using oil-contaminated sand in construction. However, an understanding of the details of its physical and mechanical properties is warranted.

2.8 Factors affecting the properties of mortar and concrete

Certain structural characteristics need to be investigated in order to use oil contaminated sand in building and construction. Compressive strength is the most important mechanical property of concrete. This property is affected by mixing methods, curing methods, water-to-cement ratio, time of curing, and types of cement binder. These factors are described in the sections that follow.

2.8.1 Mixing methods

An adequate strength of concrete can be achieved by the consistency of mixing (Aguwa, 2006). From a technical point of view, rich concrete mix may lead to high shrinkage, and the evolution of high heat as part of hydration process in mass concrete may cause cracking (Nataraja, 2002). The hydration process of Ordinary Portland Cement (OPC) concrete has already been investigated by many researchers and is very well documented (Lea, 1970). The main components of Portland cement, tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF), react with water to form complex hydrates. The end products of C_2S and C_3S phases can be presented approximately as follows:

$C_2S + H \longrightarrow C\text{-}S\text{-}H + CH$ and

$C_3S + H \longrightarrow C\text{-}S\text{-}H + CH$

where C-S-H is calcium silicate hydrate and CH is calcium hydroxide.

As heat is generated in this mixture, three principal reactions occur (Al-Harthy et al., 2005). Firstly, during hydration and hardening, the concrete develops certain physical and chemical qualities such as strength, low moisture, permeability and chemical composition, each of which affects the properties of produced concrete (Borger et al., 1994; Bishr et al., 1995). When contaminated sand is used, there is a probability that the hydration process may be hindered due to the presence of crude oil. Hence, the effect of mixing methods, as suggested by the ASTM-C305-14 (2013) and the AS-1012.2 (2014), termed cement, water, then sand (CWS) and cement, sand, then water (CSW) respectively, were considered in this study.

2.8.2 Curing methods

Adequate curing is very essential for concrete to obtain its optimum structural and durability properties. This process promotes cement hydration and controls the temperature and moisture in the concrete. During hydration of cement, all the chemical and physical processes take place after the cement particles come into contact with water (Stark, 2011). As such, it is important to saturate the calcium silicate hydrate (CSH) gels with water in order to commence the hydration (Taylor, 2013). Proper curing reduces the rate at which moisture is lost during the hydration process, and thus, a continuous source of moisture is needed to reduce the porosity and provide a fine pore size distribution in concrete (Alamari, 1988).

The influence of curing conditions on normal mortar/concrete have been widely studied (Neville, 1995; Kocaman et al., 2011; Mehta, 1986), whereas the effects of curing methods on the properties of concrete contaminated with crude oil are relatively unknown. Therefore, determination of the most appropriate curing method for concrete with oil contamination is required in order to achieve the optimum mechanical properties. This research investigates how the commonly used curing methods, i.e. cured in water (W), in air (A), in plastic bags (PB), and in a fog room (FR), affect the development of the compressive strength of mortar containing crude oil. A brief description of these four curing methods is provided below.

- Water curing (W): This is done by immersing the cast mortar/concrete in water to prevent the loss of moisture from the concrete. This curing method is also effective for maintaining a uniform temperature in the concrete during curing.
- Air curing (A): In this method, specimens are left in open air to cure until testing at 28 days. The specimens are exposed to the ambient air in the laboratory at room temperature.
- Plastic bags (PB): This represents the method whereby plastic sheets, which are normally made of polyethylene film, are used to cover the concrete during the curing process. As specified by the ASTM C 171 (Kosmatka et al., 2002), the polyethylene film should have a thickness of 0.1 mm, which it had in this study.
- Fog room (FR): This method is considered to be an excellent curing method when the humidity is low and the ambient temperature is well above freezing point (Kosmatka et al., 2002). In practice, the fog is applied through nozzles or sprayers in order to raise the relative humidity (RH), and hence, the evaporation from the surface of the specimen is reduced.

2.8.3 Water cement ratio

Water-cement ratio is a very important factor in concrete production, and hence, the strength decreases with an increasing water cement ratio, as shown in Figure 2.11, because the capillary porosity increases. To increase strength, and thus reduce w/c, it is more efficient to reduce the water content than to use more cement. The compressive strength at any specific age is a function of the water cement ratio and the degree of hydration, because both cement paste and the interfacial transition zone between the coarse aggregate and cement paste, can be affected by w/c and the degree of hydration (Wassermann et al., 2009; Mindess et al., 2003; Kosmatka et al., 2002; Mehta and Monteiro, 1993).

The effect of the water to cement (w/c) ratio on the properties of concrete has been studied widely and is considered to be one of the most important factors in concrete production, as it affects the fresh and hardened properties of concrete (Živica, 2009). The strength at any particular age is a function of w/c and the degree to which the cementitious materials have hydrated, because they affect the porosity of both cement paste, and the interfacial transition zone between the coarse aggregate and the cement paste (Wassermann et al., 2009; Mindess et al., 2003; Kosmatka et al., 2002). Strength decreases with an increasing w/c ratio because the capillary porosity increases (Kosmatka et al., 2002; Wassermann et al., 2009). Thus, it is more efficient to reduce the water content than to use more cement in order to increase the strength of the produced concrete (Popovics, 1990). While it is widely known that the strength of normal concrete at a given age, and proper curing, are strongly dependent on the w/c ratio, the effect of this parameter has never been examined for a concrete mix with oil contaminated sand. Kostecki et al. (Kostecki, 1997) indicated that oil contamination interferes with the hydration process and results in a low strength concrete. Thus, to enable the production of concrete using oil contaminated sand with optimal mechanical properties, an appropriate w/c ratio should be determined, as well as the effect of the w/c ratio on the compressive strength of concrete. For instance, Shamsai et al. (2012) have shown that decreasing the w/c ratio from 0.5 to 0.33 increases the compressive strength by 34.4%. Waziri et al. (2011) achieved a maximum strength of 23.7 MPa with a mix proportion of 1:2:4, and a water cement ratio of 0.5, at 28 days hydration. Furthermore, Rao (2001) and Schulze (1999) stated that the strength, durability, and other engineering properties of concrete increased when the w/c ratio decreased. Felekoğlu et al. (2007) have indicated that a w/c ratio between 0.9 and 0.1 in volume is usually acceptable, although decreasing the w/c ratio decreases the workability of the concrete.

According to Simeonov and Ahmad (1995) the porosity is strongly related to the w/c ratio, while Yuan and Gud (1998) indicated that a local increase in w/c in the aggregate cement paste interface is proportional to the amount of free unbound water, and any action that increases the content of the solid phase reduces the strength of the concrete. It follows then that the w/c ratio can also be correlated to the spacing between the particles in the cement paste such that the smaller the spacing, the faster the cement hydrates and fills the gaps between the particles; it also creates links between hydrated particles to form a stronger concrete (Bentz and Aitcin, 2008), as shown in Figure 2.10.

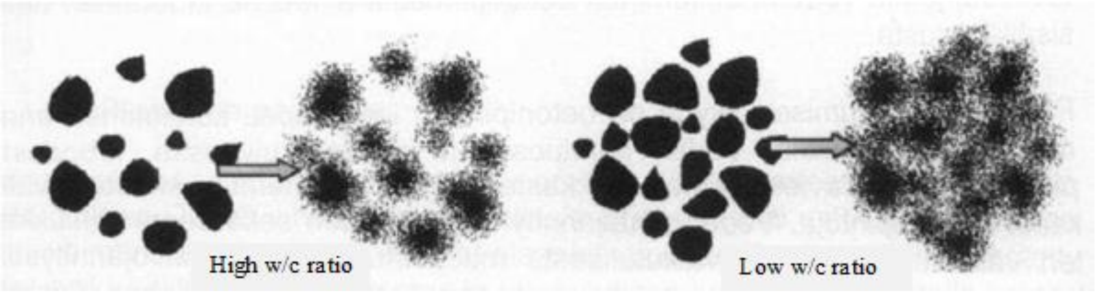


Figure 2.10 Lower water cement ratio means stronger concrete (Betoniyhdistys and Risto, 2004)

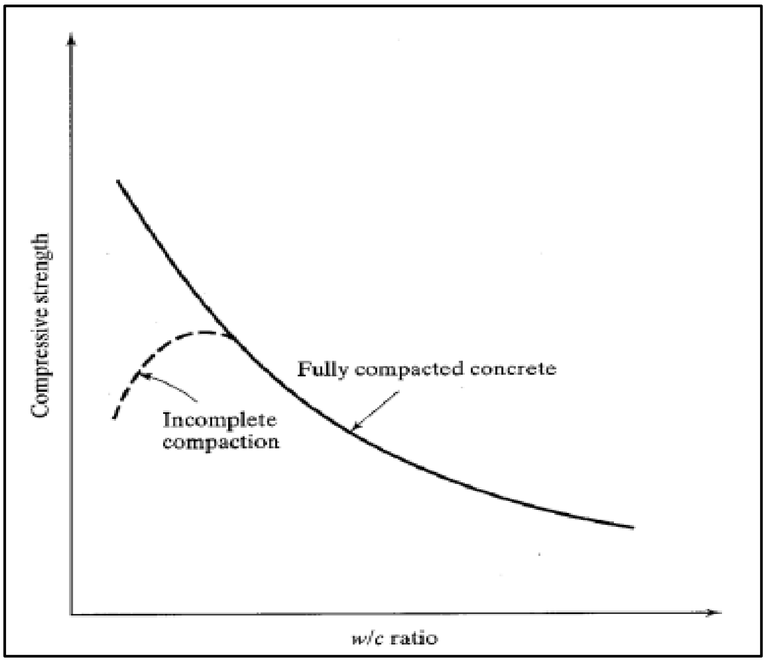


Figure 2.11 Relationship between compressive strength and w/c ratio (Betoniyhdistys and Risto, 2004)

Compressive strength can be affected by several factors as shown in Table 2.6.

Table 2.6 Shows the main factors that affect the strength

Factors	Effect	Ref.
Water cement ratio	Increasing w/c will decrease strength	(Mindess et al., 2003, Kosmatka et al., 2002, Mehta and Monteiro, 1993)
Hydration	Increasing the degree of hydration will increase strength	
Age	Strength increases as concrete age increases	
Supplementary cementitious material	Increasing the supplementary cementitious material will increase the strength	
Entrained air	Increasing the entrained air will decrease the strength	
Aggregate	Rough and angular aggregates will increase the strength	
Type of cement	Increasing the cement fineness will increase the early strength	

Since some of these factors will be fixed, such as age, supplementary cementitious material, entrained air, aggregate, and type of cement, this research will focus on the effect of the water cement ratio on the strength, using oil contaminated sand. The effect of the w/c ratio on the strength properties of mortar and concrete has been widely investigated, but its properties with the presence of light crude oil is unknown; hence, the effect of water cement ratio on compressive strength with oil contaminated sand will be investigated using different w/c ratios 0.4, 0.5, and 0.6, and these percentages have been selected based on previous studies (Kharita et al., 2010).

2.8.4 Curing time

Curing of concrete is the process of maintaining the proper moisture condition and temperature in the concrete for a definite period of time (Mamlouk and Zaniewski, 2011; Neville, 1981). Proper moisture conditions are critical because water is necessary for the hydration of cementitious materials. If curing stops for some time and then resumes again, then strength gain will also stop and reactivate (Bushlaibi and Alshamsi, 2002); though the detrimental effects of early improper curing are irreversible (Gowripalan et al., 1992). When concrete is properly cured, water retained in concrete helps continuous hydration and development of enough tensile strength to resist contraction stresses. The continuous development of strength reduces shrinkage and therefore reduces the potential initial cracks or micro-cracks (Kolyvas, 2007). Concrete curing starts soon after concrete hardens and the aim is to control temperature and moisture movement from and into the concrete; it essentially promotes cement hydration (Abalaka and Okoli, 2012). Since cement hydration takes place only in water-filled capillaries, it is important to keep concrete saturated, or as nearly saturated as possible, until the water filled pores in the fresh cement paste are filled to the desired extent by hydrating calcium silicate hydrate gels and other solid hydration products (Neville, 1981; Taylor, 2013). Hydration of cement can be defined as the combination of all chemical and physical processes that take place after contact of the anhydrous solid with water (Stark, 2011; Han et al., 2014).

The main factors for appropriate curing are temperature of curing and moisture curing time, because the rate of hydration is controlled by the quality, quantities of the cementitious materials present in the mixture, the ambient temperature and the availability of moisture in the mixture (Tasdemir, 2003). The strength increase at the early stages is due to higher temperatures during placing and setting, but undesirably affects the strength at later ages, while they are continuously cured in water at 21°C (Erdoğan, 2003). At the early stages, the way temperature increases performance of mortar/concrete but decreases at a later age, was investigated in terms of the changes of mechanical and physical properties of mortars (El-Nemr, 2011). During the hydration time, many solid hydration products are created, but the major hydration product responsible for the compressive strength of concrete is a rigid C-S-H gel (Abalaka and Okoli, 2013). The atomic structure of Calcium silicate hydrate (C-S-H) gel, the nature of its formation, and its molecular bonding are mainly responsible for the compressive strength development in concrete (Harris et al., 2002). Nevertheless, it is known that the growth of C-S-H gels and other solid hydration products in concrete is promoted by curing, and studies have shown that the strength of concrete and microscopic pore structures is also affected by the degree of hydration (Abalaka and Okoli, 2013).

Previous studies (Saul, 1951; Kim et al., 1998; Uddin et al., 2012) have concluded that the strength gain of concrete is subject to a combined effect of curing time and temperature during the hardening process. They found that the concrete gain strength at early-age is subject to a high temperature in moisture. The effect of curing time on compressive strength development is presented in Figure 2.12. From this Figure, it can be seen that moisture curing and time curing are essential for concrete to achieve the approximate maximum strength. Furthermore, Parrott (1991) investigated the effect of curing time at 1, 3, and 28 days at 60% Relative humidity (RH) on the permeability of concrete. Results showed that the permeability of concrete samples subjected to 3 days curing was about one-sixth of the samples cured for only one day. Moreover, Uddin et al. (2012) concluded that adequate curing at early ages as well as at later ages is essential to the strength development of PCC concrete.

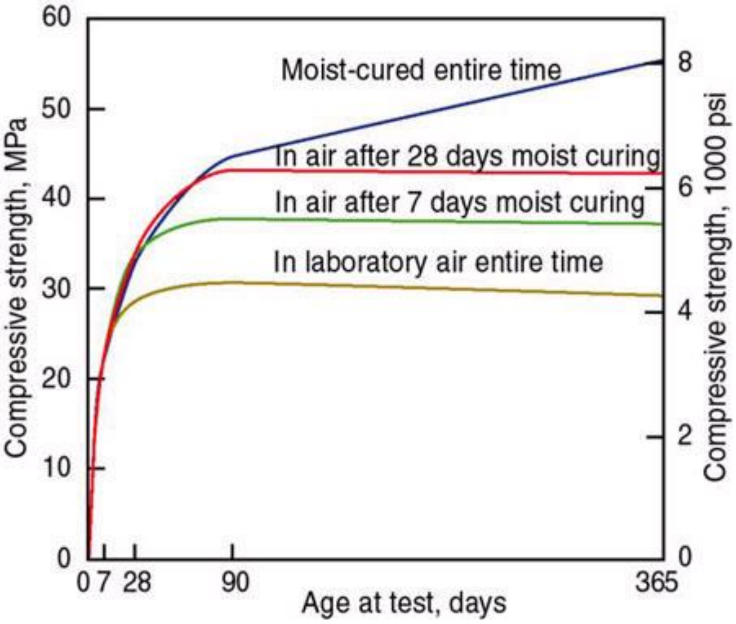


Figure 2.12 Shows the variation of concrete with curing time (Mamlouk and Zaniewski, 2011)

As shown above, many previous researchers have studied the effects of curing time on strength and have agreed that concrete properties are significantly influenced by curing, since it greatly affects the hydration of cement (Uddin et al., 2012; Uddin et al., 2013; Saul, 1951; Kim et al., 1998). Therefore, investigating this factor is important in order to investigate the effects of curing time on the strength of concrete containing light crude oil.

2.8.5 Types of cement binder

Ordinary Portland cement and geopolymer are used as a binder in producing concrete. Portland cement is defined as a ground product of Portland cement clinker, usually inter-ground with a modicum of calcium sulphate, to bring the total content of sulphate of the cement to about 2.5%-4% by weight. Portland cement clinker is made from a mixture of finely-ground calcareous and siliceous components, together with a proportion of alumina and iron, with some impurities, which is then heated in an oven up to 1450 ºC. Another explanation is that clinker is composed of rounded and either grey-green or dark grey nodes, with sizes that vary from less than 1 mm to 30 mm or more. There are four main principals in the main clinker content: Alite, belite, a calcium aluminate phase, and a calcium alumina-ferrite phase (Winter, 2012).

2.8.5.1 Ordinary Portland cement

Cement hydration is the process whereby cement and water react when they are mixed together (Winter, 2012; Pane and Hansen, 2005). The mixture of cement and water in a suitable ratio leads to a chemical reaction, which results in a solid mass composed of gel and crystalline material, which in turn binds the constituents of a concrete mix together. A mix of cement and water produces a hard cement paste, while the concrete is a mixture of cement, water, and aggregate (i.e. sand and gravel or crushed stone). The cement paste binds all the constituents together into a single solid mass. The properties of the concrete (strength and durability) are critically influenced by the properties of the cement paste (Winter, 2012).

As soon as cement and water are mixed, cement hydration starts. Cement hydration is the totality of reactions taking place in the cement/water mixture, resulting in setting and hardening of the paste. Setting is the loss of plasticity of the paste, making it solid, but without measurable strength. Setting is immediately followed by hardening, meaning that the paste develops hardness and measurable strength. The properties of the final hardened product are strongly determined by (1) the composition of the initial cement/water mixture, (2) the progress of hydration, i.e. the amount of cement that has reacted and is converted into solid hydration product, and (3) the environmental conditions such as temperature and humidity.

The progress of hydration can be characterised by the fraction (m/m) or (V/V) of cement that has reacted to, and converted to, hydration product at the corresponding moment. This fraction is called the degree of hydration, denoted α, where α is a function of time.

$$a = \frac{m_c^r}{m_c^0} = \frac{V_c^r}{V_c^0} = 1 - \frac{V_c}{V_c^0} \tag{2.1}$$

where

a = degree of hydration

m_c^0 = initial cement mass

m_c^r= reacted cement mass

$V_c^0 =$ initial cement volume

V_c^r = reacted cement volume

$V_c =$ current cement volume (=$V_c^0 - V_c^r$)

When cement is mixed with water, a large number of dissolution and precipitation processes is initiated. The water present in the original mixture will be strongly bound in the stable hydration products, while the remaining water is left in a fine network of water filled pores. Because the volume of the hydration product is higher than the volume of the original binder, it will replace the space that was first occupied by water. The formation of stable hydration products, at the expense of water, results in the fluid cement/water mixture being converted into a stony material. Cement hydration is often described as the hydration of separate clinker phases (Edmeades and Hewlett, 1998; Taylor, 1997).

Silicates hydrate to calcium silicate hydrates (C-S-H) and calcium hydroxide (Ca (OH) $_2$ or CH). C-S-H is a nearly amorphous product of the general formula

CxSHy, where x is the C/S ratio and y is the H/S ratio, both varying over a wide range. C-S-H gel is also referred to as cement stone. It is the main contributor to strength in all cementitious systems. CH is a crystalline compound, also referred to as portlandite. Dicalcium silicate (C_2S) will produce relatively less CH compared to Tricalcium silicate (C_3S).

$$2\,C_3S + 6\,H \longrightarrow C_3S_2H_3 + 3\,CH \tag{2.2}$$

$$2\,C_2S + 4\,H \longrightarrow C_3S_2H_3 + CH \tag{2.3}$$

Aluminate hydrates to hydrogarnet (C_3AH_6). This rapid reaction arises when there is no sulphate present and it causes “flash set”.

$$C_3A + 6\,H \longrightarrow C_3AH_6 \tag{2.4}$$

Aluminate and gypsum react to ettringite ($C_6A\bar{S}\,3H_{32}$).

$$C_3A + 3\,C\bar{S}H_2 + 26\,H \longrightarrow C_6A\bar{S}_3H_{32} \tag{2.5}$$

Ettringite is a mineral that is structurally similar to the ($Al_2O3\text{-}Fe_2O_3$-tri) mineral group and therefore is often referred to as the Ettringite (AFt) phase.

2.8.5.2 Geopolymer concrete

Geopolymer is considered to be the result of reactive material that is rich in silica and alumina, with alkaline liquid. This material has been studied widely and shows some promise as a greener substitute for ordinary Portland cement in some applications. It has been concluded that geopolymer concrete has good engineering properties and it has reduced the potential for global warming, resulting from the total replacement of ordinary Portland cement (Lloyd and Rangan, 2010). Geopolymer concrete was developed as a result of research into heat resistant materials after a series of catastrophic fires (Davidovits, 1991), and it has the advantage of not using any Portland cement in its production. The research also discovered that geopolymer resins and binders are non-flammable and non-combustible.

Geopolymer has shifted from being in the field of chemistry to engineering applications and commercial production, where it has been found that geopolymer concrete has good engineering properties (Rangan, 2008; Sumajouw and Rangan, 2006). Furthermore, the use of fly ash has further environmental advantages because the volume of fly ash produced annually is too high compared to the percentage utilised in beneficial ways. For instance, in Australia in 2007 almost 14.5 million tonnes were used, of which only 2.3 million tonnes were utilised in beneficial ways, principally as a partial replacement for Portland cement (Lloyd and Rangan, 2009). The improvement of geopolymer technology and applications will lead to a further increase in the beneficial use of fly ash, as has been observed over the last 14 years with the use of fly ash in concrete and other building materials.

Geopolymer concrete was developed as a result of research into heat resistant materials, after a series of catastrophic fires (Davidovits, 1991), and it has the advantage of not using any Portland cement in its production. The same research also documented that geopolymer binders are non-flammable and non-combustible. Additionally, there are several economic benefits, such as the cost of geopolymer concrete materials, which are estimated to be 10 to 30% cheaper than Portland cement concrete, due to the lower cost of fly ash compared to the same weight of Portland cement. Other benefits can be obtained through carbon credit trading because the appropriate use of one ton of fly ash creates approximately one carbon credit, with a redemption value of 10 to 20 Euros. All these advantages have encouraged me to develop a deeper investigation in order to show the beneficial use of geopolymer. Geopolymer concrete has gone beyond being simply an emerging technology and has become a viable structural concrete. For these reasons, investigating how sand contaminated with oil affects geopolymer concrete is one of the objectives of this research, an investigation that appears to be the first of its kind.

In contrast, factors such as the curing temperature, the mixing ratio, and the molarity of alkaline may play a large role in the compressive strength of geopolymer cement. Nevertheless, a high strength geopolymer concrete can be developed in the earlier stages when a high curing temperature is used (Guo et al., 2010), and this gains its target strength after 28 days under ambient conditions when slag material is added to the mix (Temuujin et al., 2009). This enhancement of its physical properties is related to the intrinsic structure, which has developed due to improved geopolymerisation (Kumar et al., 2010). A very rapid compressive strength can be obtained (from 47 to 53 MPa) after 24 hours with 60 ºC (Yost et al., 2013). It has been stated that the compressive strength can be increased by increasing the duration and temperature of oven curing, where it can achieve more than 60 MPa just 24 hours after casting, according to (Satpute et al., 2012). Based on their results, geopolymer concrete can suit many structural applications. These advantages of using geopolymer are considered in this study to investigate the reactions of oil contaminated sand and how they affect its mechanical properties. Despite the fact that the effect of oil on the cement solidification process, and its consequent effect on the performance of fresh and hardened properties of the resultant cementitious mix, have been investigated (Almabrok et al., 2013), a study on the effect of oil contaminated sand on the mechanical properties of geopolymer is a new approach. Therefore, the effect of light crude oil on the physical and mechanical properties of geopolymer mortar was investigated in this study.

2.9 Research need

The extensive review of literature has revealed that there is a general lack of agreement regarding the effect of hydrocarbon compounds on the properties and behaviour of sand and in turn on mortar and concrete containing oil contaminated sand. This may be related to the fact that pollution with crude oil is not identical in terms of its effect, as it is based on a number of factors such as the permeability and absorption properties of the sand (Nudelman et al., 2002), and the level and the sources of the oil contamination (Fine et al., 1997). Some studies conducted in this area have focused mostly on the characterisation of the physical and mechanical properties (Hamad et al., 2003; Ayininuola, 2009; Almabrok et al., 2013; Almabrok et al., 2011; Osuji and Nwankwo, 2015; Attom et al., 2013; Ajagbe et al., 2012; Diab, 2011; Nuruddin et al., 2010; Jasim and Jawad, 2010) but very few have gone beyond understanding the microstructure of the produced mortar and concrete to explain the changes in the properties due to oil contamination. Moreover, none of the current studies have evaluated the effects of light crude oil contamination on the properties of fine sand and produced concrete, which are the most common types of crude oil and sand in oil producing countries. The effects of this type of oil contamination on the important geotechnical properties of fine sand, the physical, mechanical and microstructure of the produced mortar and concrete, therefore warrants further investigation. Furthermore, a better understating of the effects of mixing and curing methods, water-to-cement ratio, strength development, and types of cement binder on the properties of hardened mortar and concrete containing oil contamination is required. These are critical parameters that need to be investigated in order to expand the understanding in this new research area and thoroughly evaluate the effectiveness of using oil contaminated sand in building and construction.

In Chapter 3, an extensive investigation into the important geotechnical properties of fine sand with different levels of light crude oil contamination is presented.

Chapter 3

Physical and Mechanical Properties of Fine Sand Contaminated with Light Crude Oil

3.1 Introduction

The extensive literature review in Chapter 2 highlighted that an investigation of sand contaminated with oil is very important because, a) very few studies in the literature have dealt with its mechanical properties Mashalah et al. (2007), b) it is useful in ensuring that the soil can bear the applied load Khosravi et al. (2013), c) crude oil pollution affects the permeability and absorption properties, and the coefficient of partition of the soil Nudelman et al. (2002), and d) the extent of the contamination based on its chemical composition and the properties of the soil varies from place to place Fine et al. (1997). Moreover, there is an inconsistency in the results on the effect of many factors, such as the type of crude oil, sand properties, absorption properties, chemical composition, and spillage quantity, on the properties of oil contaminated sand Fine et al. (1997); Nudelman et al. (2002); Tuncan and Pamukcu (1992).

Large areas of the Libyan Desert are contaminated with light crude oil due to the exploration and production of oil and gas. Light crude oil causes more adverse environmental effects compared to medium and heavy crude oil as it easily penetrates and migrates through the sand particles. This is due to the high percentages of light hydrocarbons and lower percentage of heavy components such as asphalts. The penetration and migration through the sand particles is faster compared to medium and heavy crude oil (Venosa and Zhu, 2003). As a consequence, significant public concern is has built up about the wide variety of toxic organic chemicals that are either deliberately or inadvertently being introduced into the environment by light crude oil contamination. As suggested by a number of researchers, mixing contaminated sand with cement and using it in construction is an alternative and cheap remediation method to reduce its environmental impact. However, there is very limited information available on the effects of this type of oil contamination on the physical and mechanical properties of fine sand. Thus, this warrants further evaluation in order to carefully consider the re-use of light crude oil contaminated fine sand for building and construction.

In this chapter, an investigation to determine the effects of light crude oil contamination on the important physical and mechanical properties of fine grained sand is reported on. Important properties related to the construction application such as particle size distribution (PSD), moisture content, water absorption, permeability, contact angle, and shear strength were determined.

3.2 Materials and Method

3.2.1 Materials

The methods used for the experiments in this study are those specified in the Australian Standard AS 1726 (1993). Fine sand was chosen because of its similarity to the sand in the Libyan Desert, which is where the author is from. Fine sand was air dried to meet the conditions of fine Libyan Desert sand and mixed with a different percentage of oil as shown in Figure 3.1. Particle Size Distribution (PSD) of the fine sand in this study, based on AS 1141.11.1 (2009), and PSD of Libyan fine sand (Charman and West, 2011), which demonstrates its similarity to the fine sand, used in this study are shown in Figure 3.2. At the same time, mineral Fork w2.5 motor cycle oil (MOTUL-Oil) was selected due to the following:

- The density and viscosity of selected oil (fork oil) is similar to the light crude oil as shown in Table 3-1. The difference of the flash point, between the fork oil and light crude oil because the fork oils are missing the low end petroleum components. This is evidenced in the significantly lower flash point between the fork oils and Blended Crude. However this factor has been neglected because the oil leakage usually in open area which indicates that almost of the light hydrocarbons was evaporated. Thus, previous studies as well as this study considered the similarity of density and viscosity between the light crude oil and fork oil used.

- Several studies (Almabrok et al., 2015b, Almabrok et al., 2015a, Almabrok et al., 2011, Almabrok et al., 2013) used fork oils to represent crude oil.
- Safety precautions, as this oil can be used safely

On the other hand, in terms of the cement used Table 3.2 presents the compound composition of Portland cement used in this study.

Drying sand

Oil used

(a) Adding oil to fine sand

(b) Mixing

Figure 3.1 Drying and mixing procedures

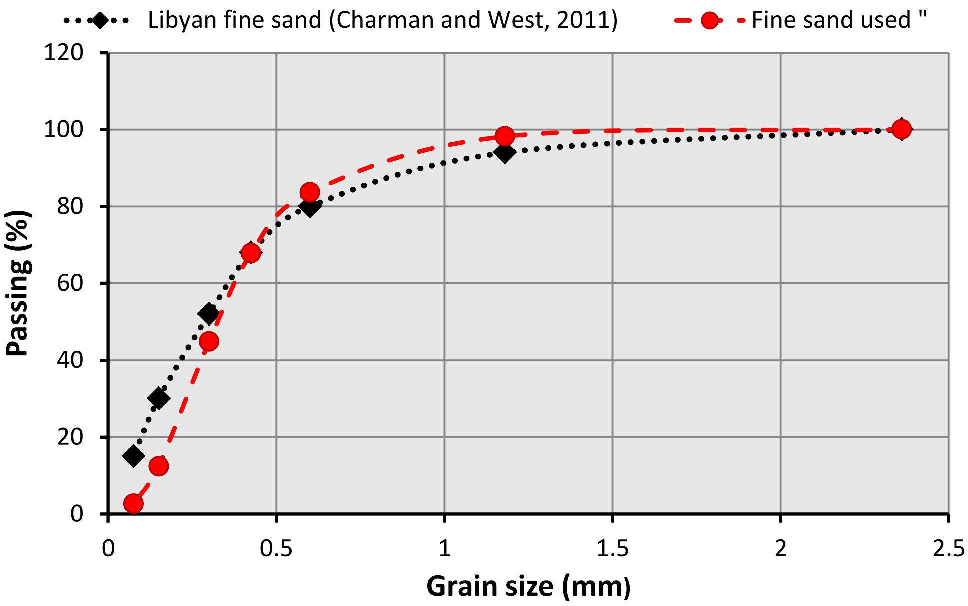


Figure 3.2 Particle size distribution curves of sand used and Libyan fine sand

Table 3.1 Comparison between light crude oil and Fork w2.5 Motorcycle oil (Ltd, 2009; SImetric., 2011)

Specifications	**Light crude oil**	**Fork w2.5 Motorcycle oils**	**Ref.**
Density (kg/L)	0.825	0.827	(Ltd, 2009 , SImetric., 2011, Fingas, 2014)
Viscosity (mm²/s)	5.96	6.74	
viscosity index	-	112	
Flash point °C	95	205	
Aromatics	8	-	
Temperature (°C)	40	40	

Table 3.2 Compound composition of Portland cement

Name of compound	Oxide composition	Abbreviation
Tricalcium silicate	$3CaO.SiO_2$	C_3S
Dicalcium silicate	2CaO.SiO2 C2S	C_2S
Tricalcium aluminate	$3CaO.Al2O_3$	C_3A
Tetracalcium aluminoferrite	$4CaO.Al_2O3.Fe_2O_3$	C_4AF
Free lime	CaO	C

3.2.2 Preparation of contaminated samples

The contaminated samples were prepared by mixing the dry sand with different percentages of light crude oil (0.5%, 1%, 2%, 4%, 6%, 8%, 10%, 15%, and 20%) according to the weight of the dry sand. In addition, the uncontaminated (0%) sand was prepared as the control sample (Figure 3.3). A maximum percentage of 20% was selected because the contaminated sand was already saturated and any additional oil would just drain from the sand. This would make some tests, for example for shear strength and permeability, difficult to conduct and difficult to obtain reliable results from. The oil was mixed manually with the dry sand and then the samples were placed inside a plastic container for 72 hours to allow the mixture to attain a homogenous condition. A lid was placed on the plastic container to prevent the crude oil from evaporating during the period of incubation.

Figure 3.3 Contaminated sand with different percentages of oil (0%-20%)

3.3 Test methods

3.3.1 Moisture content

During the test, the moisture content of the uncontaminated sand was measured following the procedure recommended by AS 1289.2.1.1 (1992). The moisture content measurement was conducted 3 times on sand samples of approximately 100 g. Figure 3.4 illustrates the oven and samples used. The water content of the sand was calculated using the following:

$$w\% = \frac{M_w}{M_s} \times 100 \qquad (3\text{-}1)$$

where

M_w = Mass of water obtained from a sample after being left in an oven for 24 hours

M_s = Mass of the sample of sand before placement in the oven (g)

Figure 3.4 Samples and oven used in moisture content

3.3.2 Microstructure of samples

A microscope (Motic SMZ-168 series, Motic China Group Co., Ltd.), was used to examine the microstructure of the uncontaminated and oil-contaminated sand as shown in Figure 3.5. The sand sample (50 g) was placed and observed under the microscope through the depression slide. This slide is of a rectangular shape (approximately 25 x 75 mm) with an indentation in the centre to hold the sand sample in position during placement and mechanical observation.

Figure 3.5 Microscope (Motic SMZ-168 series)

3.3.3 Water absorption test

The following tools were used in the water absorption test: a balance and a set of weights, a glass container 400 mm in diameter and 600 mm high, a 500 ml volumetric flask, a drying oven complying with a 350 g tamping rod, with a 25 mm tamping face and a mould made from 0.8 mm sheet metal in the shape of the frustum of a cone 73 mm high, with a large diameter of 90 mm decreasing to a small diameter of 38 mm as shown in Figure 3.6. An approximately 500 g sand sample was obtained and passed through a 4.75 mm sieve. The sample was weighted and the water absorption test was conducted following the AS-1141.5 (2000).

The dry and saturated surface dry bulk densities and percentage of water absorption were calculated following equations 3-2 to 3-4, respectively:

$$Bulk\ Density\ (Dry) = \frac{A2}{B2-(C2-D2)} \times 100\,\frac{Kg}{m^3} \qquad (3\text{-}2)$$

$$Bulk\ Density\ (S.S.D.) = \frac{B2}{B2-(C2-D2)} \times 1000\ Kg/m^3 \qquad (3\text{-}3)$$

$$Water\ absorption = \frac{B2-A2}{A2} \times 100 \qquad (3\text{-}4)$$

where A2 = Oven dry mass of aggregate

B2 = Mass of S.S.D. aggregate in air

C2 = Mass of S.S.D aggregate + wire basket in water

D2 = Mass of wire basket in water

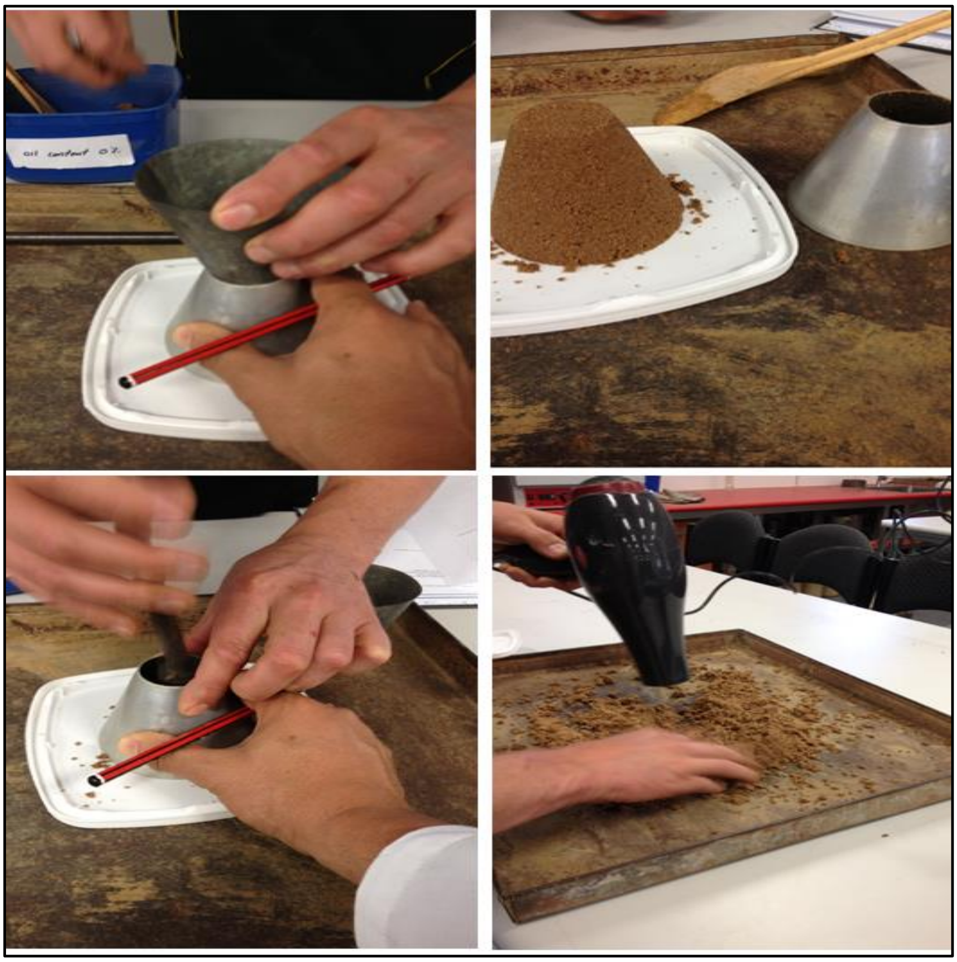


Figure 3.6 Procedure of water absorption test based on AS 1141.5

3.3.4 Contact angle measurement

The contact angle measurement was conducted using the standard sessile drop method by a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ). Milli-Q water was used as the reference solvent. Milli-Q Water is the purified water using a Millipore Milli-Q lab water system. A smooth surface of contaminated sand was prepared for all samples and at least 3 droplets on each sample were applied to measure the contact angle. The smooth surface of the contaminated sand was achieved by placing the sample between two rectangular glass slides. When the slide was placed on top of the sand, a soft manual press was applied to flatten the surface and make the surface of the sample smooth.

Figure 3.7 shows the sample preparation for the contact angle measurements while Figure 3.8 shows the hydrophilic and hydrophobic status of the surface of oil-contaminated sand. If the contact angle of water is less than 30°, the surface is designated hydrophilic since the forces of interaction between water and the surface of the sand nearly equal the cohesive forces of bulk water, and water does not cleanly drain from the surface. If water spreads over a surface, and the contact angle at the spreading front edge of the water is less than 10°, the surface is often designated as super hydrophilic, provided that the surface is not absorbing the water, dissolving in the water, or reacting with the water (Rudawska, 2012). As the hydrophobicity increases, the contact angle of the droplets with the surface increases. Surfaces with contact angles greater than 90° are designated as hydrophobic.

Figure 3.7 Sample preparations for the contact angle measurement

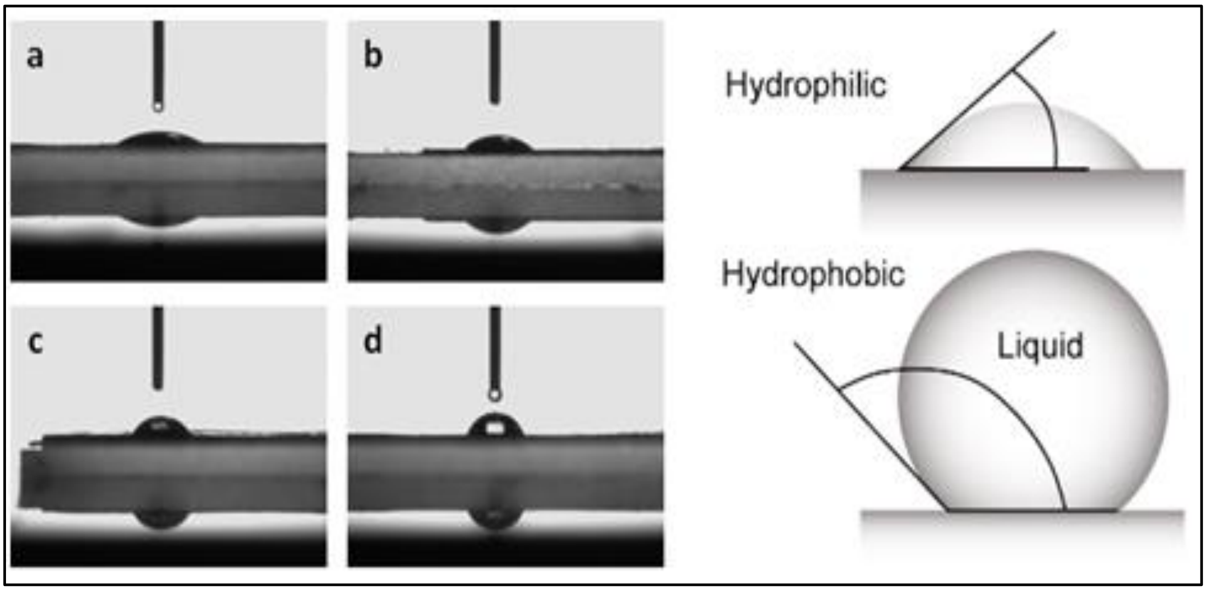


Figure 3.8 Shows the water absorption on the surface of the oil-contaminated sand (Rudawska, 2012)

3.3.5 Constant-head permeability

The permeability of fine sand was measured using the constant-head permeability test method based on AS 1289.6.7.3 (1999). The permeability apparatus consisted of a cylindrical cell body (75mm in diameter by 250mm high), a perforated base plate with straining rods and wing nuts that support the cell body, and a top cap with an inlet for a tube, and an air release valve (Figure 3.9). In the permeability test, the coefficient of permeability value (*k*) is determined, which is the amount of water flow through the soil, and it is expressed in metres per second (m/sec).

Figure 3.9 Constant-head permeability test

3.3.6 Direct shear test

A direct shear test was conducted in accordance with AS 1289.6.2.2 (1998) using the ShearTrac-II system called “Geocomp” (Figure 3.10). A shear force was applied to the contaminated sand under constant vertical loading. The test specimen was 24mm thick and 63.5mm in diameter. The specimen was carefully loaded into the shear box with the aligning pins and bottom porous stone in place. This test was thus conducted to ensure that the oil contamination would not drain out from the fine sand. From this test, the cohesion and frictional angle of sand could be determined.

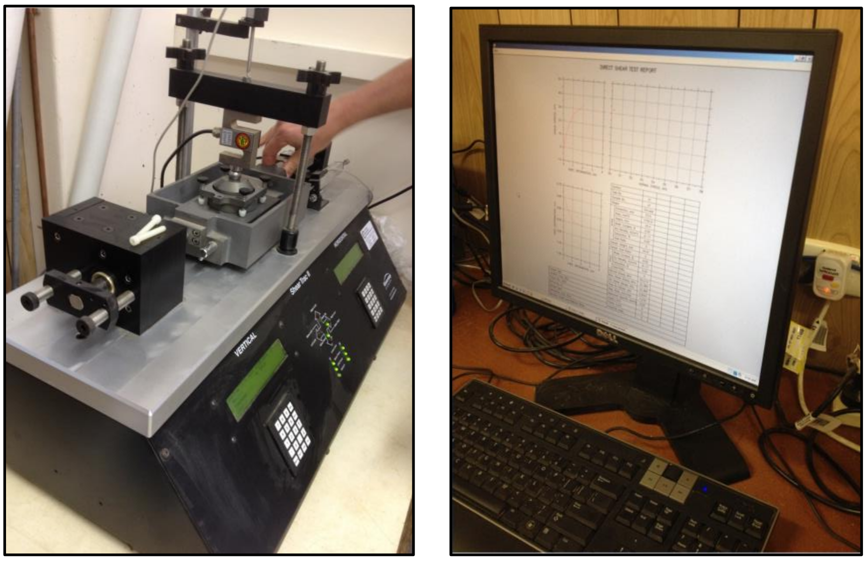


Figure 3.10 Direct shear (ShearTrac-II system hardware and software)

3.4 Results and observations

3.4.1 Moisture content

The moisture content of the uncontaminated sand sample was zero. This indicated that the sample was totally dry, which met the specification and represented the actual condition of the fine sand in the Libyan Desert (Ben-Mahmoud, 1995; El-Barasi and Barrani, 2012).

3.4.2 Water absorption

The dry and saturated surface dry, bulk densities and the percentage of water were calculated and are presented in Table 3.3. It can be seen that the water absorption decreased by nearly 16% when 0.5% of crude oil was added to the dry sand. This percentage decreased by more than 70% at 1% of crude oil contamination. On the other hand, the samples with crude oil contamination of 2% and above were already saturated with oil and it took the shape of the cone, even without adding water, as shown in Figures 3.11 and 3.12. Thus, the SSD conditions for these samples were already achieved and the water absorption could not be measured.

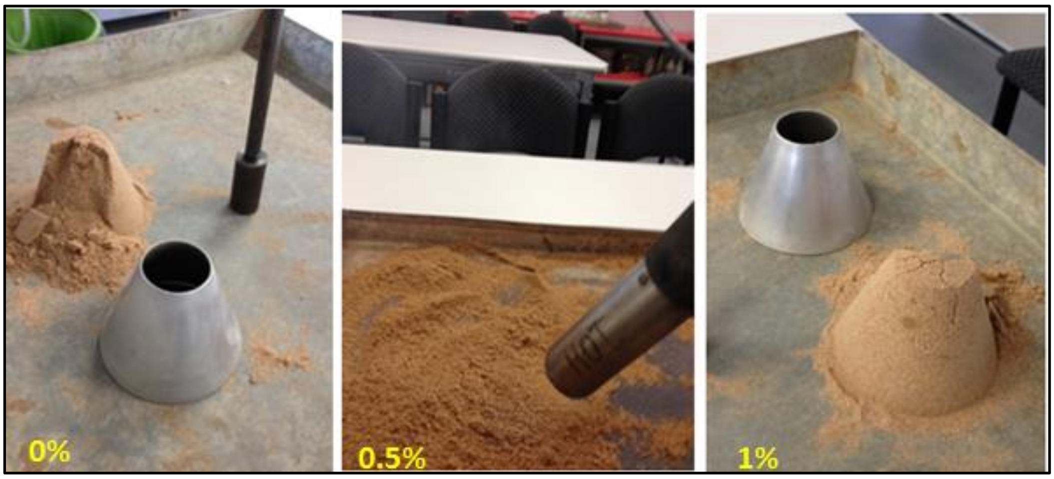


Figure 3.11 Water absorption test for 0, 0.5 and 1% oil-contaminated sand.

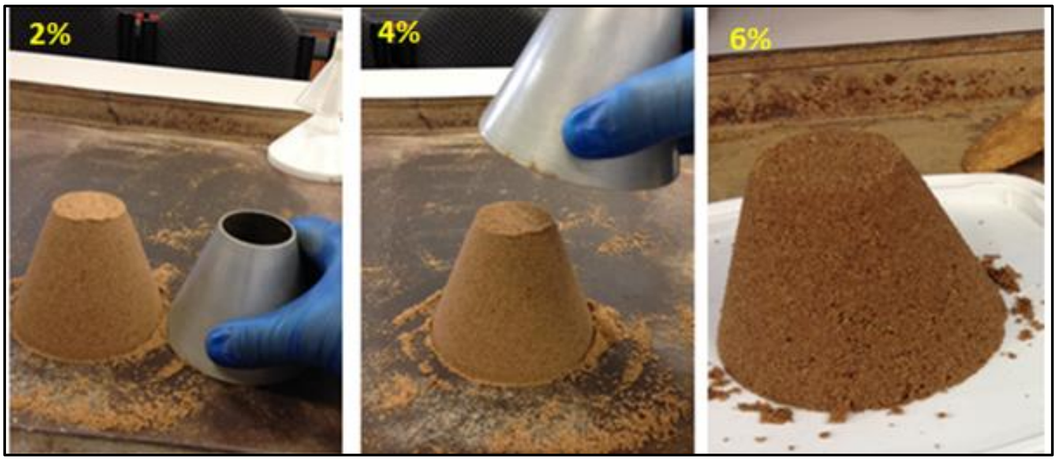


Figure 3.12 Shape of contaminated samples above 2%

Table 3.3 Water absorption of different contaminated sand

Oil content	0%	0.5%	1%	2%	4%	6%	8%
A1(Kg)	0.465	0.467	0.481	0.485	0.487	0.49	0.492
B1(Kg)	0.478	0.478	0.485	0.485	0.487	0.49	0.492
C1(Kg)	0.89	0.89	0.894	0.905	0.905	0.901	0.896
D1(Kg)	0.656	0.656	0.656	0.656	0.656	0.656	0.656
Bulk density (Dry)	1905.7	1913.9	1947.4	2055	2046	2000	1952.4
Bulk density (S.S.D)	1959	1959	1963.5	2055	2046	2000	1952.4
Water absorption	2.796	2.355	0.8316	0	0	0	0

where A1= Oven dry mass

B1= Saturated Surface Dry (S.S.D) mass

C1=Mass of flask + aggregate + water

D1=Mass of flask + water

3.4.3 Contact angle

The contact angle was measured in order to determine the hydrophobicity of oil-contaminated sand. It was observed that the increment of oil content significantly increased the hydrophobicity. The contact angle for sand samples with 0, 0.5, 1, and 2% oil contamination was hard to measure because the water was absorbed easily by the fine sand just after its application. On the other hand, the samples with oil contamination above 2% showed hydrophobic properties as can be seen in Table 3.4. As also shown in the table, the contact angle of fine sand, contaminated with 4% light crude oil, is around 13° and this increases to 42° for fines sand with 20% oil contamination. This outcome showed that the hydrophobicity of oil-contaminated sand increases with increasing crude oil content.

Table 3.4 Contact angle of oil-contaminated sand

Oil content (%)	Contact angle
0 0.5 1 2	Hard to measure
4	13.84
6	25.6
8	27.1
10	28.37
15	39.5
20	42.72

3.4.4 Permeability test

The permeability of fine sand contaminated with light crude oil is listed in Table 3.5. The permeability test showed that there was a slight reduction in the permeability coefficient (*k*) values for oil-contaminated fine sand, up to 1% compared to the uncontaminated sample (0%). From a k of 20.55 m/sec for uncontaminated sand, this was reduced to 13 m/sec for 1% oil contamination. The k value then gradually increased from 2% to 6% oil contamination with a peak value (k = 30.02 m/sec) at 6% of contaminated soil. It began to decrease again by increasing the oil content from 8% to 20% where the lowest value was measured at 0.58×10^{-5} (m/sec).

Table 3.5 Permeability of oil contaminated sand

Oil content (%)	$k \times 10^{-5}$(m/sec)
0	20.55
0.5	14.51
1	13.00
2	15.93
4	26.50
6	30.02
8	27.26
10	21.72
15	4.69
20	0.58

3.4.5 Shear strength test

The shear strength of the soil is an important property because it plays a great role in terms of its bearing capacity and the stability of the foundation system of any engineering structure. The shear strength can be influenced by a number of factors such as water content, stress history, effective stress, stress path, and soil structure (Barbour and Yang, 1993). Figure 3.13 presents the shear stress of oil-contaminated sand for the different levels of applied normal stresses (50, 100 and 200 kPa). The difference between the shear strength of the specimens increases with the applied vertical stress. These results substantiate the statement that the soil element in a flocculated state has higher shear strength than that in a dispersed state. From these results, the cohesion (c), frictional angle ($ø^{o}$) and the shear strength of oil contaminated fine sand were found. The higher these values are, the higher the shear strength of the soil is. The results obtained are summarised in Table 3.6, which clarifies how the oil affected the strength parameters cohesion and friction angle. It can be seen that the cohesion increased significantly from 0 to 1%. A decrease in the cohesion was then observed for samples with 2 to 20% oil contamination. An increase of oil contamination from 2 to 20% decreased the cohesion from 8.91 to 1.82 kPa. However, the contact angle decreased from the uncontaminated sample to 31° for sand with oil contamination. On the other hand, increasing crude oil content above 0.5 % (up to 20%) did not cause any significant variation.

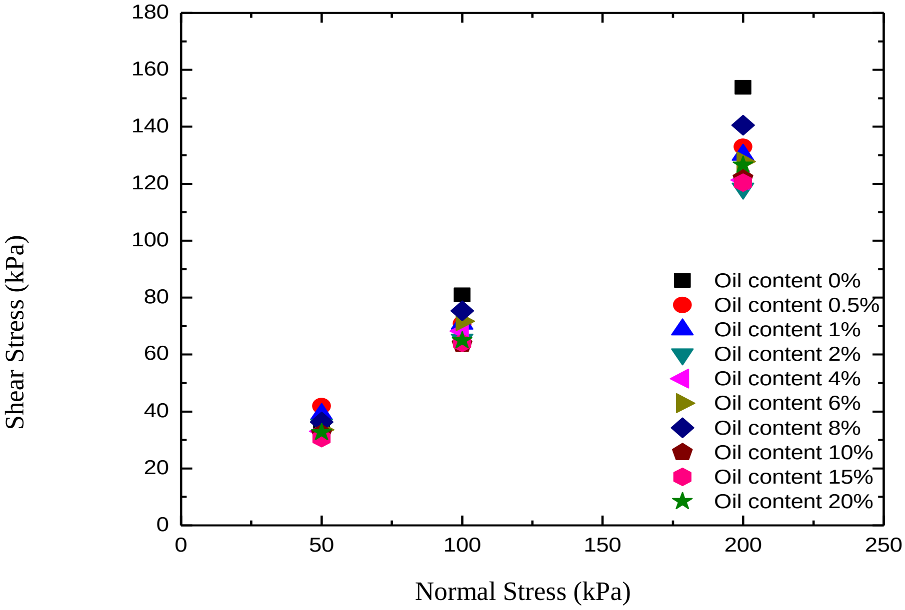


Figure 3.13 Shear stress (kPa) as a function of normal stress (kPa) with different oil content

Table 3.6 Result of cohesion and frictional angle

Oil content %	Cohesion (kPa)	Friction angle ø°
0	0.75	38.0
0.5	9.41	31.0
1	10.7	31.0
2	8.91	29.0
4	6.51	30.0
6	5.54	32.0
8	3.71	31.0
10	3.10	31.0
15	2.42	31.0
20	1.82	32.0

3.5 Discussion

3.5.1 Effect of oil contamination on water absorption

Figure 3.14 shows the water absorption of fine sand with different levels of oil contamination. The saturated surface dry (S.S.D) condition of fine sand was only achieved for samples containing 0, 0.5, and 1%. In these samples the amount of absorbed water was measured and the water absorption was calculated. The uncontaminated sand had the highest percentage of water absorption at 2.79%. This percentage decreased with the increasing content of crude oil. With 0.5 % of oil, the water absorption was 2.35%, while at 1% the water absorption decreased to 0.8%. However, water absorption became zero for sand with crude oil contamination of 2% and higher. This was attributed to the state of the sand which had changed from a dry to a wet state. This aligns with the contact angle results which indicate that the hydrophobicity increases by increasing the content of crude oil. The contact angle of crude oil above 2% becomes readable and this increased with the increasing content of crude oil, whereas the sand with crude oil from 0 to 2% was hard to measure due to the high water absorption of sand.

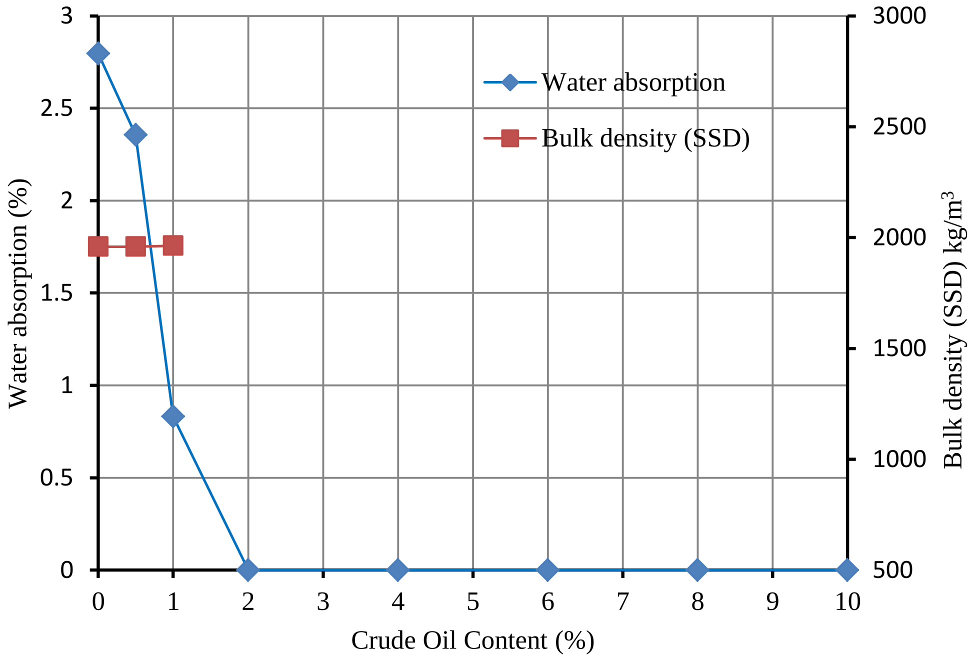


Figure 3.14 Water absorption and Bulk density as a function of oil content

3.5.2 Effect of oil contamination on permeability

The results of the permeability test presented in Figure 3.15 revealed a significant reduction in the coefficient of permeability (*k*) value between the uncontaminated sand and contaminated sand, i.e., between 0% and 1%. The decrease in permeability between the uncontaminated and contaminated samples (by up to 1%) was due to a reduction in the pore volume, as the droplets of light crude oil were already occupying the pore spaces between and within the sand particles. Similarly, the pore fluid was also occupied by water and crude oil, as shown in Figure 3.16. The reduction in the permeability coefficient of contaminated sand, compared to uncontaminated sand, can also be attributed to the blockage of some inter-particle space with light crude oil. The sand particles were packed closely together as the content of crude oil increased up to approximately 1%, owing to the suction (negative surface tension) between them. Furthermore, the system is treated as a three phase system with solids, (oil) and water assuming air has been eliminated during compaction and/or column saturation (Lenhard and Parker, 1988). This phenomenon is shown in Figures 3.16 (a-c). The increase of cohesion between the sand particles, due to contamination with light crude oil, reduces the permeability value. Furthermore, the trend at greater than 6% oil is consistent with 2 fluid phases and relative permeability. The two fluids interfere with each other to reduce flow.

For fine sand contaminated with 2% light crude oil, the void space increases because the particles of soil become coated with oil as shown in Figure 3.16 – d, which decreases the bond and increases the permeability. A previous study by (Obeta and Eze-Uzomaka, 2013) has investigated the effect of waste engine oil on permeability (*k*). They observed that the coefficient of permeability (*k*) reduced continuously from 0% to 12%. This reduction in the value of *k* was attributed to the properties of the soil used, where they claimed that the soil with the least amount of fine/gravel ratio would have more oil content at each percentage contamination, and hence, the *k* value decreased. Furthermore, the effect of crude oil contamination on the permeability *k*, using two different types of soil, sandy loam and silty loam, were investigated by Rahman et al. (2010). They concluded that the permeability of both soils was reduced as crude oil content increased. The decrease in permeability of the contaminated soils was likely associated with the clogging of some inter-particles space by oil. Thus, increasing crude oil content in contaminated soil will reduce the available inter-particles spaces for water seepage. Similar results were observed byAl-Sanad et al. (1995); Mashalah et al. (2006), where a similar trend was identified in the coefficient of permeability of soil contaminated with oil.

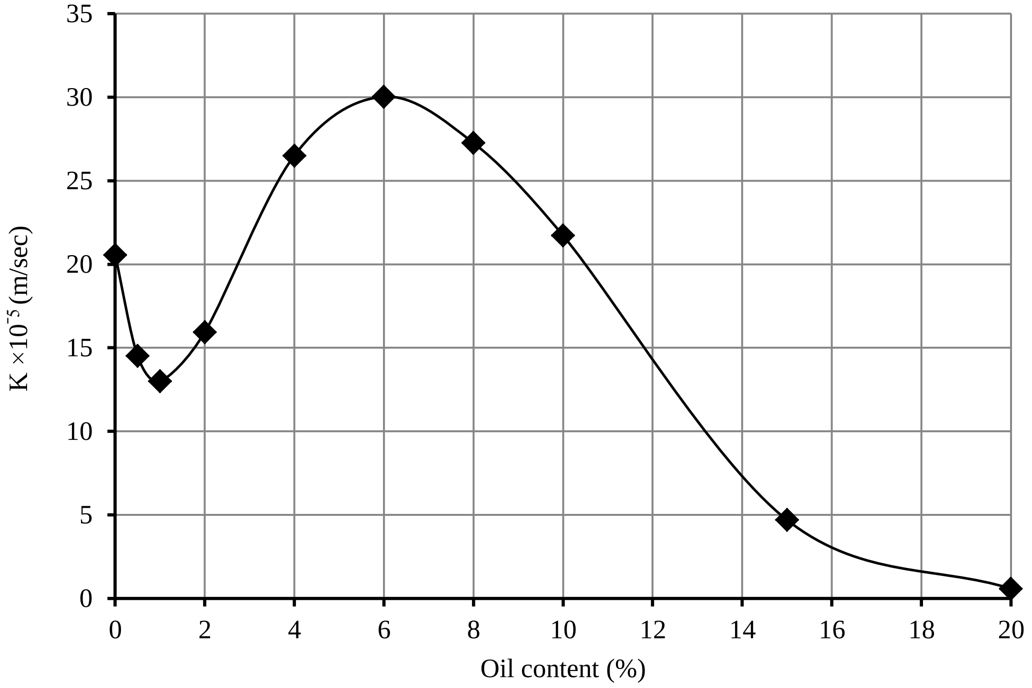


Figure 3.15 Permeability of fine sand with light crude oil contamination

Nevertheless, there was an increase in the permeability coefficient value of contaminated sand when the percentage of oil contamination (1% to 6%) gradually increased (Figure 3.9). This results contradict the above mentioned studies by Al-Sanad et al. (1995); Mashalah et al. (2006);(Rahman et al., 2010b) and (Obeta and Eze-Uzomaka, 2013) who illustrated that the permeability coefficient decreased by increasing the crude oil content. In this study the decrease in permeability through increasing the content of oil contamination may be related to an increase in the void filled with oil. In uncontaminated sand, the particles mainly consisted of face to face and edge to edge contacts (Figure 3.16-a) and inter-particle pores are more common. However, with contaminated soil, edge to face contacts (Figure 3.16 b-d) and inter-micro aggregate pores were more frequent as also indicated by Izdebska-Mucha et al.

(2011). In addition, by increasing the percentage of crude oil (1% to 6%), the sand particles became coated with oil, which increased the hydrophobicity of the sand and accelerated the passage of water during the permeability test. The particles of soil coated with oil were seen in the microscopic images (Figure 3.16 d-h). This observation pointed to one of the reasons for an increase in the permeability coefficient value when the percentage of crude oil was increased by up to 6%, see Figure 3.16 (d-f). Furthermore, the trend at greater than 6% oil is consistent with 2 fluid phases and relative permeability. The two fluids interfere with each other to reduce flow. This outcome explained the trend observed in the cohesion (Figure 3.16 a-c) which showed a significant increase of up to 1%, compared to the control sample. This indicates that an increase in cohesion leads to a decrease in permeability in terms of its unsaturated state. In contrast, there was a significant reduction in permeability when the percentage of oil contamination increased from 6% to 20%. This reduction in the *k* value can be explained by the saturation state of sand with oil, which means that the oil has occupied all the voids between the particles. As the sand is already saturated with oil, as shown in Figure 3.16 (g-j), it hinders the flow of water and hence, the *k* value is decreased.

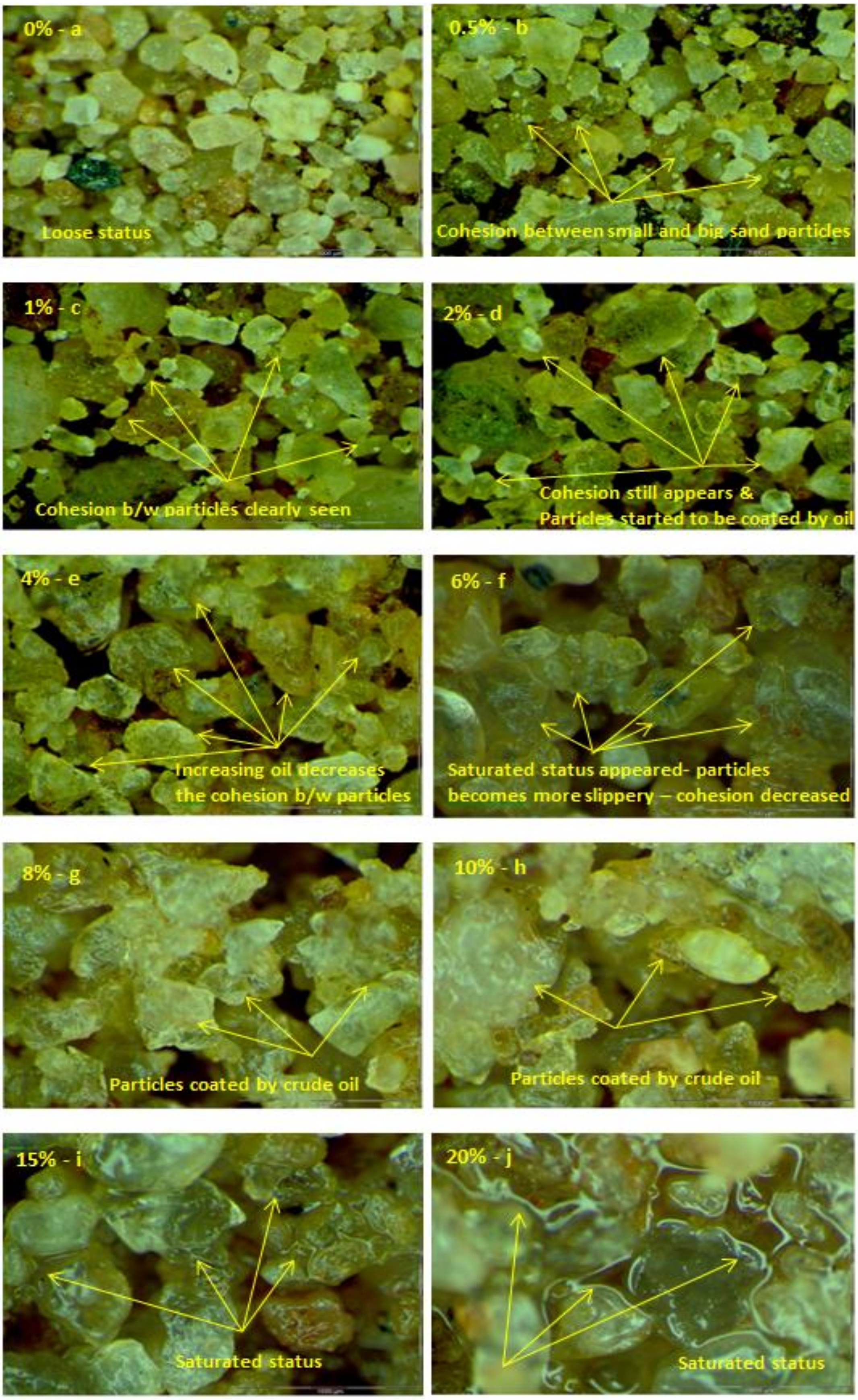


Figure 3.16 Images of fine sand with different contamination percentage

3.5.3 Effect of oil contamination on cohesion

There was a significant increase in the cohesion (c) from uncontaminated sand (0%) to sand with 1% oil contamination as shown in Figure 3.17. The sand with 1% light crude oil contamination exhibited the highest cohesion at 10.76 kPa, but the cohesion decreased when the percentage of crude oil contamination was increased. The lowest value of cohesion was measured for fine sand with 20% oil contamination, with a value of 1.82 kPa. Regardless of the crude oil content (%), the increment of the cohesion agreed with a previous study (Khosravi et al., 2013), which indicated that the cohesion gradually increased by increasing the crude oil content. In our study the optimum cohesion value observed was at (10.76 kPa) and it occurred with 1% of crude oil contamination. By contrast, the optimum cohesion value observed by Khosravi et al. (2013) was around 11 kPa, which occurred with 20% of crude oil contamination, when they investigated the effect of gas oil on the clay soil. The increment of the cohesion in their case was due to the influence of the polar covelent bonds in the clay cohesion. This influnce was due to the organic materials and hydrocarbons reducing repulsive forces between clay particles which resulted in higher cohesion (Zhao, 1996). This is not the case in our study where fine sand and light crude oil were used. In our study the increase in cohesion was reasonable because the moisture content of the dry sand used in the experiments was zero, so the addition of light crude oil would increase the wetness of the fine sand, which in turn increased cohesion between the sand particles as shown in Figure 3.16 (b-d). The trend towards cohesion that was observed in this study is supported by a previous study conducted by Cokca et al. (2004) where they indicated that the cohesive component of shear strength attained its peak value at an optimum moisture content and then decreased as the amount of oil increased. This apparent cohesion stemmed from capillary tension inside the voids, but adding oil prevents water from making contact with the particles of sand due to oil aversions, so increasing the crude oil to a certain amount reduced the capillary tension and increased the apparent cohesion of the soil.

However, these results contradict Al-Sanad et al. (1995) findings who found no cohesion when they investigated the effect of 3% to 6% of heavy crude oil contamination on windblown, predominantly fine to medium sand. Furthermore, the effect of different percentages (0, 4, 8, 12 and 16%) of crude oil on the three soil type (CL, SP, and SM) was investigated by (Mashalah et al., 2006) and they found that there was extreme reduction in cohesion when the crude oil content in CL was increased, while this correlation does not have any distinct path in SM. Simalary, SP samples showed a low cohesion due to oil contamination that can be the result of viscosity and inherent cohesion of oil. Generally it has been concluded that effect of oil contamination on shear strength parameters is not uniform and it depends on the soil type as well as the crude oil contamination type. These factors have been considered to be among the most significant factors that affect the mechanical properties of sand (Nudelman et al., 2002; Fine et al., 1997; Tuncan and Pamukcu, 1992).

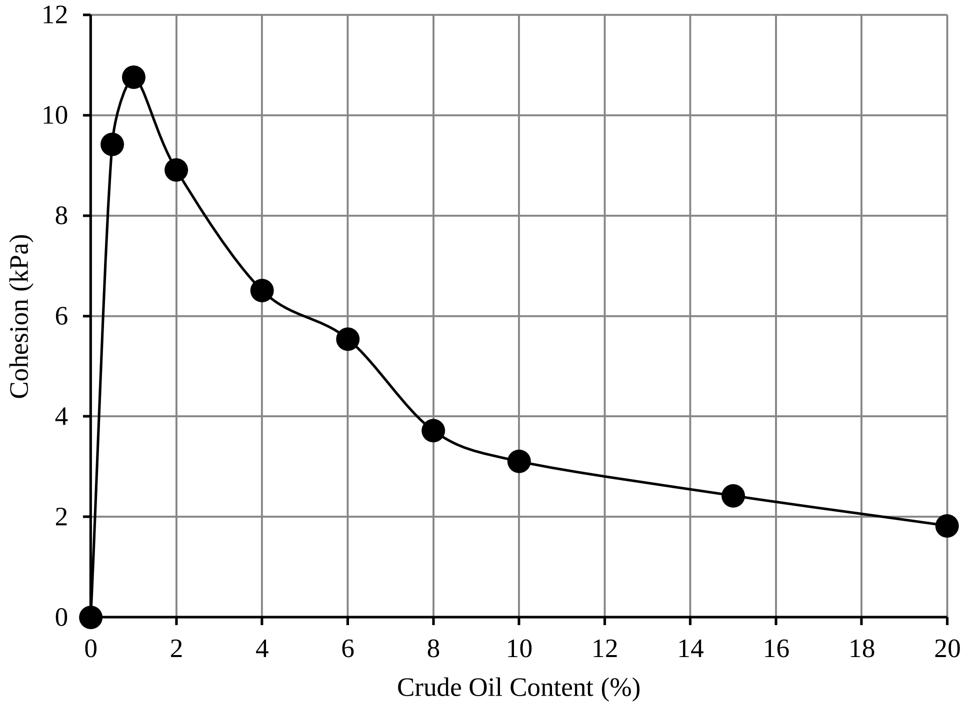


Figure 3.17 Cohesion as a function of the percentage (%) of contamination with crude oil

On the other hand, the reduction in cohesion on the wet side was attributed to the particles of sand being coated with crude oil, which reduced the interaction between them, as shown in Figure 3.16. At 4% contamination with crude oil the particles became coated with oil and became slippery, which decreased their cohesion, as shown in Figure 3.16-e. Increasing the amount of crude oil from 4 to 10% resulted in a similar saturated state where the particles became even more slippery and even less cohesive, as Figure 3.16 f-h shows. However, Figure 3.16 i-j shows that the saturated status was apparent when the amount of oil was increased up to 15 and 20%, and there was even less cohesion. Seed et al. (1961) indicated that the reduction in cohesion was due to thicker films of oil around the particles of soil, and by increasing the content of crude oil, the chance of inter particle slippage would also increase and thus result in a decrease in the shear strength.

3.5.4 Effect of oil contamination on frictional angle

Figure 3.18 illustrates the frictional angle of fine sand with different percentages of crude oil contamination, and shows a significant reduction in the frictional angle from uncontaminated (0%) to contaminated samples (0.5%) (from 38º to 31º). This reduction occurred because the crude oil acted as a lubricant that enabled the particles to slip and slide against each other; but crude oil products reduce the friction between the particles better, which decreases the space between them, and also reduces the frictional angle. In contrast, there was no significant variation in the frictional angle in those samples that had 2% to 20% of oil contamination, which indicated that above 2% the particles were coated with crude oil, as shown in Figures 3.16 d-j, which resulted in the same frictional angle. Thus, the decline in shear strength of sand contaminated with oil can be specified by the mechanical interaction caused by high pore fluid viscosity. Al-Sanad et al. (1995) also observed a significant decrease in the frictional angle when fine to medium sand was contaminated with heavy crude oil. On the other hand, Khosravi et al. (2013) concluded that the frictional angle was only slightly affected by the gas oil. Furthermore, in the investigation by Mashalah et al. (2006), they observed that there was a direct correlation between crude oil content and frictional angle in lean clay (CL) where the frictional angle increased by increasing the crude oil content. On the other hand, in the inverse correlation between crude oil content and the frictional angle in silty sand (MS), poorly graded sand (SP) was observed. They concluded that the effect of crude oil on the frictional angle is not uniform, but depends on the soil type and the type of the contaminant (type of the crude oil) (Nudelman et al., 2002, Fine et al., 1997, Tuncan and Pamukcu, 1992).

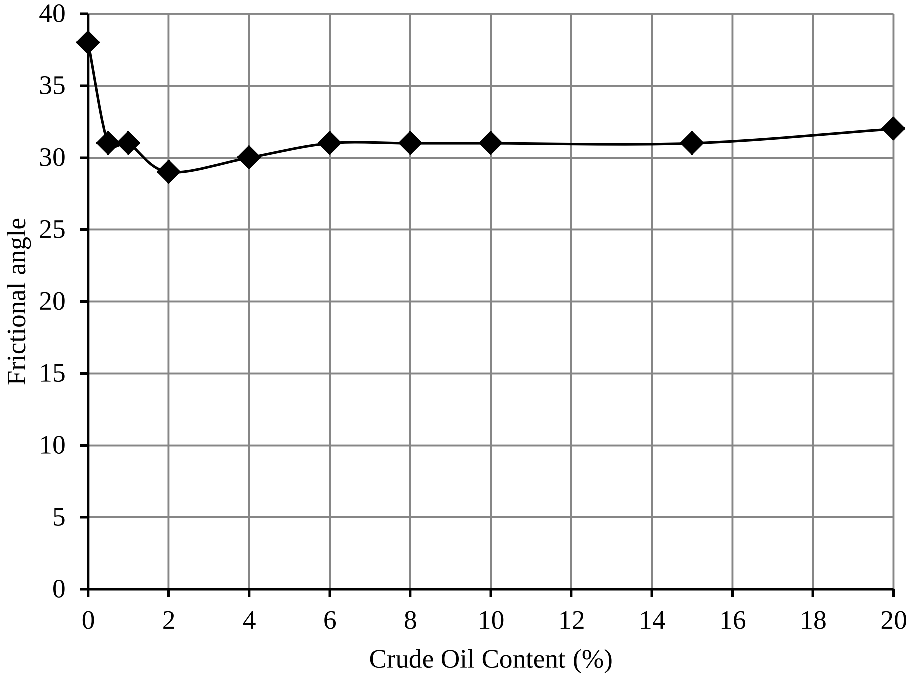


Figure 3.18 Frictional angles for fine sand with light crude oil contamination

3.5.5 Effect of oil contamination on shear strength

The effect on shear strength was determined using the cohesion and frictional angle of fine sand contaminated with light crude oil, and by using the Mohr-Coulomb equation. Figure 3.19 shows the sand shear strength as function of light crude oil contamination and an applied normal stress of 50 kPa. It can be deduced from the Figure that light crude oil contamination affects the shear strength of fine sand. The shear strength increased for fine sand with 1% oil contamination, which was due to the significant increase in the apparent cohesion of the fine sand contaminated with light crude oil as discussed in section 3.5.3. In contrast, at a high level of crude oil contamination, the shear strength decreased significantly with a further addition of oil content beyond 1% of crude oil content in contaminated sand. Thus, it can be inferred that the presence of a high percentage of oil increased the viscosity, and as a consequences the sand particles started to be coated by the crude oil as shown in Figure 3.16. By increasing the amount of oil content in particular sand, the chance of inter-particle slippage will also increase, and subsequently the shear strength of soil, will decrease (Rahman et al., 2010). This indicates that higher oil contamination resulted in lower shear strength values.

Nevertheless, these results are contradicted by Khosravi et al. (2013) finding, who concluded that the shear strength of kaolinite (clay) is not significantly influenced by gas oil. Furthermore, Puri (2000); Shin and Das (2000) both concluded that the shear strength of sand can be adversely affected by oil contamination. Moreover, Rahman et al. (2010) have investigated the effect of hydrocarbons components on two types of soil granitic soil and sedimentary soil. They concluded that the shear strength values of both soils significantly dropped from 0% to 4% of hydrocarbon content. Then, the shear strength values decreased slightly beyond 4% of hydrocarbon content. This implies that the sample will easily be slipped or sheared with higher oil content when the shear strain is applied. Moreover, Mashalah et al. (2006) concluded in their study of the effect of crude oil contamination on three types of soils (CL, SM and SP), that the shear strength decreased by increasing the crude oil content.

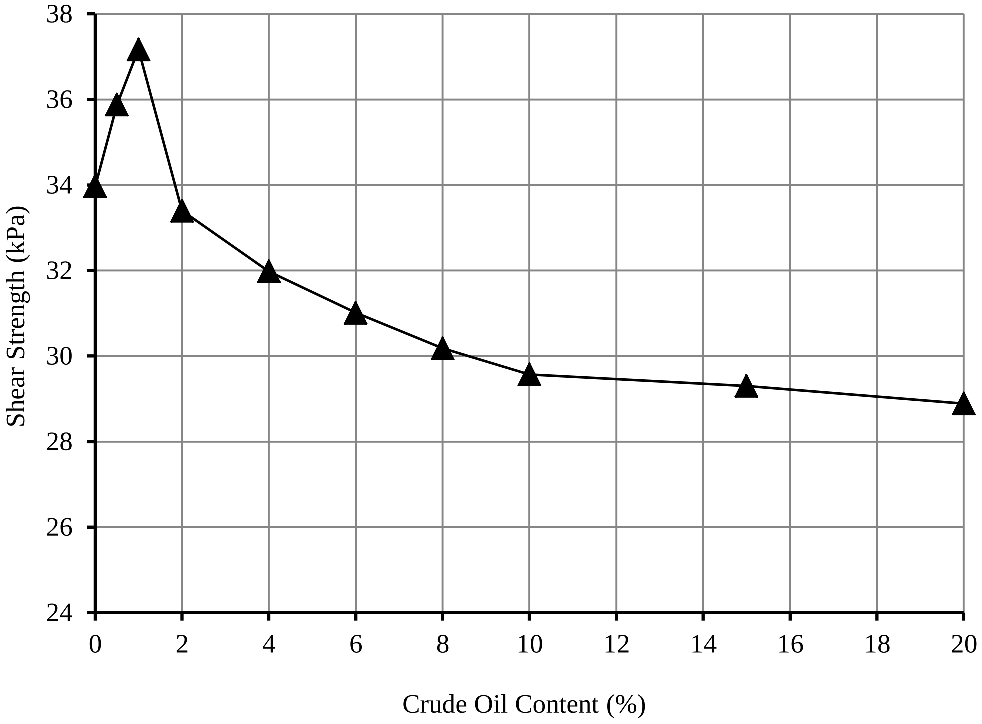


Figure 3.19 Shear strength of contaminated fine sand at 50kPa normal stress

3.6 Conclusions

The effect of light crude oil contamination on the physical and mechanical properties of fine sand was investigated in this chapter. Based on the results, the following conclusions are drawn:

- Water absorption was highest at 2.79% for dry fine sand but decreased with increasing light crude oil content of up to 2%. From 2%, the fine sand was already coated with oil and did not absorb any more water, indicating that the hydrophobicity increases with the increase in oil contamination.

- The permeability of fine sand contaminated with 1% light crude oil was reduced due to the increment of cohesion. The permeability then started to increase for fine sand with up to 6% oil contamination, as the sand particles were already coated with crude oil. This increased its hydrophobicity and accelerated the passage of water. For fine sand contaminated with more than 6% of light crude oil, the permeability decreased as all pores were already filled and saturated with oil.

- The cohesion of fine sand increased significantly at 1% light crude oil contamination due to the increased surface wetness of the fine sand particles. The cohesion then decreased from 2 to 20 % oil contamination due to the sand particles being fully coated with crude oil, which reduced the interaction between sand particles.

- A slight reduction in frictional angle was observed for contaminated fine sand due to the inter-grain lubrication of the sand particles by the crude oil. By contrast, no significant variation in the frictional angle of contaminated sand was observed for samples with oil contamination from 2% to 20%. After increasing the crude oil above 2% the sand particles started to be coated with crude oil, which resulted in the same frictional angle.

- A 10% increase in shear strength was observed for fine sand with 1% light crude oil contamination. The shear strength started to decrease at a higher level of oil contamination, with 20% oil contamination showing around 14.7% lower shear strength than uncontaminated sand.

The results obtained in this chapter are useful benchmarks for further investigation into oil contaminated sand as an alternative remediation method and to reduce its adverse impact on the environment. The results further indicate that the mechanical properties of fine sand are enhanced at an optimal level of light crude oil contamination, which shows its high potential for use in building and construction. Therefore, in chapter 4, an extensive investigation is conducted to gain an understanding of the effects of oil contamination on the physical and mechanical properties of cement mortar containing oil contaminated sand.

Chapter 4

The Influence of Mixing and Curing Methods on the Mechanical Properties of Cement Mortar with Oil Contaminated Sand

4.1 Introduction

Combining oil contaminated sand with cement and using it for construction is considered to be an effective method of re-using this waste material and reducing its impact on the environment. The results of Chapter 3 clearly demonstrated that the physical and mechanical properties of fine sand can be enhanced with low levels of oil contamination, indicating their suitability for re-use as a construction material. In this chapter, the mechanical properties of cement mortar, using fine sand contaminated with light crude oil, are investigated. The chapter focuses on determining the most appropriate mixing and curing methods that will result in optimal mechanical properties for hardened cement mortar.

Mixing and curing methods are considered to be the most critical factors that affect the strength development of concrete mix (Kocaman et al., 2011). Moreover, the workability of freshly mixed concrete is required for them to be properly placed in practice to obtain a specific compressive strength (Neville, 2000) and this largely depends on the consistency achieved during mixing (Jézéquel and Collin, 2007). Generally for any type of concrete, it is recommended to mix the constituent materials until the mix is consistent and uniform in nature. For instance, ASTM-C305-14 (2013) and AS 2350.12 (2006) suggest procedures for preparing mortar wherein they recommend to “pour water into bowl and add the cement before adding the sand slowly”. On the other hand, AS-1012.2 (2014) and ASTM-C192/C192M-14

(2007) recommend mixing the dry ingredients (cement, fine aggregates, and course aggregates) first. When these materials are thoroughly blended, water is then added until the concrete is homogeneous in appearance and has the desired consistency. This recommendation of mixing priority, i.e. cement and water, followed by sand (CWS), or cement and sand, followed by water (CSW), may not significantly affect the mechanical properties of the hardened concrete if a normal concrete mix is prepared. However, the mixing procedure may play an important role, and may affect the mechanical properties of the hardened mortar or concrete for the mix with oil contaminated sand.

Several studies (Abalaka and Okoli, 2012; James et al., (2012); Safiuddin et al., 2007) have also shown the importance of a suitable curing method in order to produce a strong and durable concrete. For instance, Henrichsen and Laugesen (1994) stated that proper curing of concrete is paramount for obtaining optimum performance from a given set of mix proportions. For high-performance concretes, curing becomes even more important, due to the typically lower water-cement ratios and the increased propensity for early age cracking due to thermal and self-desiccation stresses. As a result, James et al. (2012) have suggested immersing and sprinkling water into the concrete while curing to obtain high compressive strength. They also mentioned that this curing method is better than that of concrete covered with a plastic sheet. Similarly, Abalaka and Okoli (2012) have concluded that a higher compressive strength concrete can be achieved for water-cured specimens than for air-cured specimens. In contrast, Kocaman et al. (2011) obtained a higher compressive strength for concrete specimens produced with lightweight aggregate cured in air, compared to water and steam curing. For the concrete mix with normal aggregates, the highest compressive strength was obtained when cured in water, followed by steam curing, and the lowest strength was achieved when air-cured. The appropriate curing method for cement mortar using oil contaminated fine sand, however, has received limited attention nor has its effect on the properties of the hardened mortar been investigated.

In this chapter, two mixing methods and four commonly used curing conditions were considered and their effects on the mechanical properties of cement mortar with oil contaminated sand (0%, 2% and 10% by weight of sand) were investigated. The basic properties such as hydration process, compressive strength, and porosity and failure modes were investigated. In addition to that the microscopic observations were performed to analyse the microstructure of the cement mortar with oil contaminated fine sand.

4.2 Experimental program

4.2.1 Preparation of oil contaminated sand

The method used in the preparations of oil contaminated sand was similar to the method described in Section 3.2.2. In this chapter, the focus was on oil contaminated sand with two different percentages of light crude oil (2 and 10 % by the weight of dry sand). In addition, uncontaminated (0%) sand was prepared as a control sample.

4.2.2 Specimen sampling procedure

A total of 72 specimens were prepared covering three samples for each specimen type, two different mixing methods, four different curing conditions, and three percentages of light crude oil contamination. The preparation of mortar and the moulding of specimens were conducted following AS 2350.12 (2006). Plastic moulds (50 mm diameter and 100 mm high) were used to avoid using any agent or grease to release the specimens that could affect the properties of the hardened mortar. This also prevented any crude oil leaching from the mix.

The flow chart in Figure 4.1 shows the experimental plan for this study. As presented, mortar with three levels of oil contamination (0%, 2% and 10%) were mixed either by CWS or CSW, and were either cured in water (W), in air (A), in plastic bags (PB), or in a fog room (FR). Those percentages were selected to represent the effect of low and high crude oil contamination on the mixing and curing methods and compare them with uncontaminated samples.

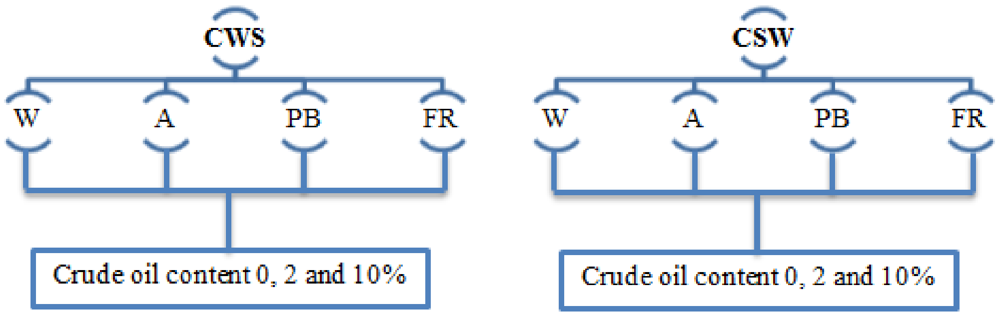


Figure 4.1 Flow charts of the experimental plan

4.2.3 Preparing and casting of mortar

The composition of the mortar was based on AS 2350.12 (2012) with mix proportions of 1 part of cement and three parts of sand (by mass), and a water cement ratio (w/c) of 0.50. Each batch was prepared separately in order to avoid any contamination between mixes. The mould filled in three approximately equal layers, and a compacting bar is used for compacting the mortar. It is a 380 mm long steel bar, weighs 1.8 kg and has a 25 mm square end for ramming. During the compaction of each layer with the compacting bar, the strokes distributed in a uniform manner over the surface of the mortar and each layer compacted to its full depth. All laboratory work was conducted at a room temperature of around 22ºC, while the curing in the fog room was conducted at a temperature of around 25ºC and humidity of 85%. The specimens were de-moulded after 24 hrs and were cured either in water, air, plastic bags, or in a fog room for up to 28 days. Figure 4.2 shows the preparation of the mortar.

Dry sand Manual mix Storage

Plastic container with lead Mixture Compaction

De-moulding Plastic sheets Curing

Figure 4.2 Sample preparation protocol

4.2.4 Curing

The procedures adopted for the four different curing methods considered in this study are described below and shown in Figure 4.3:

- Air curing (A): The specimens were left in open air to cure for 28 days (Figure 4.3a). The specimens were exposed to the ambient curing conditions in the laboratory with a temperature of around 22ºC.
- Water curing (W): This was done by continually storing the specimens at a temperature of around 22 ºC inside a plastic bag filled with tap water, as shown in Figure 4.3b. The plastic bag was used to avoid any oil leaching, which could have reduced the overall oil content of the sample.

- Plastic bags (PB): In this method, the specimens were placed inside sealed UV Stabilised Polypropylene plastic bags, with a thickness of 125 µm, and cured in air, as shown in Figure 4.3c. This represents the method whereby plastic sheets are used to cover the concrete during curing.
- Fog room (FR): The specimens were stored in a fog room (Figure 4.3d) at 25 ºC and humidity of 85%. The temperature and relative humidity (RH) were monitored by using a digital thermometer and humidity meter. The deviation of temperature and humidity was ±2°C and ±5% respectively during the curing period of specimens.

(a) In air A

(b) In water W

(c) In plastic bags PB (d) In fog room FR

Figure 4.3 Curing methods

4.2.5 Measuring heat production

The isothermal calorimeter I-Cal 4000 (Calmetrix Incorporation, USA) was used in this study. This apparatus directly measures the heat production rate that is proportional to the rate of the reaction. As shown in Figure 4.4 the I-Cal 4000 consists of a calorimeter unit and a temperature control unit, four mortar samples, and variable reference cells to accommodate variable samples sizes, as shown in Figure 4.4 (a-c). Based on the manual, the thermal mass of the reference should be similar to that of the sample; thus, two metal cylinders were used with about 100 grams of the mortar sample (Figure 4.4 (c).

Figure 4.4 I-Cal isothermal calorimeter (I-Cal 4000)

The calorimeter was connected to the computer and the temperature control unit was turned on and set at 25°C for 24 hours, before testing based on (ASTM-C1679, 2014). Approximately 100 grams of mortar was placed in a clean plastic cup. To minimise heat exchange, the lid was kept open while loading the samples and closed immediately after the sample was loaded inside the unit. Measurement of thermal power was started immediately after the specimen was placed in the calorimeter. A suction cup was used to place and remove the plastic cups to prevent damaging the unit or spilling the sample, as shown in Figure 4.4 (d). The test duration and data collection was extended to two days (48 hours).

4.2.6 Compressive test

Compressive strength tests of all specimens were carried after 28 days of casting. The specimens were tested to failure, using a loading rate of 1.5 kN/min, and utilising the 2 Channel Automatic Cube and the Cylinder Compression Machine CT340-CT440 based on AS-1012.9 (2014), as shown in Figure 4.5. The failure mechanisms of each specimen were also observed and recorded. In addition, microscopic observation of the failure surface of each specimen was performed.

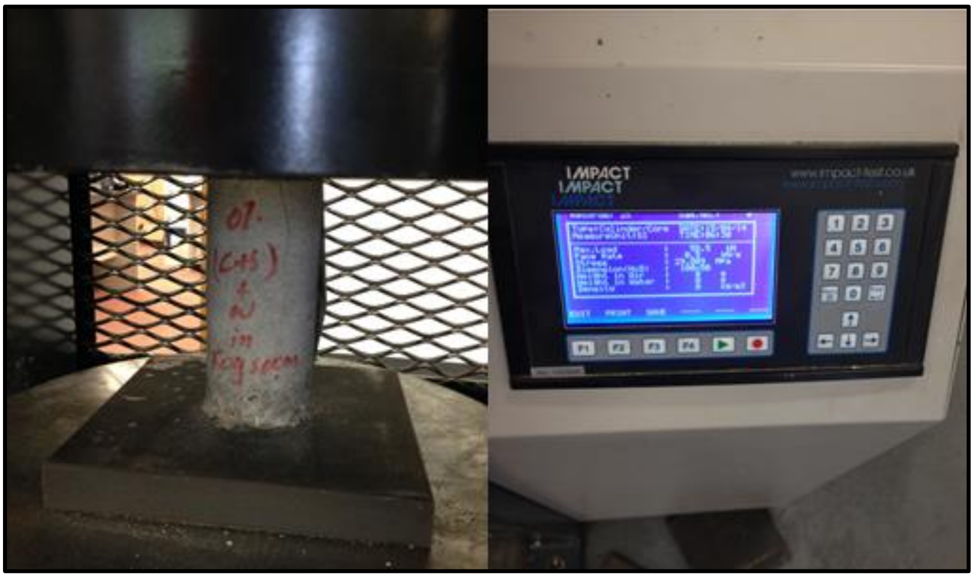


Figure 4.5 Compressive strength testing

4.2.7 Porosity

The interior part of the specimen sections were imaged (Figure 4.6) under a microscope set at a magnification of 65 times, and analysed using TBitmap software (Figure 4.7). The image analysis involved resin colour analysis to identify the pixels in the image as pores. Microscopy was conducted 28 days after the compression test.

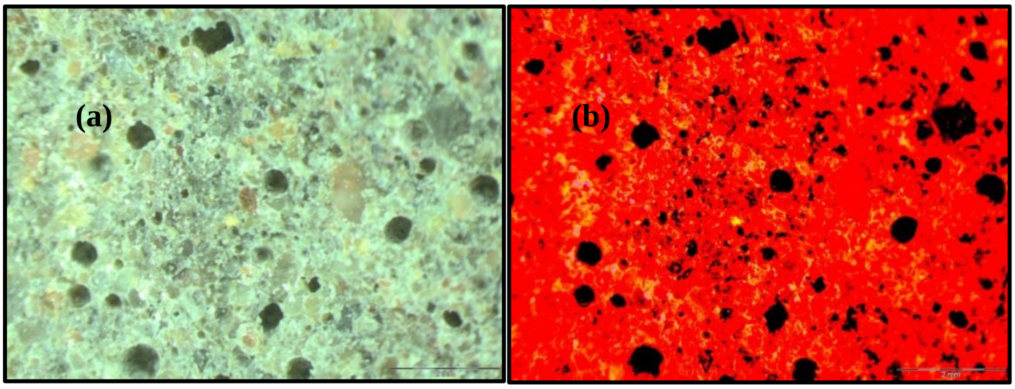
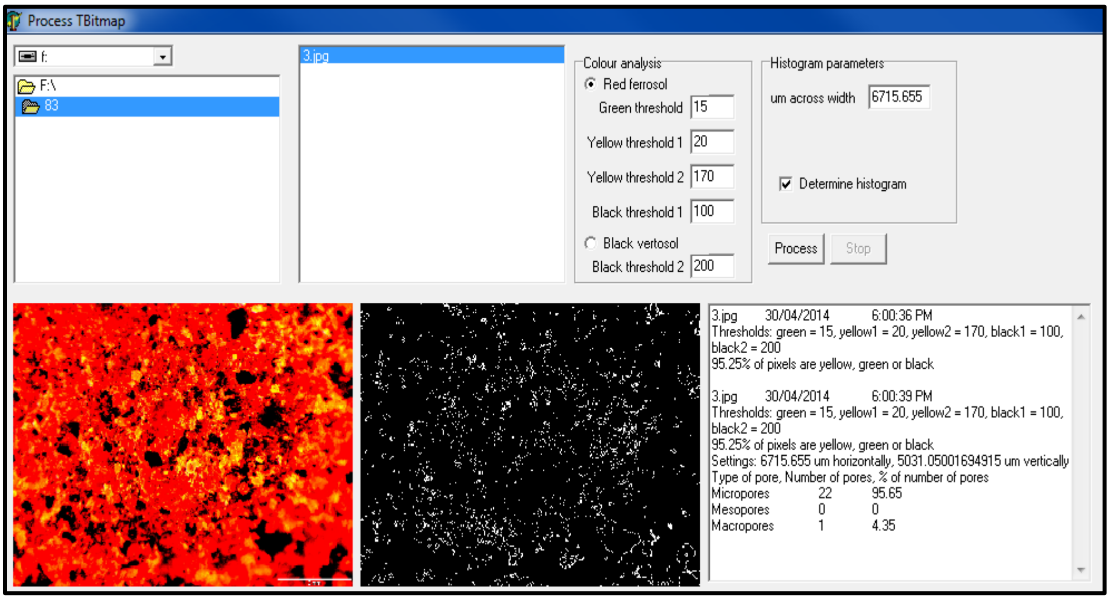


Figure 4.6 Example image of specimens' surface showing pores ((a) natural colour of the surface and (b) after readjust the colour to be readable by the software)



● Red ferrosol
Green threshold 15
Yellow threshold 1 20
Yellow threshold 2 170
Black threshold 1 100
○ Black vertosol
Black threshold 2 200

um across width 6715.655
☑ Determine histogram

```
3.jpg      30/04/2014          6:00:36 PM
Thresholds: green = 15, yellow1 = 20, yellow2 = 170, black1 = 100,
black2 = 200
95.25% of pixels are yellow, green or black

3.jpg      30/04/2014          6:00:39 PM
Thresholds: green = 15, yellow1 = 20, yellow2 = 170, black1 = 100,
black2 = 200
95.25% of pixels are yellow, green or black
Settings: 6715.655 um horizontally, 5031.05001694915 um vertically
Type of pore, Number of pores, % of number of pores
Micropores          22          95.65
Mesopores           0           0
Macropores          1           4.35
```

Figure 4.7 Example analysis screen using TBitmap software for a surface image

4.2.8 Scanning Electron Microscope (SEM) observations

The microstructure of all the samples was observed using a scanning electron microscope (SEM) (JEOL JCM-6000, Tokyo, Japan), in order to investigate the effect of light crude oil. All the specimens for SEM observation were first cut, polished, and coated with a thin layer of gold–palladium, using a vapor-deposit process (Robert and Benmokrane, 2010).

4.3 Results and observation

4.3.1 Compressive strength of mortar

The compressive strength of mortar was calculated by dividing the maximum failure load by the actual cross sectional area of the samples. Table 4.1 shows the average compressive strength (MPa) of mortar with oil contaminated sand. The results show that the largest coefficient of the variation is only around 13%, which indicates the consistency of preparing the specimens. The specimens mixed by CWS exhibited a compressive strength ranging from 23.3 to 27.3 MPa for 0%, 26.9 to 28.9 MPa for 2%, and 11.7 to 21.5 MPa for 10% of crude oil contamination. On the other hand, the compressive strength of mortar prepared by CSW varied from 22.9 to 27.4 MPa for 0%, 23.1 to 23.7 MPa for 2%, and 10.2 to 16.5 MPa for 10 % of crude oil content. In contrast, in terms of curing methods, it can be observed that specimens cured in water under the two mixing methods showed a compressive strength from 26.4 to 27.2 MPa for 0%, 23.4 to 27.8 MPa for 2%, and 13.1 to 15.3 MPa for 10% of crude oil contamination. A lower compressive strength was observed for the air cured specimens compared to the water cured specimens. The compressive strength obtained varied from 25.2 to 26.5 MPa for 0%, 23.1 to 26.9 MPa for 2%, and 12.4 to 14.8 MPa for 10%. In comparison with the PB cured specimens, the compressive strength varied from 22.9 to 23.3 MPa for 0%, 23.7 to 27.7 MPa for 2%, and 10.2 to 11.7 MPa for 10% of crude contamination. Furthermore, it can be observed that the highest compressive strength was obtained for FR cured specimens, prepared under the two mixing methods, with the strength ranging from 27.3 to 27.4 MPa for 0%, 23.4 to 28.9 MPa for 2%, and 16.5 to 21.5 MPa for 10% of crude oil contamination.

Table 4.1 Compressive strength of mortar with different crude oil content

CWS								
Crude oil %	W		A		PB		FR	
	Average (MPa)	SD	Average (MPa)	SD	Average (MPa)	SD	Average (MPa)	SD
0	27.2	1.3	26.5	0.9	23.3	1.0	27.3	0.2
2	27.8	1.9	26.9	0.9	27.7	0.5	28.9	2.0
10	15.3	0.9	14.8	0.3	11.7	0.1	21.5	0.08
CSW								
Crude oil %	W		A		PB		FR	
	Average (MPa)	SD	Average (MPa)	SD	Average (MPa)	SD	Average (MPa)	SD
0	26.4	1.5	25.2	0.5	22.9	2.1	27.4	2.2
2	23.4	0.6	23.1	1.2	23.7	3.2	23.4	0.8
10	13.1	0.8	12.4	0.2	10.2	0.02	16.5	0.6

*SD Standard deviation

The results also indicated that mixing the mortar following CWS, a higher compressive strength was obtained for samples with 2% of oil contamination compared to uncontaminated samples. This was not the case when the mortar was prepared by CSW, in which case the compressive strength of mortar with oil contaminated sand was lower than that of the uncontaminated samples. Moreover, the largest reduction in compressive strength, regardless of the mixing and curing methods, was observed for mortar with 10% of oil contamination.

4.3.2 Failure mode of mortar in compression

Figure 4.8 shows the typical failure modes for oil contaminated mortar under compression. Two different failure modes were observed, i.e. axial splitting (columnar fracture), and shear failure. There was also a transitional change between the failure modes when the combined failure modes were present; for instance, a specimen exhibiting axial splitting in some cases contained elements of shear failure, even though the dominant failure mode was axial splitting. This state occurred with specimens containing 2% of crude oil contamination and cured in air and plastic bags, whereas for the specimens that were at the same percentage, and that were cured in water and a fog room, axial splitting was the dominant failure mode. This may be correlated to the percentage of the porosity in the specimens as shown in Figure 4.8. In this figure, it can be clearly seen that the surface porosity increases as the level of oil contamination increases. Hudyma et al. (2004) have indicated that the porosity of the specimens affects the failure modes. For instance, they illustrated that axial splitting is the dominant failure mode for specimens containing a porosity of less than 10%, while the shear failure mode occurred with specimens that contained a porosity of above 10% but less than 20%. This correlated with the results of the compressive strength observed in section 4.3.1. Specimens with an axial splitting failure mode exhibited the highest compressive strength, while specimens with axial splitting containing elements of shear failure showed lower compressive strength, as shown in Table 4.1 and Figure 4.8. In contrast, the lowest compressive strength was exhibited by specimens with 10% of crude oil contamination, which failed by shear.

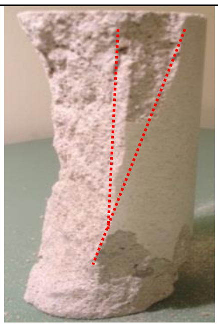
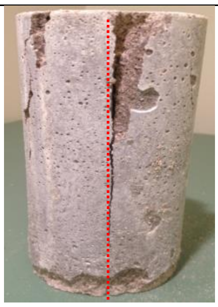
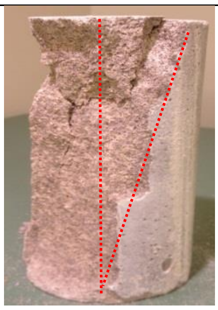
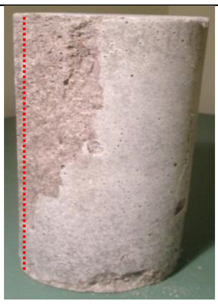
Crude oil content (%)	0	2	10
Cured in air			
	Axial Splitting		Shear Failure
Cured in water			
	Axial Splitting		Shear Failure
Cured in plastic bags			
	Axial Splitting		Shear Failure
Cured in Fog room			
	a	b	c
	Axial Splitting		Shear Failure

Figure 4.8 Failure modes of cylinder mortar in compression under different curing methods

In contrast, shear failure occurred in all specimens with sand contaminated with 10% of light crude oil, as shown in Figure 4.8-c. This type of failure is characteristic of a low strength concrete mix. This may be attributed to the air voids, which were clearly seen on the surface of the specimens, as shown in Figure 4.9, in which bigger air voids appear on mortar with sand contaminated by 10% of light crude oil than with 0% and 2% contamination. In addition, no cracking noises were heard for specimens with 10% crude oil contamination while the specimens were being loaded, and before failure. This could be due to the degree of wetness observed inside the specimens after failure, as shown in Figure 4.10. When the crude oil content was increased to 10%, the amount of crude oil that remained in the samples was higher compared to 2% and uncontaminated samples.

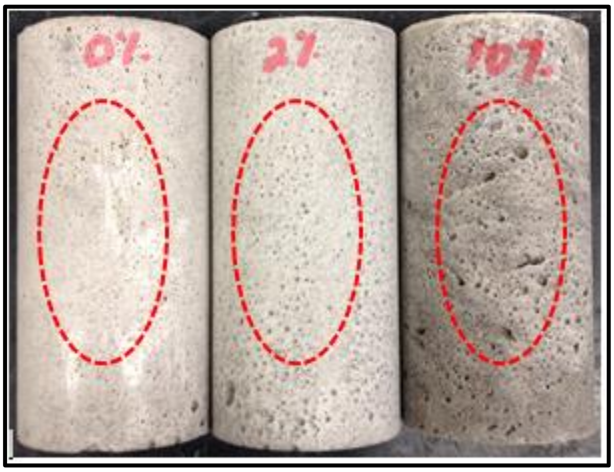


Figure 4.9 Air voids on the surface of specimens

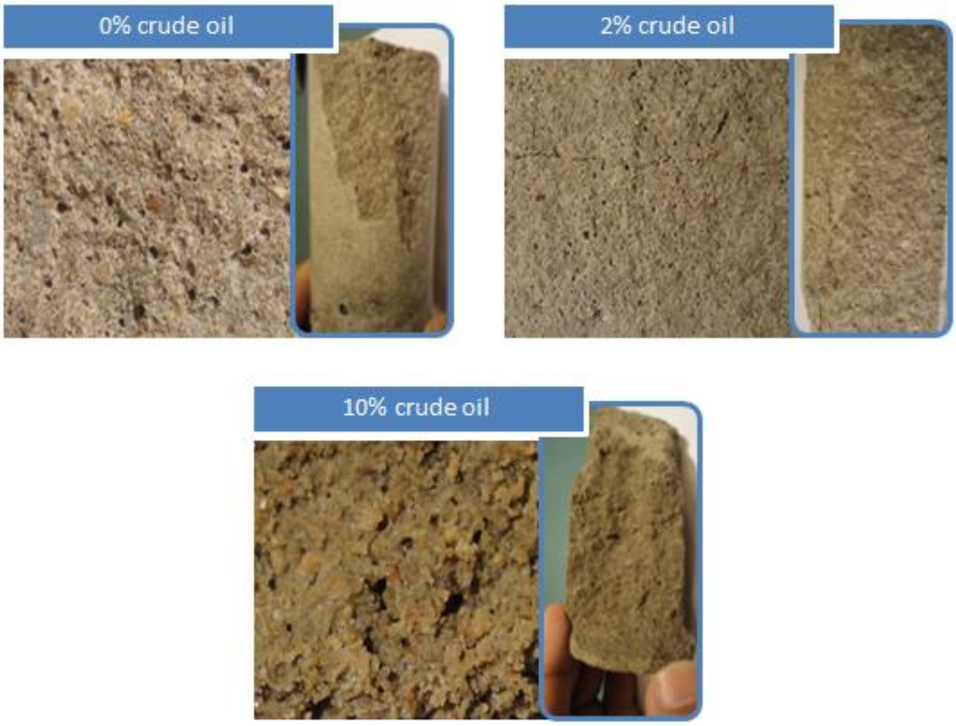


Figure 4.10 The degree of wetness inside of specimens

4.3.3 Total Porosity

Table 4.2 shows the average of the total porosity (%) of the specimen under the two mixing methods and the four curing methods. The total porosity increased by increasing the crude oil content from 0% to 10%. The highest total porosity with the two mixing methods (CWS and CSW), and under the four curing methods (A, FR, W and PB), was observed at 10% of crude oil contamination. In contrast, the lowest porosity was observed for uncontaminated samples under the two mixing methods (CWS and CSW) and the four curing methods A, FR, W and PB. The pore size was classified to three different sizes based on Kay (1990) pore classification method: (a) micropores (< 0.32 μm); (b) mesopores (0.2-30 μm); and (c) macropores (> 30 μm).

The percentages of the micropores, mesopores and macropores are also presented in Table 4.2. It can be observed that microporosity had the highest percentage under the two mixing methods and four curing methods, which comprised 81 and 82% of the total porosity in the mortar mixed by CWS and CSW, respectively. The second highest percentage was observed with macropores (around 8.8 and 11.6%), and the lowest was observed with mesopores (around 8.9 and 7.8%), respectively.

Table 4.2 Average of the total porosity (%) of the specimen under the two mixing methods and the four curing methods

Total porosity (%) CWS								
C %	A	SD	FR	SD	W	SD	PB	SD
0	3.11	0.98	2.86	3.09	5.77	0.98	5.51	1.08
2	5.48	1.21	4.42	1.05	8.52	1.2	9.76	0.86
10	10.69	0.85	10.52	0.87	11.19	0.977	12.44	1.25
Micropores (%)								
0	92.67	1.55	81.24	2.02	86.97	0.95	86.11	0.88
2	91.19	1.08	85.74	1.45	88.54	1.13	86.25	1.44
10	70.64	0.88	84.16	0.96	68.15	1.41	64.63	1.65
Mesopores (%)								
0	0	0	12.25	1.61	6.82	0.96	5.93	0.98
2	2.3	1.14	8.95	1.25	8.95	1.16	7.99	1.15
10	16.62	0.86	5.67	0.91	5.67	1.19	17.19	1.45
Macropores (%)								
0	7.33	1.4	6.49	1.81	6.19	0.95	7.95	0.93
2	6.51	1.11	5.3	1.35	4.38	1.14	5.75	1.29
10	12.72	0.87	10.15	0.93	14.72	1.3	18.17	1.55
Total porosity (%) CSW								
0	3.81	1.19	3.04	1.51	6.27	0.96	6.54	1.01
2	7.61	1.16	6.84	1.2	10.15	1.17	13.45	1.07
10	13.5	0.86	12.5	0.9	16.92	1.13	17.72	1.4
Micropores (%)								
0	83.92	1.08	84.63	1.36	80.67	0.97	74.81	1.04
2	86.71	1.18	89.09	1.12	84.62	1.18	80.22	0.96
10	81.36	0.85	82.99	0.88	71.17	1.05	72.12	1.32
Mesopores (%)								

0	3.7	1.37	6.36	1.76	10.45	0.95	9.23	0.94
2	5.02	1.12	6.37	1.32	9.29	1.15	10.02	1.25
10	3.76	0.87	5.01	0.93	12.65	1.27	6.86	1.52
Macropores (%)								
0	12.37	1.17	9	1.48	8.87	0.96	15.96	1.01
2	8.26	1.16	4.52	1.18	6.08	1.17	9.76	1.05
10	14.87	0.86	11.99	0.9	16.18	1.12	21.01	1.38

4.4 Discussion

4.4.1 Effect of mixing method on compressive strength

Figure 4.11 shows the comparison of the compressive strength between the two mixing methods for mortar with oil contaminated sand and cured under different conditions. In general, the compressive strength of specimens mixed under CWS was higher compared to CSW, especially for a higher level of oil contamination. As expected for the uncontaminated sample, the variation of the compressive strength between the CWS and CSW mixing methods had no significant effect for the mortars cured under W, A, PB, and FR. When the content of crude oil was increased to 2%, the mortar mixed by CWS had a compressive strength of at least 4.0 MPa greater than the mortar mixed by CSW. For 10% oil contamination, the compressive strength of mortar, when prepared following CWS, was 5.4 MPa higher than CSW. This indicates that the mixing method had a significant effect on the compressive strength of mortar with oil contaminated sand. This was caused by mixing the cement with crude oil contaminated sand first, which affected or inhibited the hydration process. This is due to the crude oil coating the cement particles and affecting the hydration process, which is more likely to happen for mortar that is mixed following the CSW method than for the CWS method. As indicated by Winter (2009), the cement and water react together during the hydration process. When cement and water are mixed in suitable proportions, the result of the reaction is a solid mass, composed of gel and crystalline material, which binds together the constituents of a concrete mix. However, the presence of light crude oil may have interfered with the cement-water binder reactions, delaying or preventing full hydration particles, which was also mentioned by Kostecki (1997). Moreover, Munoz et al. (2005) have indicated that the presence of oil contamination in a significant proportion in concrete reduces its compressive strength. As clearly shown in Figure 4.12, combining the oil contaminated sand and the cement first resulted in oil merging into the cement, thereby hindering the reaction between the cement and the water. This explains why the mortar mixed by CSW had a lower compressive strength than the mortar mixed by CWS. For this reason, it is suggested that the CWS mixing method should be followed when preparing a mortar or cement using sand with oil contamination.

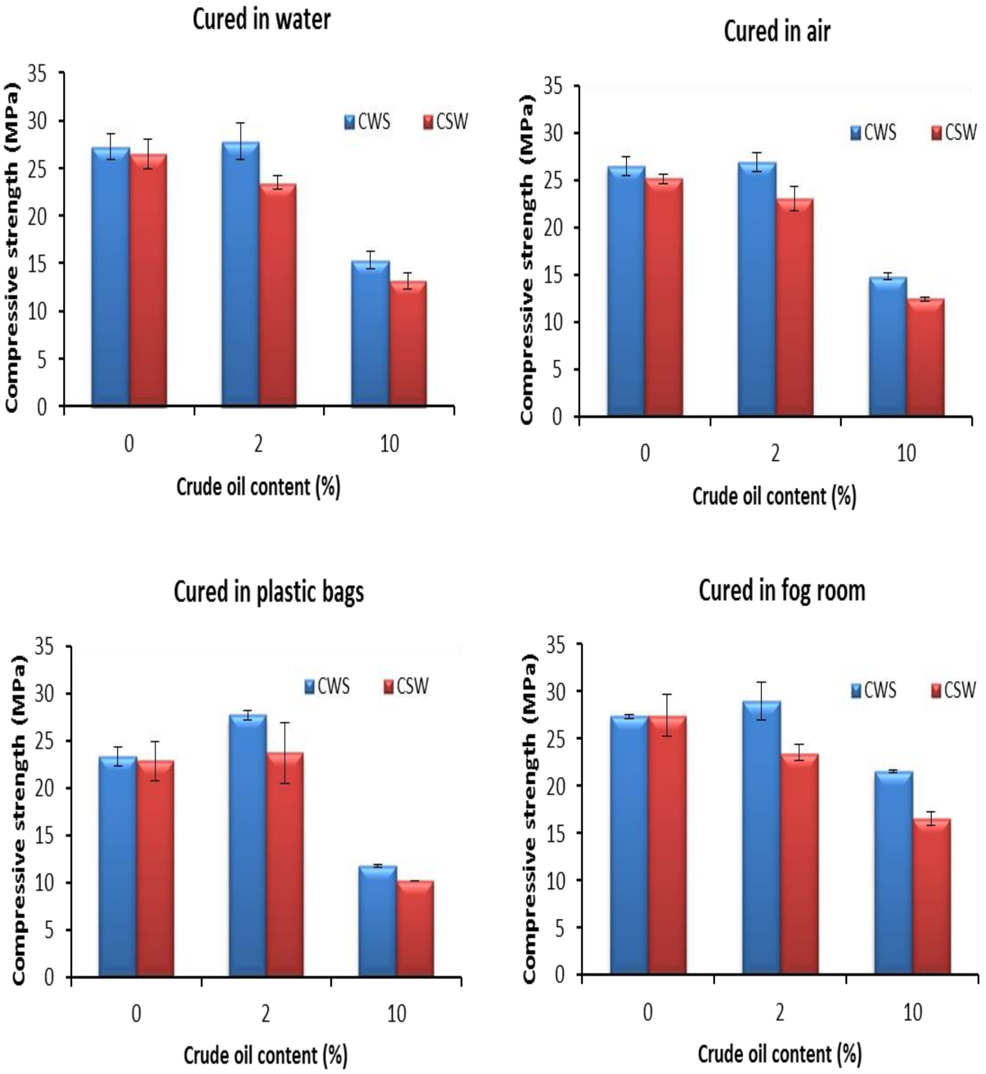


Figure 4.11 Comparison of compressive strength between the two mixing methods

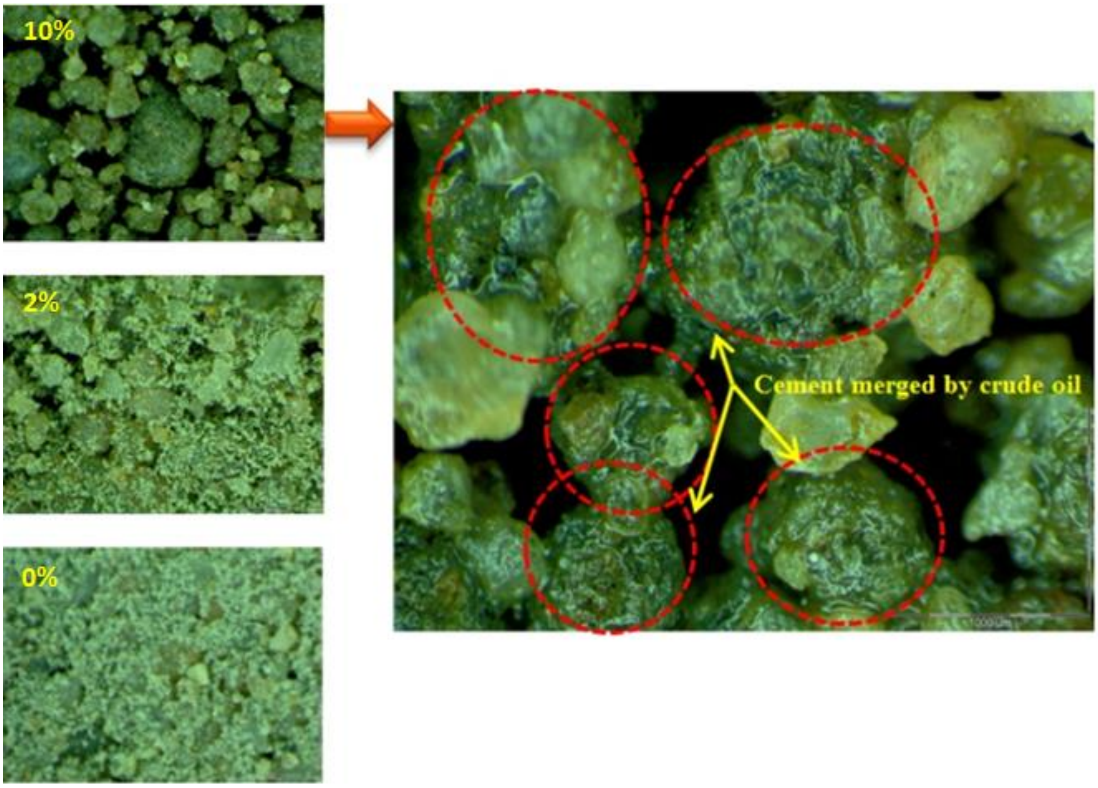
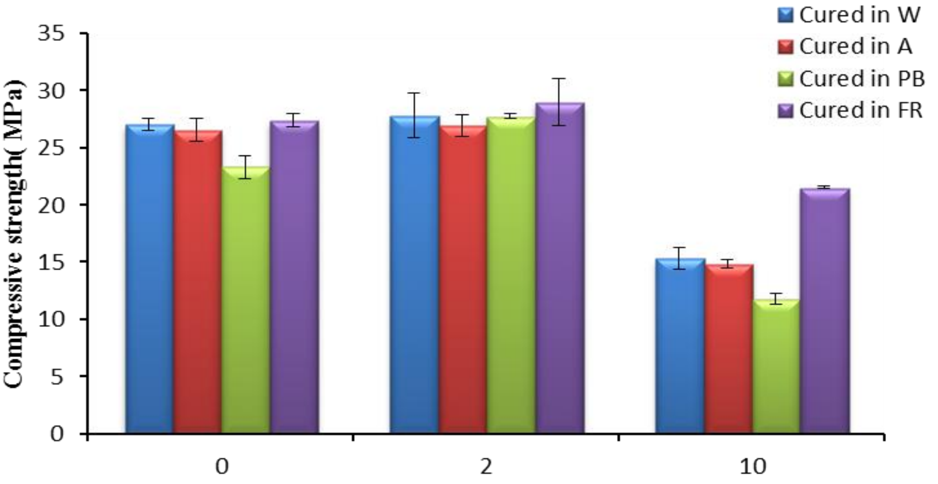


Figure 4.12 Oil contaminated sand mixed with cement

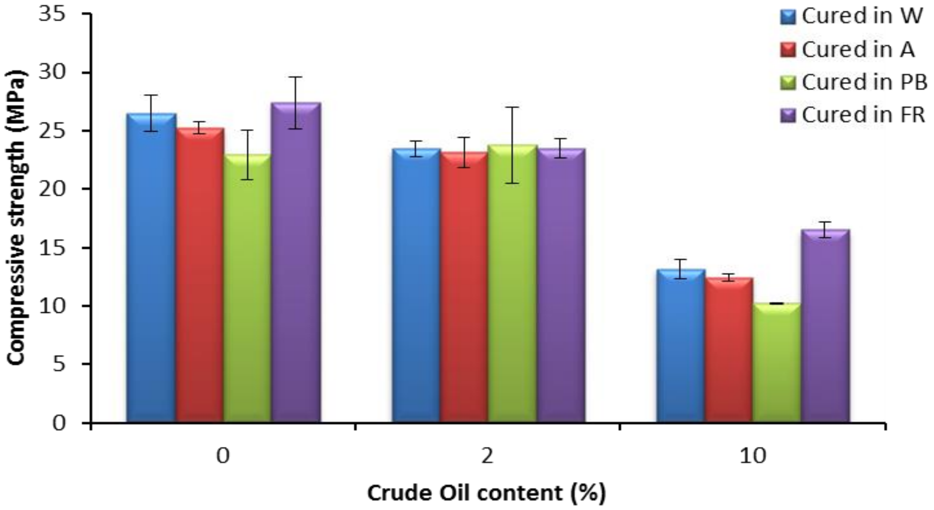
4.4.2 Effect of curing method on compressive strength

Figure 4.13 shows the average compressive strength of mortar with different crude oil content and curing conditions. In general, the compressive strength of the mortar with 0% and 2% oil contamination is almost the same when cured under A and W and prepared under different mixing methods. The highest compressive strength was attained by mortar cured in the fog room (FR). The average compressive strength of these specimens was 27.3, 28.9 and 21.5 MPa for CWS, and 27.4, 23.4 and 16.5 MPa for CSW, at 0%, 2% and 10% oil contamination, respectively. The development of higher compressive strength in mortar cured under FR, compared to the other curing methods (W, A and PB), is attributed to sufficient moisture during the curing process, which allows the hydration process to complete. This result indicates that it is very important to keep the specimens in high and constant humidity (around 85%) during curing to maintain the right level of moisture needed to complete the hydration process. This finding is supported by Spears (1983) who indicated that continued curing at relative humidity higher than 80% better facilitates the hydration in cement. Furthermore, Hayri and Baradan (2011) stated that high humidity can enhance the hydration process even under the same temperature.

In both mixing methods, a slightly higher compressive strength was observed for mortar cured in water (W), compared to air dried (A) and inside sealed plastic bags (PB). The development of higher compressive strength in W, compared to A and PB, is credited to sufficient moisture, which was maintained to assist the hydration of cement. The lower compressive strength of mortar cured under A, compared to W, agrees with the findings of Güneyisi et al. (2005), who concluded that the compressive strength of concrete cubes cured in ambient air conditions is 10-20% lower than cubes cured in water. Furthermore, Alizadeh et al. (2008) reported that the compressive strength of concrete cubes cured in water is higher compared to cubes cured in air at 7 and 28 days. Moreover, previous studies conducted by Gonnerman and Shuman (1928) and Price (1951) showed that concrete cured in air had less compressive strength than concrete cured in water, at all ages of the concrete. This increase in the compressive strength and other mechanical properties of concrete induced by water curing is due to the improved gel/space ratio inside the concrete (Neville, 1981). In contrast, only a small variation on the compressive strength is obtained between mortars cured under W and A. This may be due to the high humidity, which was around 60% during the curing period, and which results in a high possibility of moisture loss during the hydration process of the mortar.



(a) CWS



(b) CSW

Figure 4.13 Effect of different curing methods on the compressive strength

The mortar cured in PB exhibited the lowest compressive strength regardless of the mixing method. Compared to the mortars cured under W and A, the compressive strength of mortar cured under PB was almost 10% lower for mortar with uncontaminated sand and almost 20% lower for mortar with sand contaminated by 10% of light crude oil. This can be explained by the microscopic observations provided in Figure 4.14, which show that the mortar cured under PB was significantly wet with light crude oil, compared to other specimens. The low compressive strength, when cured under PB, can also be explained by the insufficient hydration of cement due to the specimens being kept in sealed plastic bags. This condition prevented the available moisture in the atmosphere to come in during curing, which would have assisted in the hydration process. This aligns with the results obtained by Bentz (1997) who compared the degree of hydration under saturated and sealed conditions. He concluded that the sealed condition reduces the hydration process, mainly during the initial 7 days of curing time. Furthermore, Neville (Neville, 1981) has stated that the main reason for keeping the concrete saturated with water during the curing process is to ensure that the water-filled space in the fresh cement paste is filled to the desired extent by the products of cement hydration. Thus, curing in sealed plastic bags, or covering with plastic sheets, in practice is not recommended for concrete with oil contaminated sand, as this prevents the available moisture in the environment to be absorbed by the mortar and to assist in the hydration process.

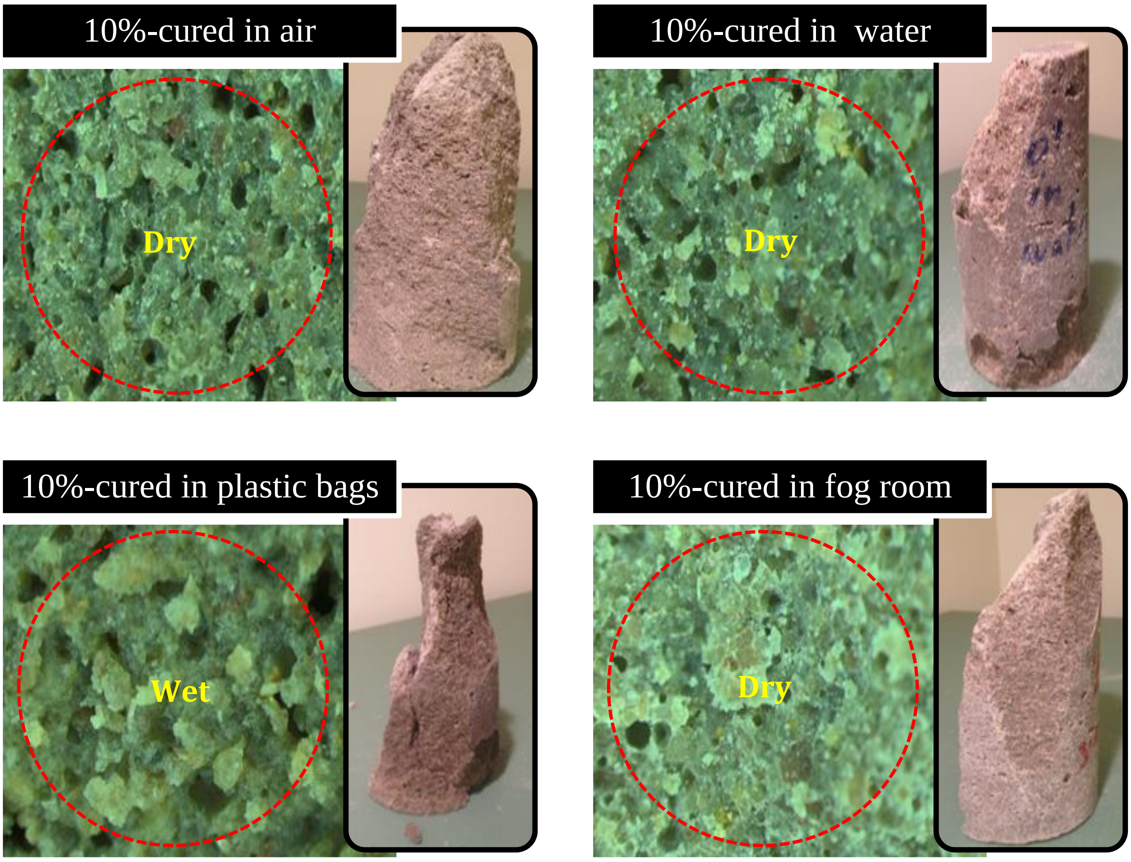


Figure 4.14 Degree of wetness under different curing methods at 10% of crude oil contamination

One interesting finding from this study regarding the effect of curing methods on the compressive strength of mortar with 0 and 10% of crude oil contamination, reinforces the results of previous studies (Neville, 1995; Kocaman et al., 2011; Mehta, 1986) who have all observed that the curing method affected the compressive strength. Notwithstanding this result, the study also revealed that 2% of crude oil contamination, even under different curing conditions, had no significant effect on the compressive strength. This result was attributed to the degree of wettability caused by adding crude oil to dry sand. Increasing the wettability of dry sand with light crude oil decreased the amount of water that the sand could absorb. In Chapter 3 it was found that the water absorption of dry and uncontaminated sand is around 2.8%, but the fine sand contaminated with 2% of light crude oil does not absorb any more water, due to the sand particles being already coated with oil. Thus, all or most of the water added in the mix during the mortar preparation came in contact with the cement particles and thus helped complete the hydration process. It is also important to note that the compressive strength of mortar with sand contaminated by 2% light crude oil, and mixed by CWS, is higher than that of mortar with uncontaminated sand. However, by considering the standard deviation, the compressive strength is similar to uncontaminated samples. This can be further explained by the results obtained in Chapter 3, the addition of a minimal amount of light crude oil up to 1% enhanced the shear strength of fine sand. This indicated that a higher compressive strength can be attained for oil contaminated sand than for uncontaminated sand, up to a certain amount of contamination, if proper mixing and curing methods were used. These results have therefore increased the potential for using a certain level of oil contaminated sand in building and construction.

4.4.3 Effect of light crude oil on the hydration process

Figure 4.15 shows the comparison of the heat evolution during the hydration between the uncontaminated (0%) and the 10% of crude oil contaminated samples. The samples were prepared using CWS because this mixing method showed a higher compressive strength than CSW, as presented in Section 4.3.1. It can be seen that the hydration process is strongly affected by the presence of light crude oil. There were lagging and decreasing in temperature peaks with 10% of crude oil contamination, compared to an uncontaminated sample (0%). This indicates that the hydration process did not complete when the fine sand was contaminated with 10% of light crude oil. The thermal profile, resulting from the isothermal calorimeter, showed a suppression of the Tricalcium Silicate (C_3S) peak (D) and a significant decrease in the height of the third hydration Tricalcium Aluminate (C_3A) peak (F). The rate of hydration of the cement was faster for uncontaminated samples at an early age compared to specimens with 10% of light crude oil contamination. This can be attributed to the presence of calcium silicates, as they are the main cement compounds (occupying about 75% of cement weight), and they are responsible for the final strength of the hardened cement paste. By contrast, the reaction of C_3A with water is very violent, with the evolution of a large amount of heat, in turn forming calcium aluminates hydrate in the form of leaf hexagonal crystals (Odler, 1998; Potgieter and Kaspar, 1999). As a consequence, the mortar formed a physical bond with the aggregate, which resulted in mortar strength. In contrast, for specimens with 10% of light crude oil contaminations, the surface area of residual sand particles, untreated in specimens, were coated with crude oil. Thus, this percentage of light crude oil delayed the reaction of C_3S, as well as to C_3A, as shown in Figure 4.15 and 4.14. The reaction of C_3A to form insoluble calcium sulfoaluminate ($3CaO.A1_2O_3.3CaSO_4.30\text{-}32H_2O$) - ettringite - around C_3A particles, which permits enough time for the hydration of C_3S, was slower. Thus, longer time and lower reaction occurred with C_3A when 10% of light crude oil was used, hence, physical bond formation between cement paste and aggregate was hindered. Furthermore, the reduction of cumulative heat evolution between 0% and 10% crude oil contamination is clearly observed in Figure 4.16. This Figure shows that the cement was not fully reacting and hence, the cumulative heat of hydration decreased.

The mix containing 10% of light crude oil has both inhibited and retarded C_3S (peak D), by 16% and 81 minutes respectively, compared to the uncontaminated sample. In terms of the third peak 10% of crude oil content had inhibited and retarded C_3A (peak F) to a significant extent, as shown in Table 4.3. The heat evolution was decreased by 48%, while C_3A retarded by 325 minutes, compared to the uncontaminated sample. This shows that at a high percentage of crude oil, both C_3S and C_3A were affected, with C_3A more affected than C_3S.

Table 4.3 Shows the hydration process using isothermal calorimeter for mortar with and without crude oil contaminations.

Crude oil	Hydration peak (D)	time	Hydration peak (F)	Time	Cumulative evolution (J/g cement)		
(%)	mW/g cement	min	mW/g cement	min	12 (hr)	24 (hr)	48 (hr)
0	3.19	391	3.93	695	131.6	185.6	245
10	2.67	472	2.02	1020	101.9	152.3	197.8

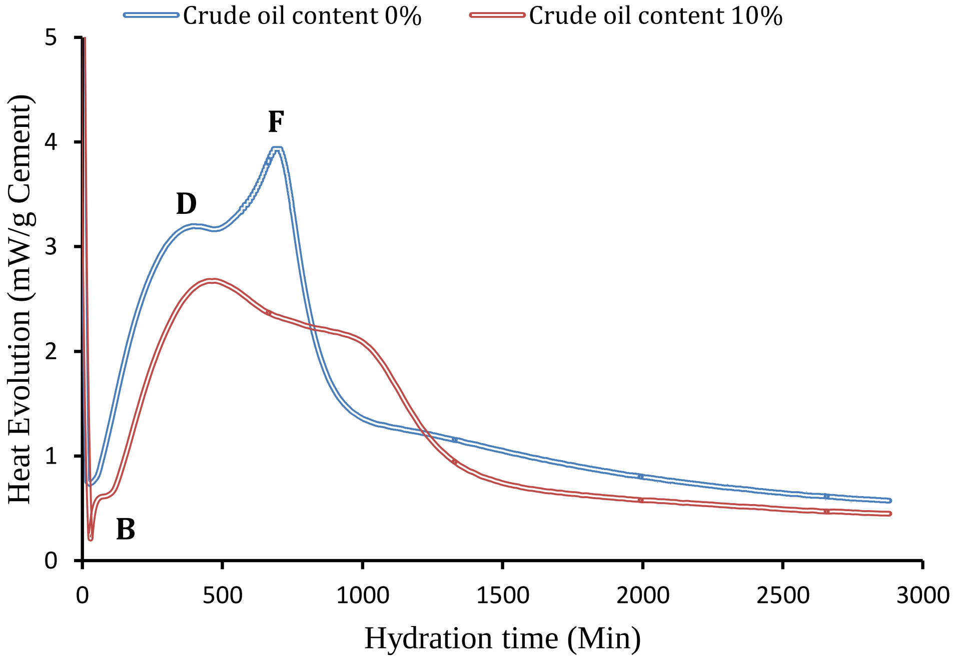


Figure 4.15 Heat evolution of mortar with 0 and 10% of crude oil contamination using isothermal calorimeter

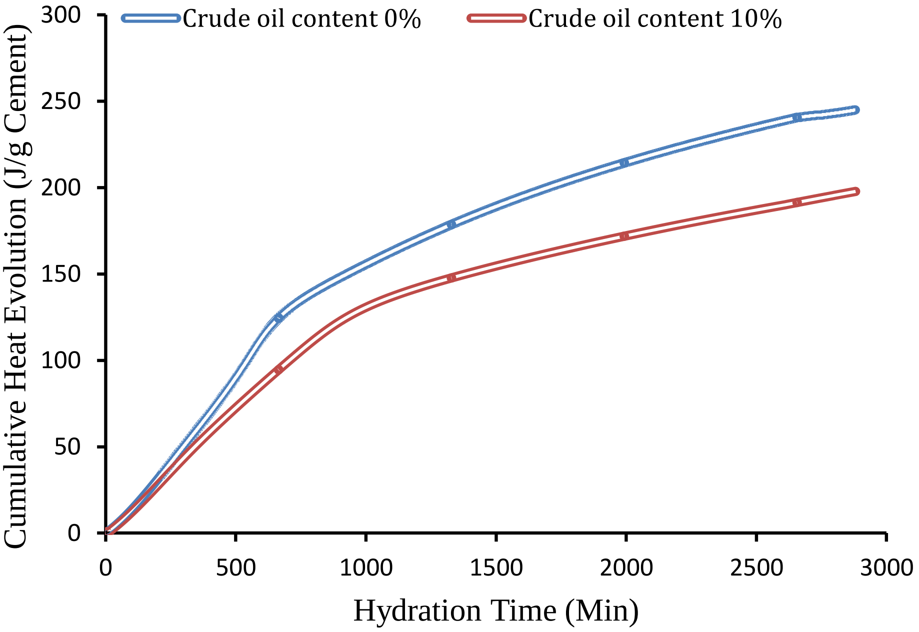


Figure 4.16 Cumulative heat evolution of mortar with 0 and 10% of crude oil contamination using isothermal calorimeter

The presence of light crude oil in high percentages (10%) inhibited both C_3S and C_3A hydration processes. The impact on the total evolved heat suggests that the light crude oil may inhibit cement hydration through coating the cement grains. The presence of crude oil decreases the reaction between the cement and water, as the sand and cement particles are coated by crude oil. This also means that most or all of the water added to the mix will remain free. Winter (2012) has indicated that a concrete mix with more water will have a higher porosity and permeability, but lower compressive strength. In this condition, the paste fraction of the concrete becomes increasingly porous and weak due to the fact that pores are interconnected.

The effects of the hydration process for the different curing methods are also apparent in the SEM images in Figure 4.17. These SEM images show the fracture surface of the mortar under different curing methods (W, A, PB and FR) for 0 and 10% crude oil contamination. It can be seen that there are more long thin crystals (x) when the mortar is cured under W, A and PB, while only a few appear on the surface when it is cured under FR. In addition, the mortar cured in W, A, and PB is more porous, with numerous capillary pores (P), partly bridged by hydration product, growing hydrating cement particles (C), in contrast to FR. On the other hand, the Calcium silicate hydrate (C-S-H) is much denser and most of the pores are filled for FR in contrast to the other curing methods. This explains the reason why the mortar cured in FR has higher compressive strength than the other curing methods considered.

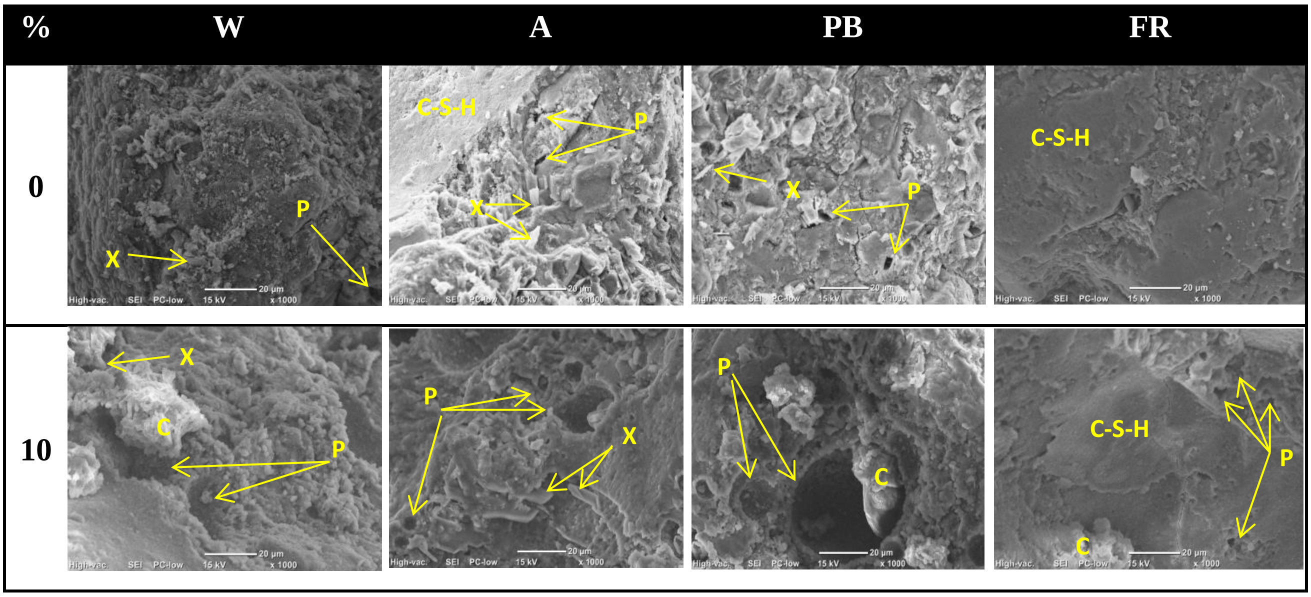


Figure 4.17 SEM images showed mortar after 28 days, made using ordinary Portland cement, w/c=0.5

Key: x- crystals; c- hydration product; C-S-H – Calcium silicate hydrate; P – Pore

The reduction of compressive strength, caused by light crude oil contamination, can be explained by the more and bigger pores in the samples, as shown in Figure 4.17. These pores are originally occupied by water and oil in the mix. For 0% oil contamination, these pores are filled by cement hydration products (Winter, 2009) and generally become small. By contrast, the contamination of the sample with light crude oil resulted in more and larger pores, due to the oil as well as the water, both of which reacted completely with the cement. This indicates that the mortar with oil contamination is more porous, and more likely to have the pores interconnected, thus resulting in a lower compressive strength (Chen and Wu, 2013).

4.4.4 Effect of total porosity on compressive strength

Figure 4.18 shows the percentage of total porosity of the specimen prepared under the CWS with three levels of oil contamination (0%, 2%, and 10%) as a function of four different curing methods (A, FR, W and PB). Furthermore, Figure 4.19 shows the average of the total porosity percentages of the specimen, prepared under CSW with three oil contamination levels (0%, 2% and 10%), as a function of four different curing methods. In general, higher porosity was observed when a CSW mixing method was used with the three different oil percentages, and under the four different curing methods, when compared to a CWS mixing method. When cement mixed with water first, the cement paste was easily able mix with the sand and create the bond between the cement past and the sand, and hence, homogenous mix was clearly observed when CWS was used resulting in lower total porosity. On the other hand, when dry mix was used (cement and sand) first and then water introduced, the mix was less homogenous compared to CWS. This may attributed to barriers made by the fine aggregate when water tried to mix with cement, resulting in lowering the interaction between the cement and water. Thus, low homogenous mix was observed which may the main reason beyond the increment of the total porosity compared to CWS. Furthermore, it can be observed that the total porosity under the two mixing methods and four different curing methods increased by increasing the amount of crude oil. In terms of the total porosity under the different curing methods (A, FR, W and PB), a higher porosity was observed when the specimens were cured with PB and A curing methods, compared to W and FR curing methods, when the three different crude oil contamination levels used, and when a CWS mixing method was used. In contrast, the lowest percentage of total porosity was observed with specimens cured in FR, and when the four curing methods were used.

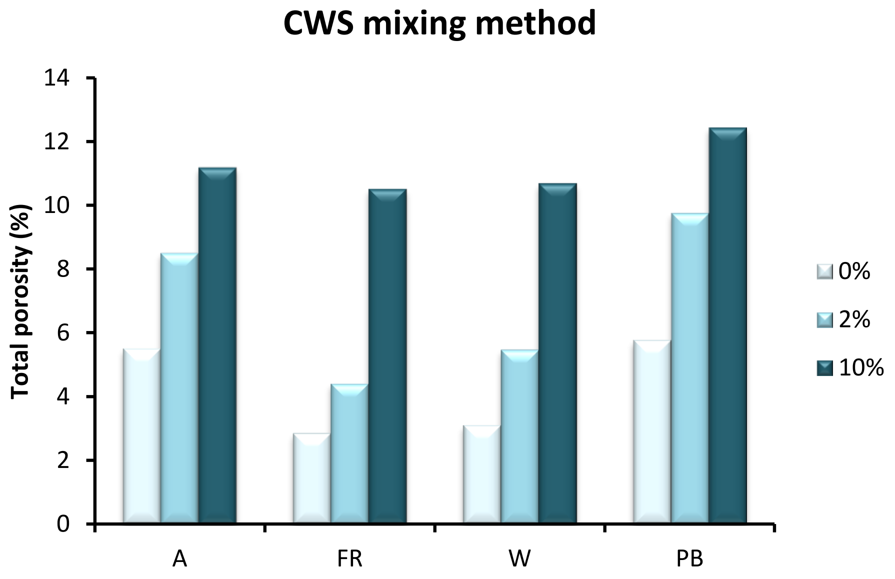


Figure 4.18 Relationship between the total porosity using CWS mixing method and different curing methods

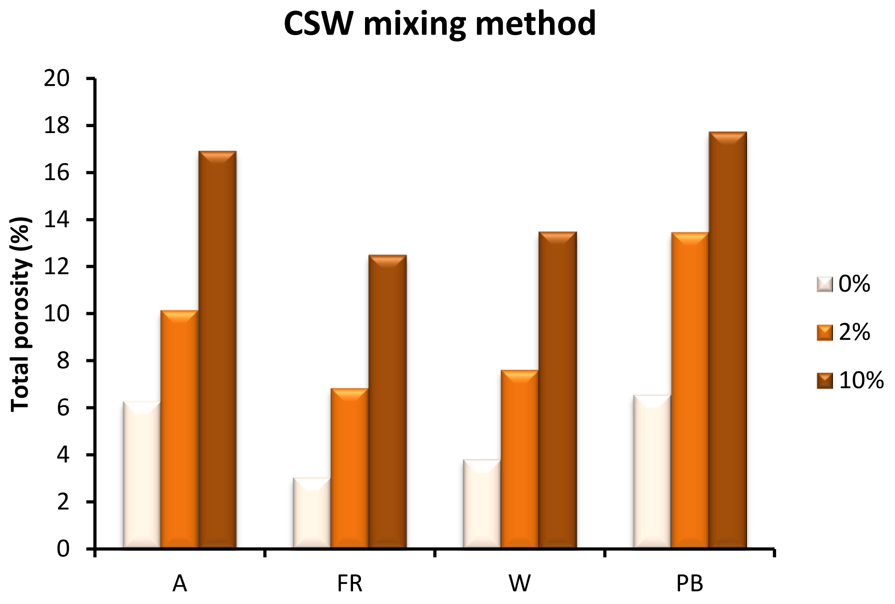


Figure 4.19 Relationship between the total porosity using CSW mixing method and different curing methods

Similar results were observed when a CSW mixing method was used. A higher percentage of total porosity was observed when PB and A curing methods were used, compared to FR and W curing methods, and when the three different contents of crude oil contamination percentages were used. While the lowest percentage of the total porosity was observed with specimens cured in FR, higher porosity was observed when a CSW mixing method was used compared to a CWS method with different curing methods. Furthermore, the higher porosity was observed when specimens were cured in PB and in A, compared to FR. This may be the main reason behind the lower compressive strength observed when a CSW mixing method was used compared to a CSW method. Mixing the cement with crude oil contaminated sand first affected or inhibited the hydration process, resulting in high total porosity. However, the presence of crude oil may have interfered with the cement-water binder reactions, delaying or preventing full hydration particles, which was also mentioned by Kostecki (1997). As a result, Munoz et al. (2005) indicated that the presence of oil contamination in a significant proportion in concrete reduces its compressive strength. This is due to the crude oil coating of the cement particles and its effect on the hydration process, which is more likely to happen for mortar mixed following the CSW mixing method than that following the CWS method.

The highest compressive strength was observed with specimens cured in FR, which showed the lowest total porosity. The low total porosity observed here, compared to other curing methods, may be attributed to sufficient moisture during the curing process, which allows the hydration process to complete, as explained in section 4.4.3. Besides that, the lowest compressive strength occurred for specimens cured in PB, as it had the highest total porosity among the specimens cured under different conditions. This can be explained by the insufficient hydration of cement, as explained in section 4.4.3.

4.5 Conclusion

This chapter has investigated the most effective mixing and curing methods for mortar containing fine sand, and contaminated with light crude oil. Based on the results, the following conclusions were drawn:

- The mortar produced by mixing cement and water, before adding the oil contaminated sand (CWS), resulted in a higher compressive strength than the mortar prepared by mixing the sand and cement before adding the water (CSW). This is due to the better reaction of cement particles and water during the hydration process, unlike in CSW where the cement particles are coated with oil, preventing them to react with water.

- A higher compressive strength is achieved for mortar with 2% oil contamination than the uncontaminated samples mixed by CWS. This is due to excess water availability to assist in the hydration process, as the fine sand is surface saturated with oil. By increasing the crude oil from 2 to 10%, the compressive strength significantly decreases, as the oil contamination in the mix hinders the cement from being hydrated.

- The mortar cured in the fog room had the highest compressive strength at all levels of oil contamination among the different curing conditions considered, i.e. cured in air, cured in water, and cured in sealed plastic bags, because there was enough moisture available to complete the hydration during the curing process.

- The curing method has no significant effect on the compressive strength of mortar with fine sand, contaminated by 2% of light crude oil. In this condition, the fine sand does not absorb any more water and all the added water in the mix reacts with the cement particles during the hydration process.

- The mortar cured in a sealed plastic bag (PB), especially with 10% oil contaminated sand, exhibited the lowest compressive strength. This is due to the prevention of movement of hydrocarbons in a confined space during the curing process, which hinders the hydration process. Microscopic observations showed that the mortar cured under PB is significantly wetter with light crude oil compared to specimens cured under different conditions.

- The hydration process was significantly affected for cement mortar containing fine sand, contaminated with 10% light crude oil, due to the suppression of C_3S and C_3A. The C_3S hardens rapidly and is largely responsible for the initial set and early strength, while (C_3A) liberates a large amount of heat during the first few days of hardening. As a consequence, the impact upon total evolved heat suggests that the light crude oil may inhibit cement hydration through coating the cement grains. This results in more and bigger pores in the cement mortar and in lower compressive strength than the uncontaminated mortar.

- SEM observations showed fewer long thin crystals (x) in the cement mortar cured under FR, rather than under W, A and PB. Similarly, the cement mortar cured under FR has smaller capillary pores (P), and is partly bridged by a hydration product growing hydrating cement particles (C), rather than W, A and PB. Moreover, the Calcium silicate hydrate (C-S-H) is much denser and most pores are filled under FR, rather than the under other curing methods.

- The mortar cured in FR was less porous than that cured in W, A, and PB. Similarly, higher porosity was observed for mortar mixed by CSW, rather than CWS. In addition, the pores of cement mortar containing light crude oil contaminated fine sand were bigger in size, and more interconnected, compared to those of uncontaminated samples.

These results demonstrate that up to a certain amount of crude oil, a higher compressive strength can be achieved compared to uncontaminated sand, if proper mixing and curing methods are used. These results have therefore increased the potential for using oil contaminated sand in building and construction. In Chapter 5, the effect of the water to cement (w/c) ratio, which is another important aspect that affects the mechanical properties of hardened cement mortar containing different percentages of crude oil contamination, is presented.

Chapter 5

The Influence of Water Cement Ratio on the Mechanical Properties of Mortar Containing Light Crude Oil Contaminated Sand

5.1 Introduction

Compressive strength is the most important property of concrete. This property can be affected by several factors such as quality of raw materials, mixing and curing of concrete, relative humidity, temperature, and water/cement ratio (Abalaka and Okoli, 2012, James et al., Safiuddin et al., 2007, Kaliyan and Vance Morey, 2009). In Chapter 4 the most appropriate mixing and curing methods for mortar containing light crude oil contaminated fine sand were determined. Mixing the cement and water first, before adding the oil contaminated sand, and curing it in a fog room to simulate the conditions of 25 °C and 85% humidity, were found to result in a cement mortar with optimal mechanical properties. This mixing and curing condition was then adopted for the specimen preparations for the rest of the studies in this thesis.

Proportioning a concrete mixture, i.e. mass ratio of the water and cement (w/c ratio) has a significant influence on hardened concrete properties, particularly with regards to its strength and durability, due to its relationship with the amount of capillary porosity in the cement paste (Neville, 1995). Therefore, the effect of the w/c ratio on the compressive strength is widely studied and very well-known (Soroka, 1980, Schulze, 1999, Oluokun, 1994). The effect of water content on physical and mechanical properties is critical, and therefore, to reach a certain workability level in order to achieve better strength, the water content of the concrete has to be carefully controlled (Rao, 2001). Excess water can seriously degrade the strength and durability of concrete; however, it will create an easier-flowing concrete with a higher slump. The excess water in the concrete mixes gradually evaporates during aging to leave an interconnected fine porous structure, which exhibits poor mechanical properties (Nematzadeh and Naghipour, 2012). On the other hand, while less water in the cement paste will yield a stronger and more durable concrete, it increases friction between the cement and aggregate particles, and brings about stiffening of the fresh mix and greater difficulty in handling, compacting, and finishing of concrete, resulting in a greater risk of cold joints and weaker areas in the overall structure (Ravina and Soroka, 1994, Yazan, 2005). These studies clearly demonstrated that w/c ratio has a significant effect on the physical and mechanical properties of uncontaminated concrete. However the effect of this mixing parameter on cement mortar with light crude oil contamination is still unknown. Thus, this chapter investigates how the w/c ratio influences the physical and mechanical properties of mortar containing light crude oil contaminated fine sand. Three w/c ratios were considered (0.4, 0.5, and 0.6) and the properties of cement mortar consisting of fine sand, with different levels of light crude oil contamination, were investigated.

5.2 Experimental program

5.2.1 Preparation of oil contaminated sand

Different levels of light crude oil contamination (0%, 0.5%, 1%, 2%, 4%, 6%, 8%, 10%, 15% and 20%) were used in this study. The preparation of oil contaminated sand was presented in detail in Section 4.2.1.

5.2.2 Preparing and casting of mortar

The mortar was based on AS 2350.12 (2006) and consisted of one part cement and three parts sand (by mass), and the water cement ratio (w/c) was 0.4, 0.5, and 0.6 respectively. Each batch was prepared separately to avoid any contamination between different mixes. All the laboratory work was conducted at a room temperature of around 22ºC, while curing in the fog room was carried out at a temperature of around 25ºC and a humidity of 85%. The specimens were de-moulded after 24 hrs and cured in a fog room for up to 28 days. Figure 5.1 shows the preparation of mortar.

Hand mixing

72 hr in plastic containers

Mortar mixture

Compaction

De-moulding

Curing- FR

Figure 5.1 Sample preparation protocol

5.2.3 Test Procedures

Compressive strength tests of all specimens were carried after 28 days of curing. The specimens were tested for failure under a loading rate of 1.5 kN/min, using the 2 Channel Automatic Cube and Cylinder Compression Machine CT340-CT440 based on AS-1012.9 (2014). Similar steps to those described in chapter 4 section 4.2.6 were carried out.

5.2.4 Porosity

The interior part of the specimen sections were imaged using TBitmap software as explained in chapter 4 section 4.2.6. In order to determine the number of images required to characterise porosity, high resolution images of specimens were used due to their ability to identify smaller pore sizes (Borges et al., 2012). High resolution means a smaller area and hence more images will be needed to characterise the porosity properly. This meant that the minimum number of representative area sample images needed was based on their physical properties (Baveye et al., 2002, Vanden and Protz, 1999). The porosity for each sample was measured by randomly selecting a subset of the total number of images, which in turn were based on the surface area. The image was taken with the highest magnification of the optical microscope where one image covers only 0.09 cm^2 of the total surface area. Therefore, at least ten images were taken to cover the 20% of the total area as recommended. These images represented around 20% of the total surface area of the specimens, so in subsequent analyses of porosity, 10 images were used for each sample. Figure 5.2 shows that the standard deviation did not change significantly when at least 10 images were used for specimens.

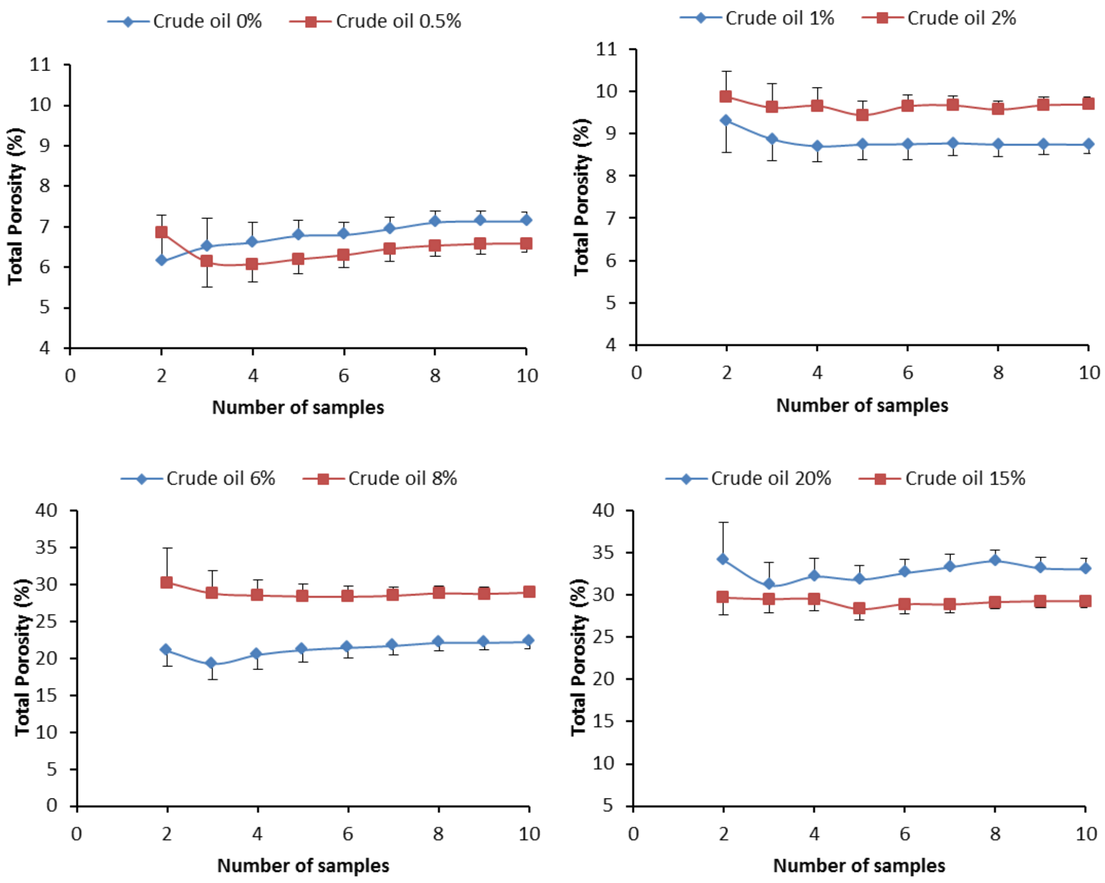


Figure 5.2 Standard deviation of samples of mortar images

5.2.5 Scanning Electron Microscope (SEM) images

The microstructure of all samples was characterised using a scanning electron microscope (SEM) (JEOL JCM-6000, Tokyo, Japan). All specimens for SEM observation were first cut and coated with a thin layer of gold–palladium using a vapor-deposit process (Robert and Benmokrane, 2010). The images were captured at a 15kV acceleration voltage, and 200 μm working distance. The images were digitised to 2560×2048 pixel, at a pixel spacing of 0.094 μm, giving an image field of view of 240×192 μm. This magnification and pixel spacing level was a compromise to obtain adequate resolution and a representative sample area. Prior to imaging, the brightness and contrast setting of the microscope were calibrated so that the brightness histogram of the recorded image was centred. Images were performed at low vacuum (40Pa), so no sample coating was needed to avoid changing effects. Microcracks due to damage caused by sample preparation should not be included, and care was taken to avoid imaging these areas, particularly close to the edges. Nevertheless, the amount of microcracking observed in the samples was small and therefore considered not to have a significant influence.

5.3 Results and observation

5.3.1 Compressive strength of mortar

The average compressive strengths at various w/c ratios 0.4, 0.5, and 0.6, and under different crude oil contamination (0%, 0.5%, 1%, 2%, 4%, 6%, 8%, 10%, 15% and 20%), are presented in Table 5.1. Under the three different w/c ratios, the compressive strength increased with up to 1% of crude oil contamination, and then decreased significantly by increasing the content of crude oil. The highest compressive strength of the three different w/c ratios occurred at 1 % of crude oil contamination: 23.5, 32.5, and 26.1 MPa, respectively. By contrast, the lowest compressive strength occurred at 20% of crude oil contamination with the three different w/c ratios of 0.4, 0.5, and 0.6, and they were 4.0, 3.9, and 4.0 MPa respectively.

Table 5.1 Compressive strength of different w/c ratios and different crude oil content

Oil content (%)	Compressive strength (MPa)	SD	Err.	Compressive strength (MPa)	SD	Err.	Compressive strength (MPa)	SD	Err.
	w/c = 0.4			w/c = 0.5			w/c = 0.6		
0	19.3	1.8	1.0	26.1	1.	0.6	24.5	1.9	1.1
0.5	19.3	2.4	1.3	30.0	1.2	0.7	25.8	1.6	0.9
1	23.5	3.9	2.2	32.5	1.0	0.6	26.1	1.4	0.8
2	19.9	0.6	0.3	28.9	3.5	2.0	24.4	0.6	0.3
4	19.8	1.5	0.8	26.2	1.0	0.5	22.6	3.6	2.0
6	18.7	2.8	1.6	23.7	2.8	1.6	19.7	0.6	0.3
8	17.5	0.5	0.3	23.3	0.6	0.3	18.3	0.8	0.4
10	13.8	0.6	0.3	21.5	0.1	0.1	14.26	0.4	0.2
15	6.9	0.1	0.07	7.5	0.4	0.2	7.02	0.4	0.2
20	4.0	0.1	0.06	3.9	0.1	0.03	3.9	0.08	0.05

5.3.2 Failure modes

Figure 5.7 shows the typical failure modes of the mortars for the 3 different w/c ratios. Only 0%, 8%, 10%, and 20% were presented because these levels of oil contamination represent the typical failure modes of cement mortars. During the test, two different failure modes, i.e. axial splitting (columnar fracture) and shear failure, occurred. With a w/c ratio of 0.4, the dominant failure mode for mortar containing from 0% to 8% crude oil was axial splitting, but from 10% to 20% of crude oil the dominant failure mode was shear failure. There was also a transitional change between the failure modes when the combined failure modes were present; for instance, a specimen exhibiting shear failure could also contain elements of axial splitting even though the dominant failure mode was shear failure. This state occurred when a w/c ratio of 0.4 was used with 10% contamination, whereas with the same percentage of contamination but with w/c ratios of 0.5 and 0.6, the dominant failure mode was axial splitting. This type of failure is also called tensile surface splitting and peeling (Andreev, 1995). Those specimens with w/c ratios of 0.5 and 0.6 exhibited axial splitting for 0% to 10% of crude oil contamination, whereas the specimens containing 15% to 20% of oil contamination exhibited shear failure as the dominant mode.

A higher compressive strength was obtained when the failure mode of axial splitting (columnar fracture) occurred rather than the shear failure mode. For instance, at 0.6, axial splitting occurred from 0% to 10% of crude oil contamination where the compressive strength varied from 24.58 to 14.26 MPa, but when crude oil contamination increased to 15% and 20%, shear failure was the dominant mode and the compressive strength decreased to 7.02 and 3.97 MPa respectively. Similarly, with a w/c ratio of 0.5, axial splitting occurred from 0% to 10% of crude oil contamination, and the compressive strength varied from 26.19 to 21.5 MPa respectively, while the dominant failure mode was axial splitting (columnar fracture). The failure mode changed to shear failure by increasing the content of crude oil to 15% and 20%. The compressive strength obtained at those percentages was 7.5 and 3.9 MPa respectively. When 0.4 was used as a w/c ratio, axial splitting was the dominant failure mode with up to 8% of crude oil contamination afterwards; this changed to shear failure from 10 to 20%, which appeared with a reduction in the compressive strength. It can be concluded that axial splitting (columnar fracture), occurred in specimens with less than 10% macroporosity, while the specimens with approximately 10% to 20% macroporosity experienced shear failure as the dominant mode. Furthermore, the wettability for those specimens from 8% of crude oil contamination up to 20% is clearly shown in Figure 5.3.

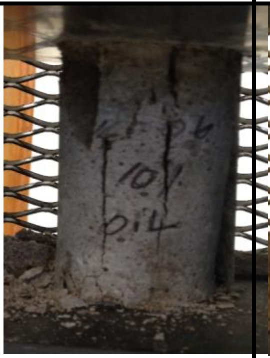
%	0	8	10	20
wc 0.4				
	Axial Splitting		*Shear Failure*	
wc 0.5				
	Axial Splitting			*Shear Failure*
wc 0.6				
	Axial Splitting			*Shear Failure*

Figure 5.3 Failure mode of different w/c ration and different crude oil content

Wetness inside the specimens may have affected the failure modes of the mortar. Figure 5.4 shows the internal surface of the three different w/c ratios of 0.4, 0.5, and 0.6, respectively for 8% of oil contamination. For a w/c of 0.5 and 0.6 the specimens were dryer than the w/c ratio of 0.4, which resulted in axial splitting. The main reason beyond the different of the colour was due to the degree of wettability. At w/c of 0.4, the mixing water was quite low compared to 0.5 and 0.6, as a consequence, the hydration process was not completed accordingly Thus, the shear failure mode for a w/c ratio of 0.4 was compatible with the high percentage of wetness observed inside the specimens.

w/c 0.4
Crude oil content
8%

w/c 0.5
Crude oil content
8%

w/c 0.6
Crude oil content
8%

Figure 5.4 Wetness of the specimens of 8% oil contamination

5.3.3 Porosity

Table 5.2 shows the average of the total porosity (%) of the specimen under the three different w/c ratio considered in this study. The highest total porosity between the three different w/c ratios used was observed for the w/c ratio of 0.4. This increment of total porosity was clearly seen up to 10% of crude oil contamination, while at 15 and 20% of light crude contamination the total porosity was almost the same with a w/c ratio 0.5, and slightly higher with a w/c ratio of 0.6. The second highest total porosity occurred with a w/c ratio of 0.6 and up to 10% of light crude oil contamination, while by increasing the crude oil to 15 and 20%, a lower total porosity occurred with a w/c ratio of 0.6 than with a w/c ratio of 0.4 and 0.5. However, the lowest total porosity occurred with a w/c ratio of 0.5 and up to 10% of light crude oil contamination, whereas increasing the crude oil to 15% and 20%, a comparable total porosity occurred with a w/c ratio of 0.4, and slightly higher than with a w/c of 0.6.

Despite a slightly lower total porosity at 1% and 2% of light crude oil contamination when a w/c ratio of 0.6 was used, compared to a w/c ratio of 0.4 and 0.5, similar to 15% and 20% of crude oil, the overall trend agreed with the compressive strength obtained under the three different w/c ratios used. For instance, disregarding the 15% and 20% percentages, the highest total porosity occurred with a w/c ratio of 0.4, which showed the lowest compressive strength. In contrast, the lowest total porosity occurred when a w/c ratio of 0.5 was used, where the highest compressive strength was obtained.

As mentioned in section 5.2.4, the total porosity was classified based on the Kay (1990) pore classification method, which agreed with the TBitmap software used in this research. Hence, the pore size was distributed into three different sizes: (a) micropores (< 0.32 μm); (b) mesopores (0.2-30 μm); and (c) macropores (> 30 μm). The percentage of the micropores, mesopores, and macropores are also presented in Table 5.2. It can be observed that the microporosity has the highest percentage under the three w/c ratios used. The average of the micropores (< 0.32 μm), with the three w/c ratios 0.4, 0.5 and 0.6, was around 79%, 80%, and 77%

respectively. Conversely, the average of the mesopores (0.2-30 μm), under the three w/c ratio used, was around 9.9%, 10%, and 11.7% respectively. In contrast, the average of the macropores (> 30 μm), among the three w/c ratio used, was 10.7%, 9%, and 10% respectively. The effect of the size of the porosity on the compressive strength of oil contaminated cement mortar is discussed in the next section.

Table 5.2 Shows the average of the total porosity (%) of the specimen under the three different w/c ratios

Total porosity						
% \ C	0.4	SD	0.5	SD	0.6	SD
0	5.82	0.86	3.11	0.48	3.62	0.35
0.5	5.65	0.66	3.95	0.36	4.92	0.38
1	8.58	0.51	5.08	1.52	4.76	1.28
2	9.43	0.79	5.48	0.71	4.55	2.23
4	10.55	0.4	5.77	0.38	7.71	0.74
6	14.98	0.99	5.49	0.54	8.88	1.15
8	17.34	0.46	6.22	0.55	10.5	0.67
10	19.82	1.23	8.9	0.58	10.52	1.14
15	25.79	1.52	26.42	1.46	23.27	1.51
20	26.31	1	27.1	1.7	27.84	1.65
Microporosity (%)						
0	88.44	1.55	81.24	1.67	83.61	1.31
0.5	82.43	1.33	88.53	1.07	81.46	1.38
1	87.82	1.69	85.61	2.25	81.53	3.53
2	88.69	1.91	85.74	1.88	81.82	2.43
4	88.96	2.9	83.32	2.3	80.36	2.37
6	79.44	1.03	85.38	2.26	85.59	1.51
8	77.8	1.04	84.62	2.56	81.85	3.02
10	70.13	1.84	85.76	0.56	72.76	3.14
15	65.26	3.06	64.8	1.7	65.83	2.97
20	64.25	2.76	65.75	1.89	63.68	2.39
Mesopores (%)						
0	3.99	0.69	12.25	1.78	9.28	1.46
0.5	10.68	2.81	6.48	1.65	12.22	2.07
1	6.29	2.7	10.37	1.42	13.42	2.17
2	4.8	2.66	8.95	0.95	11.79	2.83
4	4.3	2.15	11.34	0.89	11.03	3.3
6	10.95	1.45	6.93	1.18	4.78	1.27
8	11.37	1.07	7.05	1.9	8.26	1.75
10	15.56	1.18	5.07	1.39	15.17	2.75

15	15.54	1.38	16.68	1.51	16.12	1.38
20	15.9	1.52	15.02	1.64	15.46	0.64
Macropores (%)						
0	7.55	2.01	6.49	1.36	7.1	1.95
0.5	6.87	0.87	4.98	1.99	6.31	2.2
1	5.88	1.99	4.01	1.34	5.04	3.21
2	6.5	1.46	5.3	0.88	6.38	2.89
4	6.73	1.36	5.33	1.47	8.6	2.5
6	9.6	0.96	7.68	1.01	9.62	2.66
8	10.82	1.01	8.31	1.51	9.88	2.22
10	14.3	1.18	10.15	1.4	12.06	1.8
15	19.18	1.73	18.51	1.75	18.04	1.6
20	19.83	0.61	19.22	1.05	20.85	2.47

5.4 Discussion

5.4.1 Effect of w/c ratio on the compressive strength

Figure 5.5 shows the compressive strength of the three different w/c ratios as a function of different crude oil contamination used (0%-20%). It can be seen that the highest compressive strength was obtained with a w/c ratio of 0.5, followed by a w/c ratio of 0.6, while the lowest compressive strength was observed when a w/c ratio of 0.4 was used, and this had up to 4% of light crude oil contamination. When increasing the crude oil from 6% to 10%, the w/c ratio of 0.4 was the lowest compared to a wc ratio of 0.5, with the variation between w/c of 0.4 and 0.6 being decreased to less than 1 MPa. However, at a high percentage of crude oil contaminations (15% and 20%); similar (and the lowest) results were obtained with all different w/c ratios.

Increasing the crude oil content by up to 10%, a higher compressive strength was obtained when mortar was mixed with a w/c of 0.5, compared to a w/c of 0.4 and 0.6. For instance, higher compressive strength was obtained for a w/c ratio of 0.5 compared to a w/c 0.6 by 6.13%, 14%, 19.6%, 15.5%, 13.7%, 16.8%, 21.5%, and 33.6% respectively. The increment of compressive strength when a w/c ratio of 0.5 was used, compared to 0.6, was comparable to previous studies (Alawode and Idowu, 2011, Živica, 2009, Nwofor, 2012, Shamsai et al., 2012) where increasing the w/c ratio decreased the compressive strength. The reduction in the compressive strength that occurred with a w/c of 0.6, compared to a w/c of 0.5, was due to an increase in porosity (which will be explained in detail in section 5.5.1) because by increasing the water cement ratio, the paste fraction of the mortar becomes increasingly porous and the mortar becomes weaker, due to increased porosity and more preamble, because the pores are interconnected (Winter, 2012). Furthermore, (Vu et al., 2009) claimed that the w/c ratio, upon entering the concrete composition, is a major parameter affecting the porosity and strength of the cement matrix of hardened concrete.

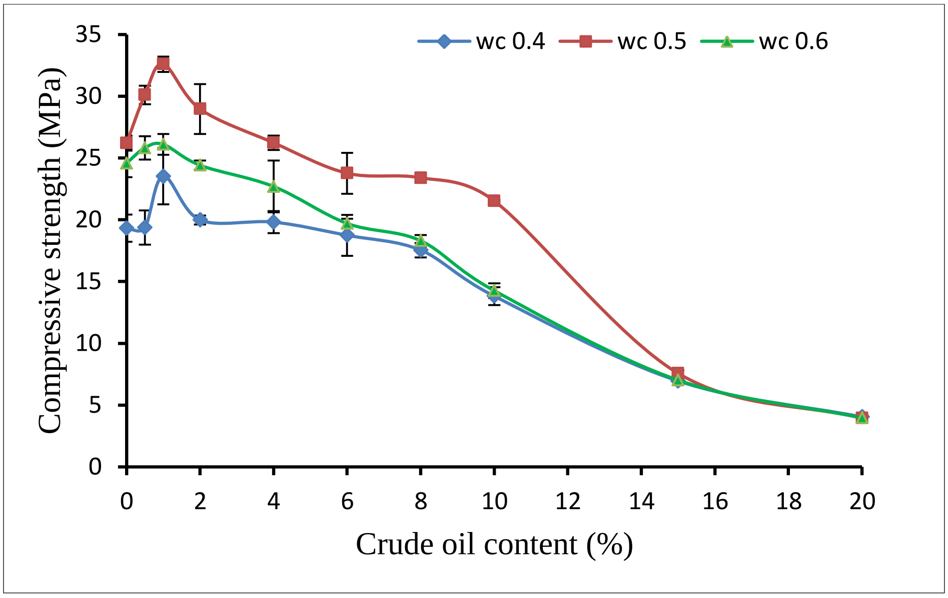


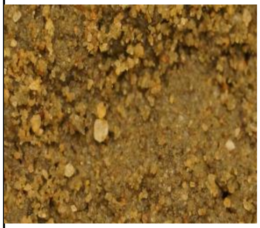
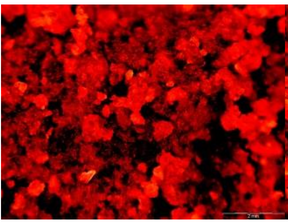
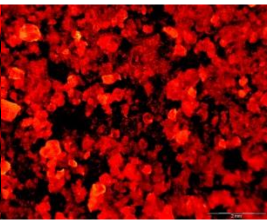
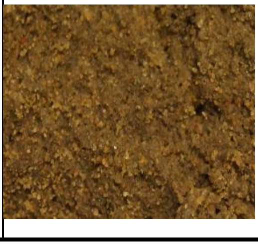
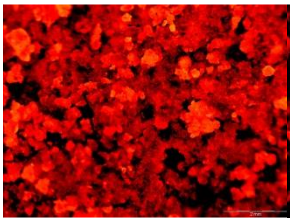
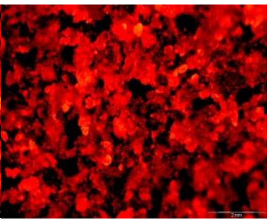
Figure 5.5 Effect of w/c ratio on the compressive strength

In contrast, under the same conditions in terms of mixing, curing and crude oil content levels (0%-10%), the lowest compressive strength occurred with mortar using a w/c ratio of 0.4. By increasing the crude oil contamination up to 10%, the compressive strength decreased by 26.0%, 35.6%, 27.6%, 31.1%, 24.4%, 21.0%, 24.8%, and 35.8% respectively when a w/c ratio of 0.4 was used compared to w/c 0.5. This may be due to insufficient water being used to complete the hydration process. Neville (1996) indicated that there is a minimum w/c ratio needed for hydration products to form because there is insufficient space at low w/c ratios. The w/c ratio should not be below 0.42 for complete hydration to occur. For a w/c ratio of 0.4, the actual water provided was less than this amount, because some was absorbed by the dry fine sand during mixing. This is supported by our initial investigation into the mechanical properties of contaminated fine sand that was presented in chapter 3, section 3.5.1. It was found that uncontaminated sand had the highest percentage of water absorption at 2.79%, but this percentage decreased as the amount of crude oil increased. This indicated that the hydration processes was not completed with a w/c ratio of 0.4, which may increase total porosity due to the lack of water needed to complete the hydration process.

Furthermore, when a w/c ratio of 0.4 was used, the workability was less than with w/c ratios of 0.5 and 0.6, which indicates that removing the air voids was much harder than with more workable mortar. Winter (2009) has stated that workability is an important factor in mortar/concrete because it indicates how easy concrete can be compacted; in other words, it indicates how easy all the air voids in the concrete can be removed to achieve maximum density. Obtaining the maximum possible density of a wet mix is important to maximise the strength of the hardened concrete and its resistance to deterioration. Furthermore, Alawode and Idowu (2011) have stated that the use of less than the optimum amount of water may make setting difficult and reduce workability. On the other hand, greater shrinkage and a reduction in strength will occur when more water than the optimum amount is used. The best water-cement ratio, therefore, depends on the particular concrete mix. This is the main reason for reducing the compressive strength when a w/c ratio of 0.4 was used rather than 0.5 and 0.6, and when the crude oil contamination varied from 0 to 10%. As a consequence, reducing the water cement ratio decreases the workability, and hence, higher porosity is expected because all the air voids cannot be removed during compaction, which means the total porosity will be higher.

The effect of porosity on the strength of hydrated cement paste has been studied widely, and there is no doubt that porosity is a primary factor influencing the strength of cement paste (Röβler and Odler, 1985). The w/c ratio determines the porosity of the hardened cement paste at any stage of hydration, because it will directly affect the volume of voids in concrete. The w/c ratio also influences the porosity of the cement matrix within the hardened concrete (Roy and Gouda, 1973, Sersale et al., 1991), which itself heavily influences the durability of concrete.

In contrast, by increasing the crude oil from 15% to 20%, the compressive strength decreased significantly under the three different w/c ratios used (0.4, 0.5, and 0.6), while the values of the compressive strength were similar. The similarity of the compressive strength values at these percentages may be due to the saturated status of the sand with crude oil, which were observed at those levels as shown in chapter 3, section 3.5.2. Increasing the amount of crude oil that appears at 15% and 20% indicated that more free water will remain, due to all sand and cement particles being immersed in oil during mixing. This may be the main reason behind the degree of wettability observed in Figure 5.6 as well as the porosity. At a high percentage of crude oil contamination, the w/c ratio did not show any significant effect on the compressive strength due to the saturated status achieved. With this condition, the oil contamination in the mix hindered the hydration process of the cement. As a consequence, lower compressive strength was obtained under the three different w/c ratios used. This reduction in the compressive strength of mortar at a high level of crude oil contamination confirmed the results of previous studies (Ahad and B, 2000, Ejeh and Uche, 2009), which observed that the crude oil decreased its compressive strength as the amount of crude oil increased.

%	*15*	*20*	*15*	*20*
c/w	Digital SLR Camera images		Microscopic images	
0.4				
0.5				

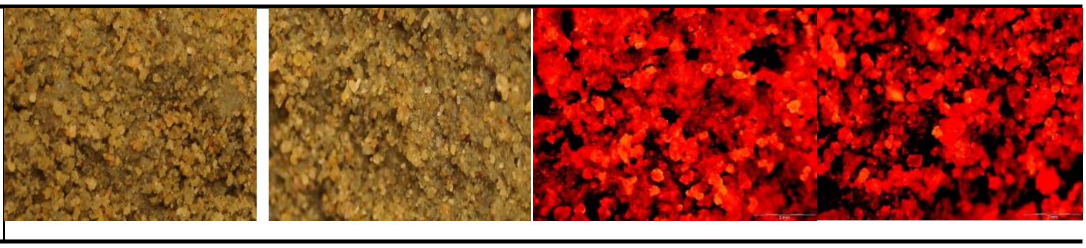
0.6	

Figure 5.6 Images show the wettability and the porosity of the specimens at a high level of crude oil contamination

5.4.2 Relationship between compressive strength and porosity

Figure 5.7 shows the percentage of total porosity of the specimens under the three w/c ratios as a function of crude oil contamination. Here the total porosity increased by increasing the amount of crude oil with the three w/c ratios of 0.4, 0.5, and 0.6. Furthermore the highest porosity occurred with a w/c ratio of 0.4, with up to 10% of contamination, compared to a w/c ratio of 0.5, and 0.6. The high total porosity occurred at a w/c ratio of 0.4 and may be due to the un-achievability of the maximum density when specimens were compacted, due to a low workable mix compared to a w/c ratio of 0.5 and one of 0.6. If concrete is not properly compacted it may contain voids which will contribute to its porosity (Kaliyan and Morey, 2009). At low w/c ratios, full compaction is difficult to achieve. Although the sand particle started to be coated by 2% and above; the extra amount of water in w/c 5 and w/c 6 compared to w/c 4 played a great role regarding the improvement of the workability. Thus when a w/c ratio of 0.4 was used, the amount of water was less than it should be, because dry sand was used which produces harsh and unworkable mixtures at a w/c of 0.4. As a consequence, reducing the water cement ratio decreases the workability, and hence, higher porosity is expected because all the air voids cannot be removed during compaction and thus, the total porosity will be higher. Khayat (1999) indicated that the higher the w/c of concrete, the higher the fluidity of concrete will be, which is one of the important factors affecting workability (Khayat, 1999). Furthermore, at a high level of crude oil contamination of between 15% and 20%, the variation of the total porosity among the three w/c ratios decreased between the three w/c ratios used. This attributed saturated state was caused by crude oil at these percentages, which improved the workability of the mortar mixes with the three w/c ratios. The porosity at these percentages of crude oil contamination was due to the amount of free water that remained in the specimens, due to the high level of crude oil contamination as explained in the previous section 5.5.

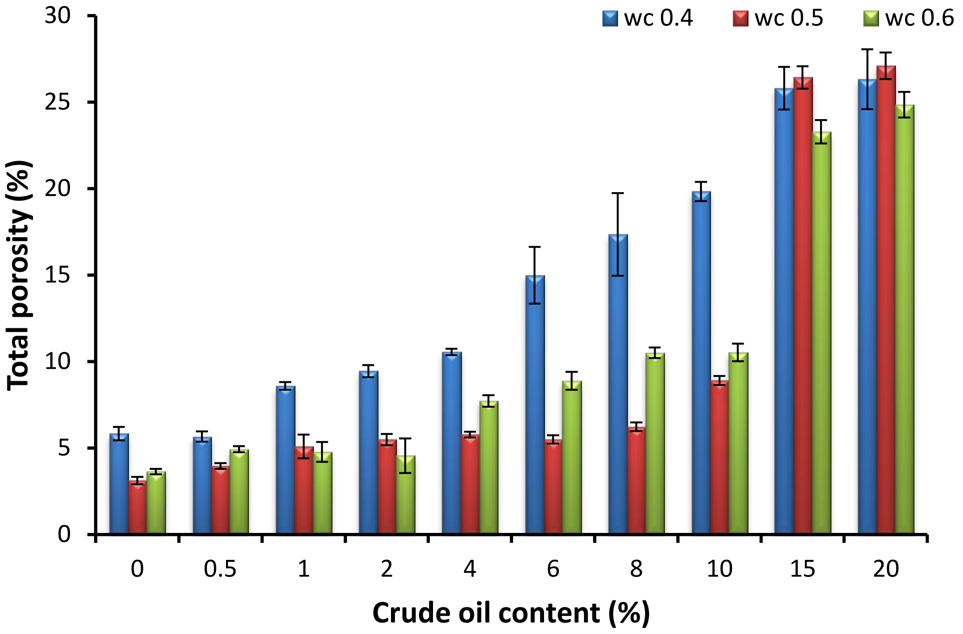


Figure 5.7 Relationship between total porosity and different crude oil contamination

In contrast, the total porosity of 0.5 and 0.6 is almost the same for 0 to 2%, which may be due to the improvement of the workability of the mortar mix caused by increasing the w/c ratio. Maximum density can be achieved if concrete is properly compacted, and thus, the air voids can be easily removed. At these percentages (0% - 2%), it is expected that no free water was caused by adding the crude oil because the SSD condition was met at 2% of crude oil contamination. All the water added in both w/c ratios 0.5 and 0.6 enhanced the fluidity of the mortar and was not so high as to increase the free water inside the specimens. As a consequence, the total porosity was almost the same at these percentages. However, the total porosity for 0.6 was higher than 0.5 for 4% to 10% of oil contamination. This could be attributed to the saturated status of the contaminated sand as it exceeded the SSD condition. Increasing the w/c ratio while increasing the crude oil percentages increases the probability of free water, which increased the total porosity at a w/c ratio of 0.6 compared to a w/c ratio of 0.5 at crude oil content of 4%-10%.

Despite the fact that increasing the crude oil content affects total porosity with the three different w/c ratios, the effect of porosity on the compressive strength will not be based on total porosity but rather on the pore size distribution. Based on Kay (1998) method, the total porosity was classified based on the pore size distribution into three different sizes: (a) micropores (< 0.32 μm); (b) mesopores (0.2-30 μm); and (c) macropores (> 30 μm). Previous studies have indicated that the compressive strength depends upon the amount of macroporosity (Al-Harthi et al., 1999) and pore structure (Price et al., 1994). The pore structure of a porous material can be characterised by parameters such as pore size, pore conductivity, pore surface roughness, and pore volume fraction (Corapcioglu, 1996). The size distribution of pores also affects the strength. (Luping, 1986) found that a material with low porosity, but with more large pores, may have a lower strength than a material with a higher porosity and less large pores. Therefore, as addressed previously in section 2.3.8, the total porosity with the pore size distribution classification of micropores, mesopores, and macropores was considered and calculated using TBitmap software.

Figure 5.8 shows the macroporosity (%) as a function of different crude oil contamination, which was considered to be the most effective pore size, compared to micropores and mesopores, on the compressive strength of concrete. The trend for macroporosity generally agreed with the compressive strength obtained with the three different w/c ratios, and total macroporosity occurred with uncontaminated sand under the w/c ratios of 0.4, 0.5 and 0.6 were 11.5%, 10.4%, and 11.1% respectively. This percentage decreased by increasing the amount of crude oil and the lowest value was achieved at 1% of contamination with percentages of 6.2, 4.0, and 5.0 respectively. Afterwards, increasing the amount of crude oil from 2% to 20% caused an increase in macroporosity, with the highest percentage occurring with 20% of crude oil, with 19.8%, 19.2%, and 20.8% respectively.

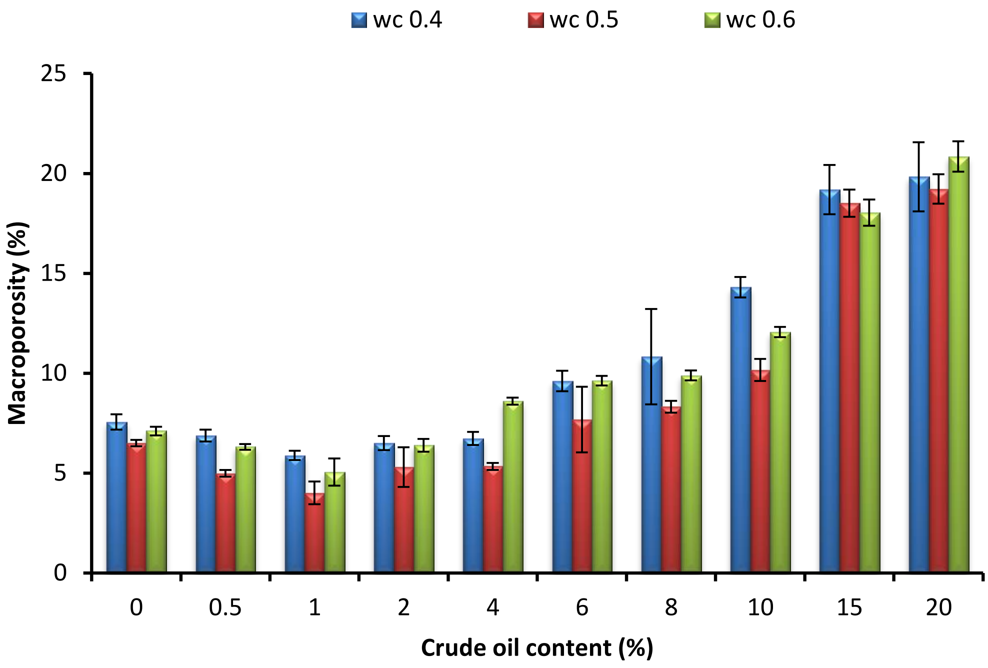


Figure 5.8 Total macroporosity as a function of different crude oil contamination (%)

Figure 5.9 showed the relationship between the macroporosity and compressive strength attained with w/c ratios of 0.4, 0.5, and 0.6, under different percentages of contamination. Increasing the amount of crude oil by up to 1% decreased the macroporosity, whereas with these three w/c ratios, the compressive strength increased. Increasing the amount of crude oil from 1 to 20% caused a significant increment in the total macroporosity and as a consequence, the compressive strength decreased significantly. A previous study conducted by Al-Harthi et al. (1999) concluded that macroporosity affects the compressive strength of concrete, while the compressive strength is based on the amount of macroporosity, while another study by Price et al. (1994) indicated that the pore structure effects the compressive strength. In this study the microporosity and mesoporosity did not have the same effect as the macroporosity.

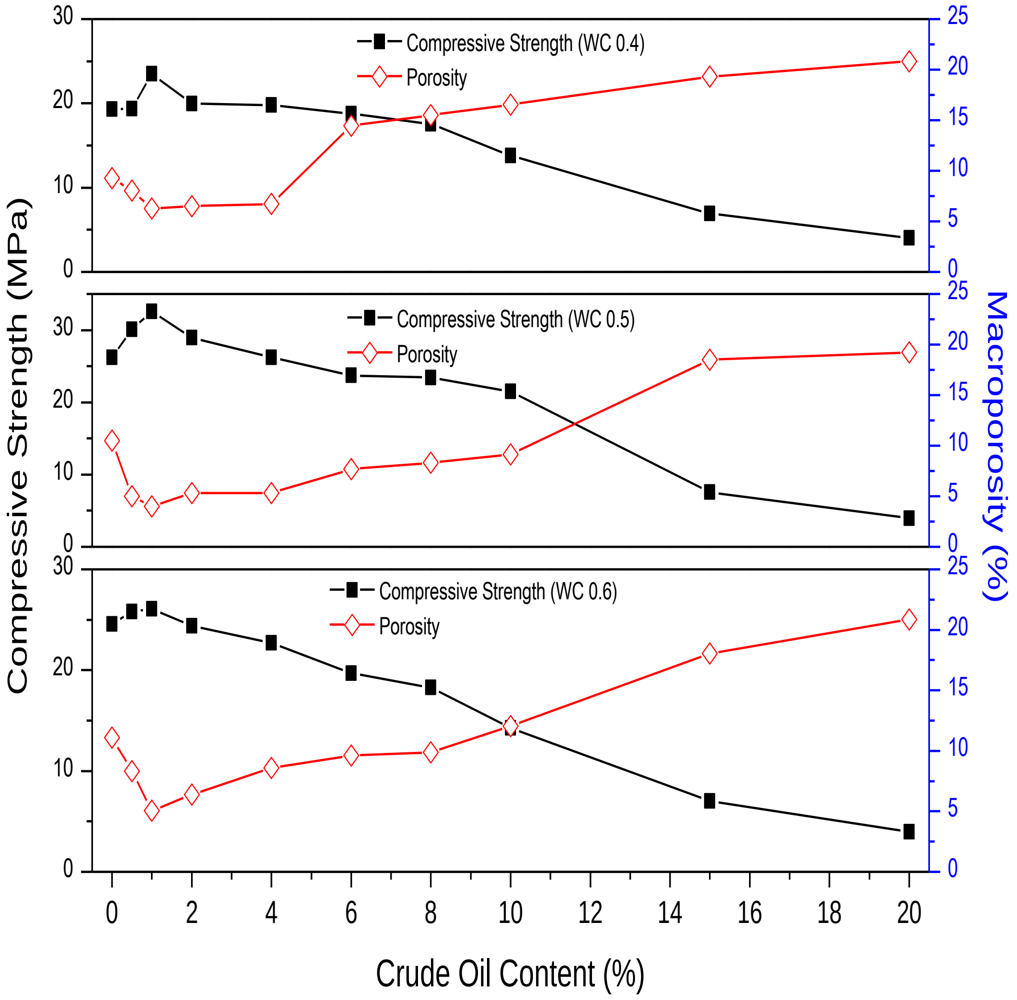


Figure 5.9 Compressive strength and macroporosity of the mortar under different w/c ratios

5.4.3 Scanning Electron Microscopy (SEM)

The SEM observations were used to better explain the observed behaviour of the cement mortar containing sand with light crude oil contamination, and the effects of the w/c ratios. From the SEM images it can be seen that there are three different parameters that can be observed. These parameters are the pore size (P), partially hydrated (P-H) cement, and full hydrated (F-H) cement, as shown in Figure 5.10. This Figure represents the sample (w/c 0.4- with 10% oil crude oil) of the full hydrated cement, partially hydrated cement and the pores by the SEM in a BEI mode.

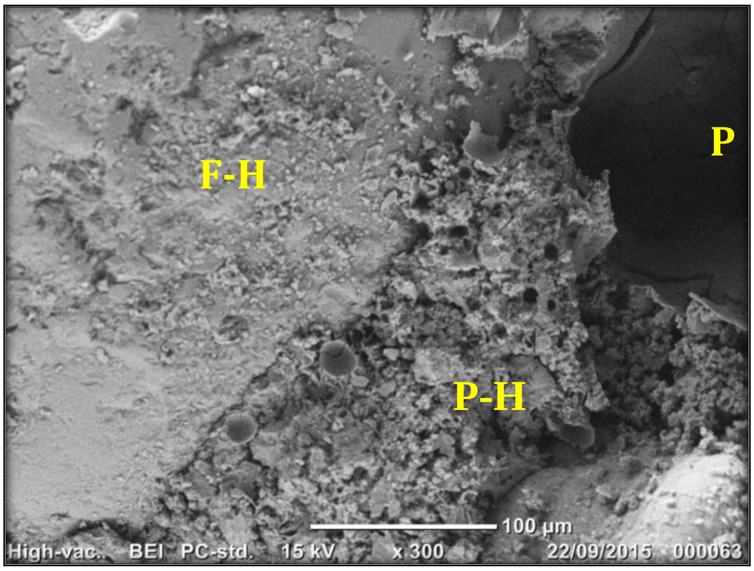
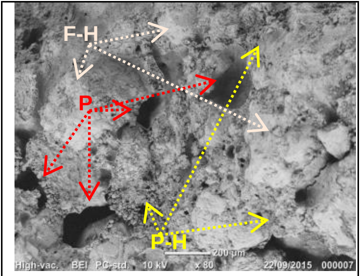
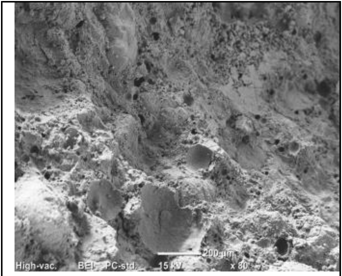
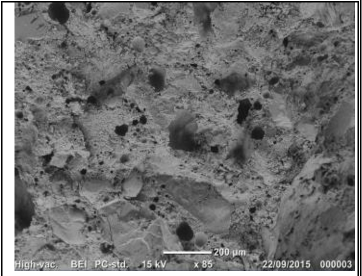
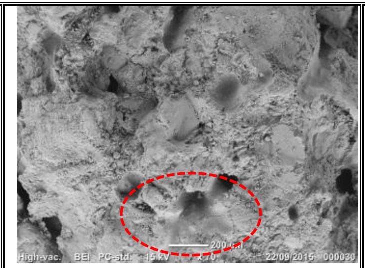
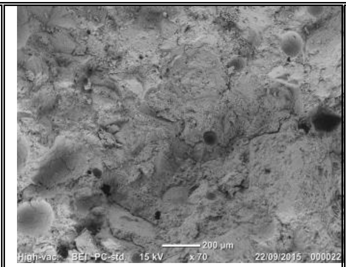
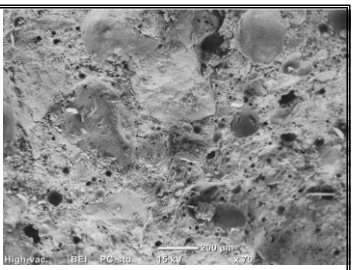
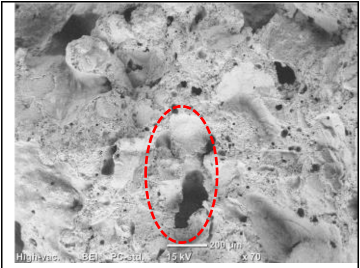
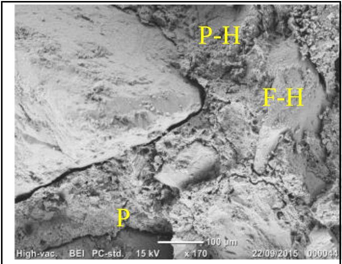
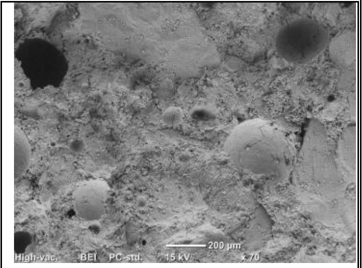
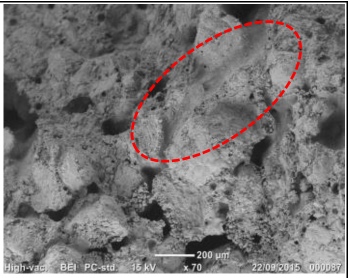
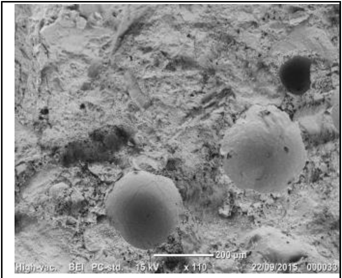
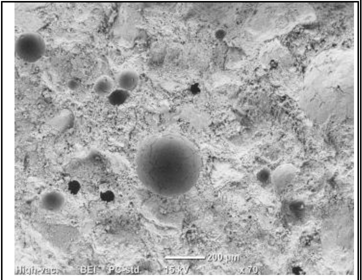
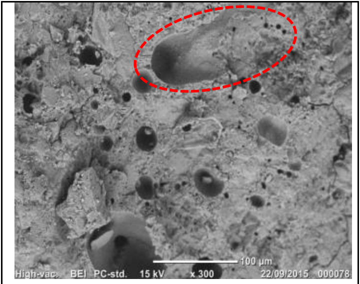
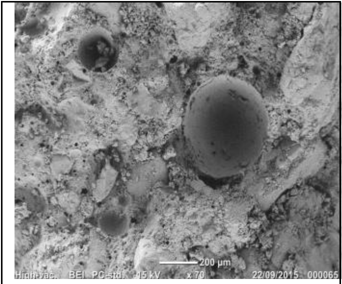
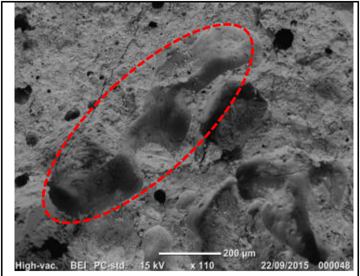
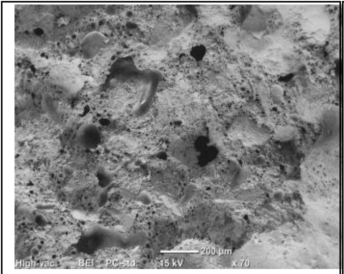
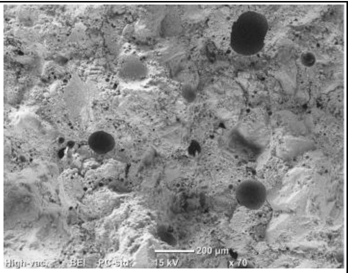


Figure 5.10 Shows a sample (w/c 0.4- with 10% oil crude oil) of the full hydrated cement, partially hydrated cement and the pores by the SEM in a BEI mode.

Figure 5.11 shows that the fully hydrated cement represents the C–S–H gel, and it formed a dense network structure. This shows that the hydration reaction of mixtures was fast enough and a lot of hydration products were formed. Thus, the mortar structure tissue became dense. The C–S–H gel formed a fibrous network structure in cement pastes (Kourounis et al., 2007). As hydration progressed, other hydration products gradually filled the network structure and hence, the mortar structure became tight at the latter stage of hydration.

wc %	**0.4**	**0.5**	**0.6**
0			

0.5			
1			
2			
4			
6			

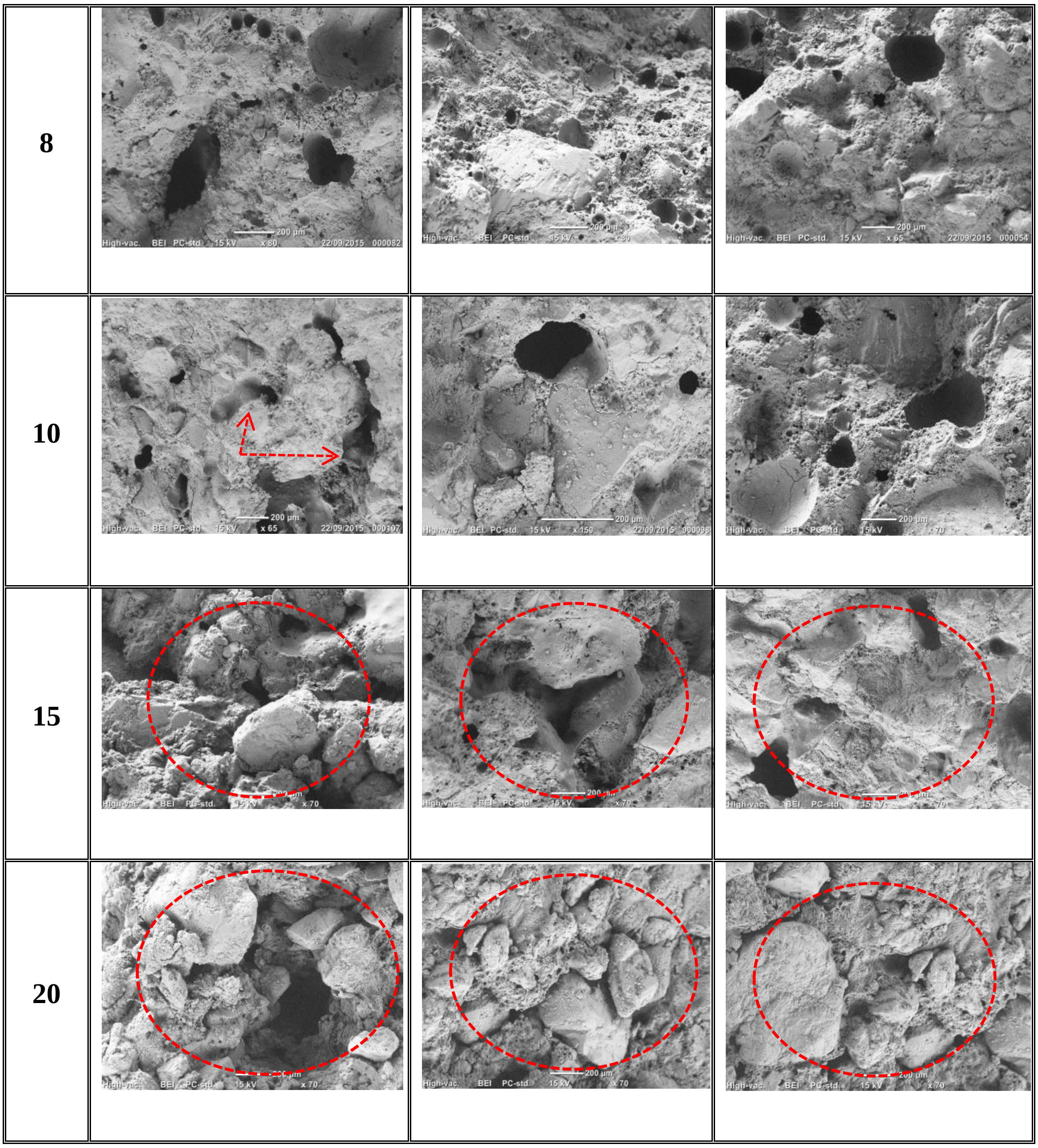


Figure 5.11 Shows the fully hydrated cement and how it formed a dense network structure

The partially hydrated cement represents an incomplete hydration process due to insufficient water. The three statuses, F-H, P-H, and P, can be seen in all the SEM images although the percentage of each status is the main difference. An initial observation was that under the three w/c ratios, the pore size decreased by increasing the crude oil content by up to 1%. At this percentage the lowest pore occurred with a w/c ratio of 0.5, followed by 0.6 and 0.4 respectively. This confirms our results conducted in section 5.4.2, as they related to the strength and the total macropores, which were expected to be the pores with the largest effect on the strength, compared to the micropores and mesopores, as shown in Figure 5.9.

The large pores and the larger area of the P-H were clearly seen with a w/c ratio of 0.4 at 0% compared to a w/c ratio of 0.5 and 0.6. This supported our discussion earlier in section 5.5 about insufficient water; because dry sand was used and as it was shown in chapter 3, section 3.5.1, that around 2.8% of water was absorbed by dry sand, this was the main reason behind the lack of water at this percentage. This indicates that the actual water used was less than 0.4 and hence, the hydration process was not completed. Winter (2012) has stated, in his book Understanding Cement, that the hydration process will not be completed at values below the critical w/c ratio because there is no space available in which an additional hydration product can form. The same author also stated that above a w/c ratio of 0.44, there is sufficient water for complete hydration and also enough space for the hydration product to form, thus, the cement can hydrate fully.

However, by increasing the crude oil by up to 1%, the pore size as well as the P-H area decreased and met the lowest percentages, while more area of F-H appeared under the three w/c ratios used. This agreed with the compressive strength obtained under the three w/c ratios used as shown in section 5.5. By increasing the crude oil content from 2% to 10% with the three w/c ratios, similar observations were made in terms of the pore size and areas of the P-H and F-H. Disregarding the percentage of the pore size and the areas of the P-H and F-H under each w/c ratio used, it can be seen that pore size, as well as the P-H area, gradually increased while the F-H area deceased. However, a higher percentage of area was partially hydrated at a w/c ratio of 0.4, compared to a w/c ratio of 0.5 and 0.6, as shown in Figure 5.14. This may be the main reason why there was a larger pore at a w/c ratio of 0.4, compared to a w/c ratio of 0.5 and 0.6, under the same condition of the crude oil contamination. This has been supported by Powers and Brownyard (1947) and Winter (2012) who stated that if the w/c ratio is below 0.44, there will always be some residual unhydrated cement if no water, additional to the original mix water, was available during curing time.

Furthermore, this explains why the lowest compressive strength was observed when a w/c ratio of 0.4 was used, compared to a w/c of 0.5 and 0.6. The interconnection between the pores, which was clearly seen with a w/c ratio of 0.4, as shown in Figure 5.14, may be due to the low workability that resulted from a lack of water, as a consequence of which, compaction was hard for the specimens with a w/c ratio of 0.4 compared to 0.5 and 0.6. However, increasing the w/c ratio from 0.5 to 0.6, higher pore size and P-H cement, and lower F-H cement, were observed when crude oil contamination was increased from 2% to 10%. This confirmed our result that showed lower strength when a w/c ratio of 0.6 was used, which in turn confirms previous results (Alawode and Idowu, 2011, Živica, 2009, Schulze, 1999, Nagaraj and Banu, 1996).

In contrast, at a high level of crude oil contamination of between 15% and 20% the status was quite similar in terms of the pore size, which shows the largest diameter. This was due to a high amount of free water kept in the mortar due to the saturation status of the contaminated sand used. Moreover, the sand particles had not bonded with the mortar, which also appears as part of P-H cement. This shows that the hydration process was affected by crude oil at a high percentage under the three different w/c ratios of 0.4, 0.5, and 0.6 respectively. The average strength at 15 and 20% was 7.4 and 4 MPa, which was the lowest strength among the different crude oil contamination used. Furthermore, the presence of hydroxide in crude oil may disturb the dissolution of a clinker mineral (hardening). Disturbing of hardening is caused by precipitation of hydroxides and other salts on the unhydrated cement particle. This prevents dissolution and reaction of the clinker minerals and retards cement hydration. Such retardation leads to a lower degree of hydration and this leads to higher porosity and lower amounts of C-S-H. This will result in poor strength development and high leachability of the solid product or there may even be no solid product at all (Eijk, 2001).

5.5 Conclusion

This chapter has investigated the effect of water cement ratio on the physical and mechanical properties of cement mortar containing fine sand contaminated with light crude oil. Based on the results, the following conclusions were drawn:

- Cement mortar consisting of fine sand with a light crude oil contamination of 0% to 10%, and a water cement ratio of 0.5, exhibited a higher compressive strength compared to a w/c ratio of 0.4 and 0.6. On the other hand, the excess water in cement mortar with a w/c ratio of 0.6 leaves a more and interconnected fine porous structure, resulting in lower mechanical properties compared to mortar with a w/c ratio of 0.5.

- The cement mortar with a w/c ratio of 0.4 exhibited the lowest properties due to more and bigger air voids observed in these specimens. This is due to its lower workability compared to w/c ratios of 0.5 and 0.6. Moreover, this mix has insufficient water to complete the hydration process. This occurred because the actual water provided was less than this amount, due to the fact that some was absorbed by the dry fine sand during mixing.

- The w/c ratio has an insignificant effect on the physical and mechanical properties of cement mortar consisting of fine sand contaminated with 15% and 20% light crude oil. The cement mortar prepared with different w/c ratios exhibited almost the same and low compressive strength. Compared to cement mortar with low percentages of light crude oil contamination, more free water remained in these samples after 28 days, indicating incomplete hydration of cement due to the sand, and the cement particles were fully saturated with crude oil.

- The cement mortar failed either due to axial splitting or shears failure. Axial splitting was observed for cement mortar with a w/c ratio of 0.4 with up to 8% of oil contamination, while this failure behaviour was observed for mortar with a w/c ratio of 0.5 and 0.6 and up to 10% oil contamination. On the other hand, shear failure was the dominant failure mode for cement mortar with higher oil contamination levels and in all w/c ratios considered in this study.

- The total porosity depends on the w/c ratio and the levels of oil contamination. The cement mortar with a w/c ratio of 0.4 has the highest total porosity for 0% to 10% oil contamination. On the other hand, the total porosity of mortars with a w/c ratio of 0.5 and 0.6 is almost the same for 0 to 2%, but became higher for a w/c ratio of 0.6 (rather than 0.5) with 4 to 10% oil contamination. Moreover, the total porosity is the same for all w/c ratios with 15 and 20% oil contamination.

- The pore size distribution influenced the developed compressive strength more so than the total porosity. More specifically, the macroporosity (> 30 μm) has a direct correlation with the compressive strength, as opposed to the micropores and mesopores. The mortar with a w/c ratio of 0.4 produced the highest percentage (%) of macroporosity followed by a w/c ratio of 0.6, while the w/c ratio of 0.5 has the lowest macroporosity, which produced its high compressive strength.

- SEM observations revealed a larger area of partially hydrated (P-H) cement for mortar with a w/c ratio of 0.4, compared to 0.5 and 0.6. On the other hand, the w/c ratio of 0.5 has the lowest P-H indicating it has a higher completion of cement hydration than the other mixes. SEM also showed more interconnected and larger pores for a w/c ratio of 0.4 than for a w/c ratio of 0.5 and 0.6.

Based on these conclusions, cement mortar consisting of oil contaminated fine sand will have better physical and mechanical properties than mortar with a w/c ratio of 0.5. Thus this w/c ratio was used in the investigation in the chapters that follow. In the next chapter, the strength development of cement mortar with oil contaminated sand is presented.

Chapter 6

Strength Development of Cement Mortar Containing Light Crude Oil Contaminated Sand

6.1 Introduction

Extensive investigations in Chapters 4 and 5 have provided information on appropriate mixing and curing methods, and sufficient water-to-cement ratio, respectively that will result in optimal physical and mechanical properties for cement mortar containing fine sand contaminated with light crude oil. However, it was also found from these investigations that oil contamination can inhibit the hydration process and reduce the compressive strength of the produced mortar.

Ajagbe et al. (2012) have indicated that the presence and degree of contaminants are very important factors that affect the compressive strength of the hardened cement mortar. They also impact on the appearance of the concrete. Moreover, Osuji and Nwankwo (2015) have concluded that high percentages of crude oil in concrete hinder the physical bond formation between cement paste and fine aggregates. Furthermore, Ajagbe et al. (2013) have concluded that lower compressive strength of concrete with oil contamination compared to uncontaminated concrete may be due to slow cement hydration. Eijk (2001) has indicated that the contaminants in concrete affect cement hydration through disturbing nucleation/precipitation of hydration products, dissolution of clinker minerals, increasing ettringite formation and the forming of new compounds (hydroxides, calcium salts, silicates, sulphates, H_2 formation). These researchers’ findings were arrived at through their evaluation of the properties of concrete with oil contamination up to 28 days. It is a common knowledge however that the concrete gains strength even after this curing time. It is important therefore to evaluate how mechanical strength is developed over time for concrete containing fine sand with light crude oil contamination. Equally important is to have a better understanding about how the curing period affects the interaction between contaminants (light crude oil), unhydrated cement particles and hydration products.

In this chapter, an investigation of the physical and mechanical properties of cement mortar containing fine sand contaminated with light crude oil, and cured at different times, was conducted. The basic properties of cement mortar such as the compressive strength, porosity and microstructure of the cement mortar were observed for up to 365 days of curing.

6.2 Materials and methods

6.2.1 Preparation of the specimens

Oil contaminated sand was prepared following the procedures described in Section 3.2.2. In this chapter, the focus was on oil contaminated sand with eight different percentages of light crude oil (0%, 0.5%, 1%, 2%, 4%, 6%, 8%, and 10%, going by the weight of dry sand). High levels of crude oil contamination (15% and 20%) have been excluded due to the significantly low compressive strength of the cement mortar produced at those percentages, as found in Chapter 5, which are deemed unsuitable for construction application.

6.2.2 Casting of mortar

A total of 144 specimens covering three samples for each specimen type were prepared. The mortar was prepared following the recommendations of AS 2350.12 (2006) with mix proportions of 1 part of cement and three parts of sand (by mass), and a water cement ratio (w/c) of 0.5, as recommended in Chapter 5. A bigger concrete mixer was used (120 L mixer) due to the relatively large volume of cement paste needed to produce 18 cylinders for testing at 6 curing times. The cement mortar was then placed in plastic moulds (50 mm diameter and 100mm high) and cured in a fog room (FR), set at 25 ºC and 85% humidity. The specimens were kept in the fog room until they were ready for testing. Figure 6.1 shows the preparation of cement mortar.

Mixing Compaction

De-moulding Fog room

Figure 6.1 Preparation steps for mortar with light crude oil

6.2.3 Test Procedures

Compressive strength tests were carried out after 7, 14, 28, 56, 168, and 365 days of curing. The specimens were tested to failure under the 2 Channel Automatic Cube and Cylinder Compression Machine CT340-CT440, at a loading rate of 1.5 kN/min, and following the AS-1012.9 (2014). The porosity of each sample was determined by using TBitmap software, following the procedures described in Sections 4.2.6 and

5.2.5. Similarly, microstructure observations were conducted using a scanning electron microscope (SEM) (JEOL JCM-6000, Tokyo, Japan), following the procedures in Section 5.2.6.

6.3 Results and observation

6.3.1 Compressive strength of mortar

The average values of compressive strength of cement mortar with different levels of light crude oil contamination at different ages of curing are presented in Table 6.1. It can be clearly observed that there was an increment of compressive strength for all specimens with the advancement of the hydration period (age). Similar to the findings in Chapters 4 and 5, the highest compressive strength was observed at 1% of crude oil contamination, while the lowest compressive strength at each curing age was exhibited by the cement mortar with 10% of crude oil contamination. However, in Chapter 6, the mixes were prepared using 120L mixing equipment that creates less homogeneity compare to the kitchen mini mixer used in Chapter 4 and 5. As a consequence, the mix was less workable and porous causes lower compressive strength than the specimens prepared by the kitchen mini mixer. Moreover, the trend of the results in both cases was found similar, indicating reliable results. For instance, the compressive strength of uncontaminated samples (0%) was 16.7 MPa after 7 days, which is 18% lower than the cement mortar with 1% light crude oil contamination. Increasing the light crude oil contamination by up to 10% resulted in a 46% lower compressive strength compared to the uncontaminated samples.

Table 6.1 Compressive strength of different age and different crude oil content

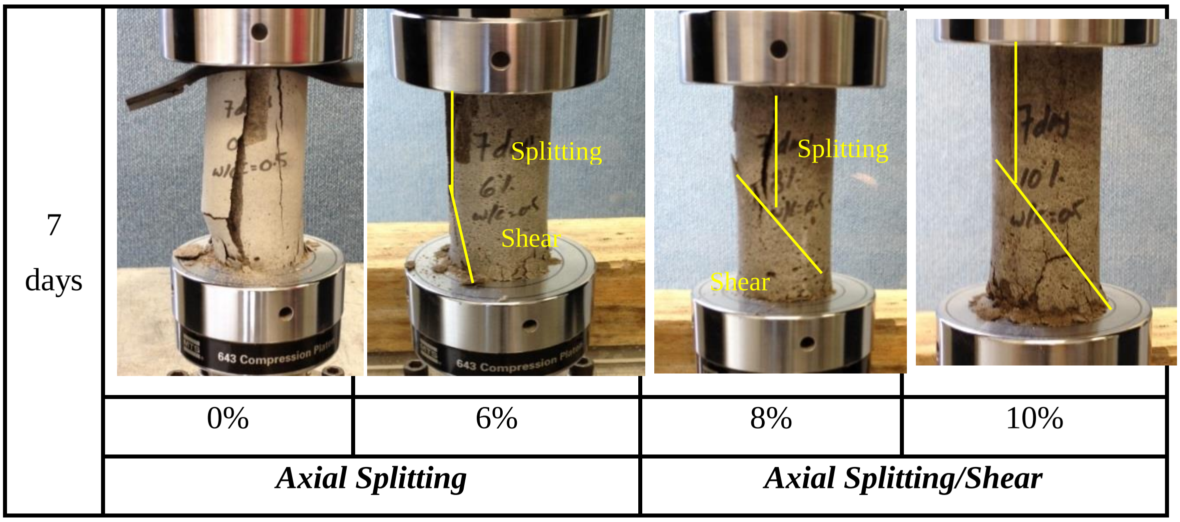
Oil (%)	C. S MPa	St.	C. S MPa	St.	C. S. MPa	St.	C. S. MPa	St.	C.S. MPa	St.	C.S MPa	St.
	7 days		**14 days**		**28 days**		**56 days**		**168 days**		**365 days**	
0	16.7	0.589	18.4	1.922	22.8	2.200	23.5	0.66	23.6	2.26	23.7	1.01
0.5	16.8	1.726	20.3	1.373	24	1.541	25.4	1.35	25.6	2.55	25.9	1.56
1	19.7	1.182	23.9	1.064	26.6	0.957	27.8	2.13	27.9	0.80	28.1	1.56
2	17.1	2.533	20.2	0.703	23.8	1.022	25.6	2.12	25.7	0.49	25.7	1.46
4	13.2	0.942	15.9	0.886	17.6	0.873	18.7	1.49	19	0.20	19.2	1.10

6	10.5	0.769	12.6	0.806	14.1	1.341	14.7	0.38	14.8	1.45	14.9	0.31
8	10.2	0.918	11.3	0.185	12.4	0.866	12.9	0.51	13.4	1.57	13.5	0.23
10	9.0	0.438	9.5	0.602	10.7	1.255	11.1	0.34	11.9	1.25	12.1	1.26

- C.S Compressive strength
- St. Standard deviation

6.3.2 Failure modes

The typical failure modes of the cement mortars tested at 7, 14, 28 56, 168, and 365 days are presented in Figure 6.2. Only 0%, 6%, 8% and 10% are presented because these levels of oil contamination represent the typical failure of cement mortars. Two different failure modes, i.e. axial splitting and shear failure, were observed. At 7 and 14 days, the dominant failure mode with up to 4% of crude oil contamination was axial splitting, while at 6% up to 10% a combination of axial splitting and shear failure was observed. At 28, 56, 168 and 365 days, the axial splitting failure mode was only observed for cement mortar with 0% to 8% oil contamination, but a combination of axial splitting and shear failure was observed for specimens with 10% oil contamination. Similar to observations in Chapter 5, axial splitting failure occurred in the cement mortar with higher compressive strength, and shear failure occurred for cement mortar with relatively lower compressive strength.



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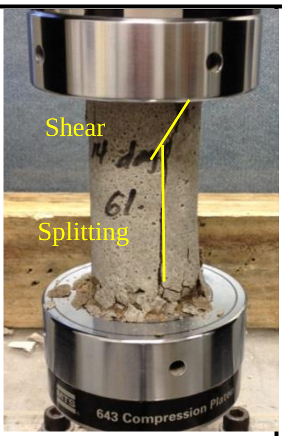
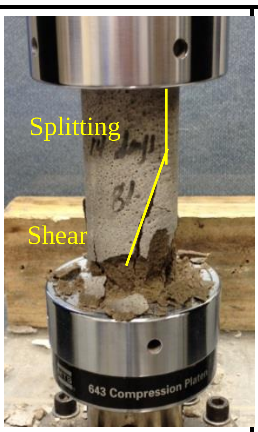
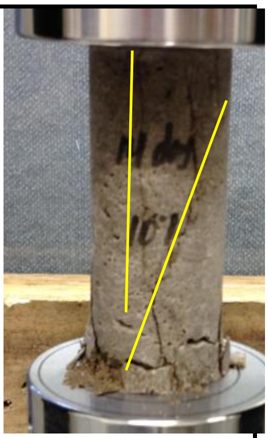
days</td><td> </td><td> </td><td> </td><td> </td></tr>
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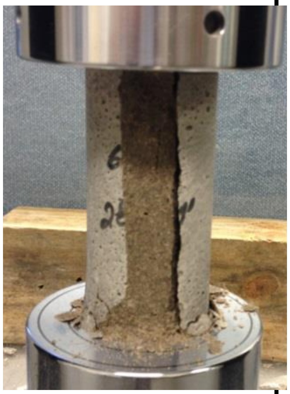
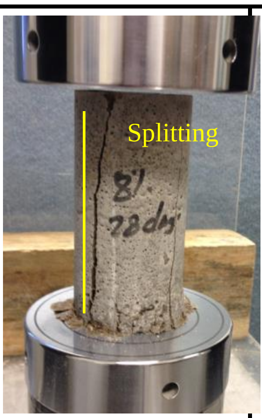
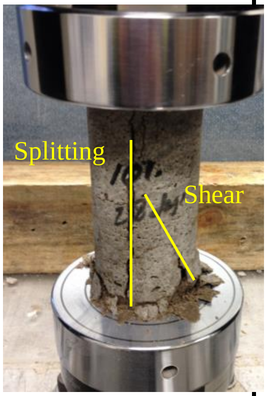
days</td><td> </td><td></td><td> </td><td> </td></tr>
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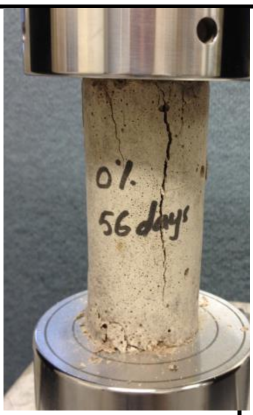
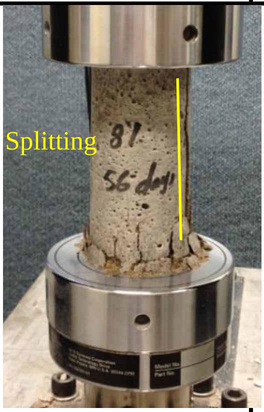
days</td><td> </td><td> </td><td> </td><td> </td></tr>
<tr><td>0%</td><td>6%</td><td>8%</td><td>10%</td></tr>
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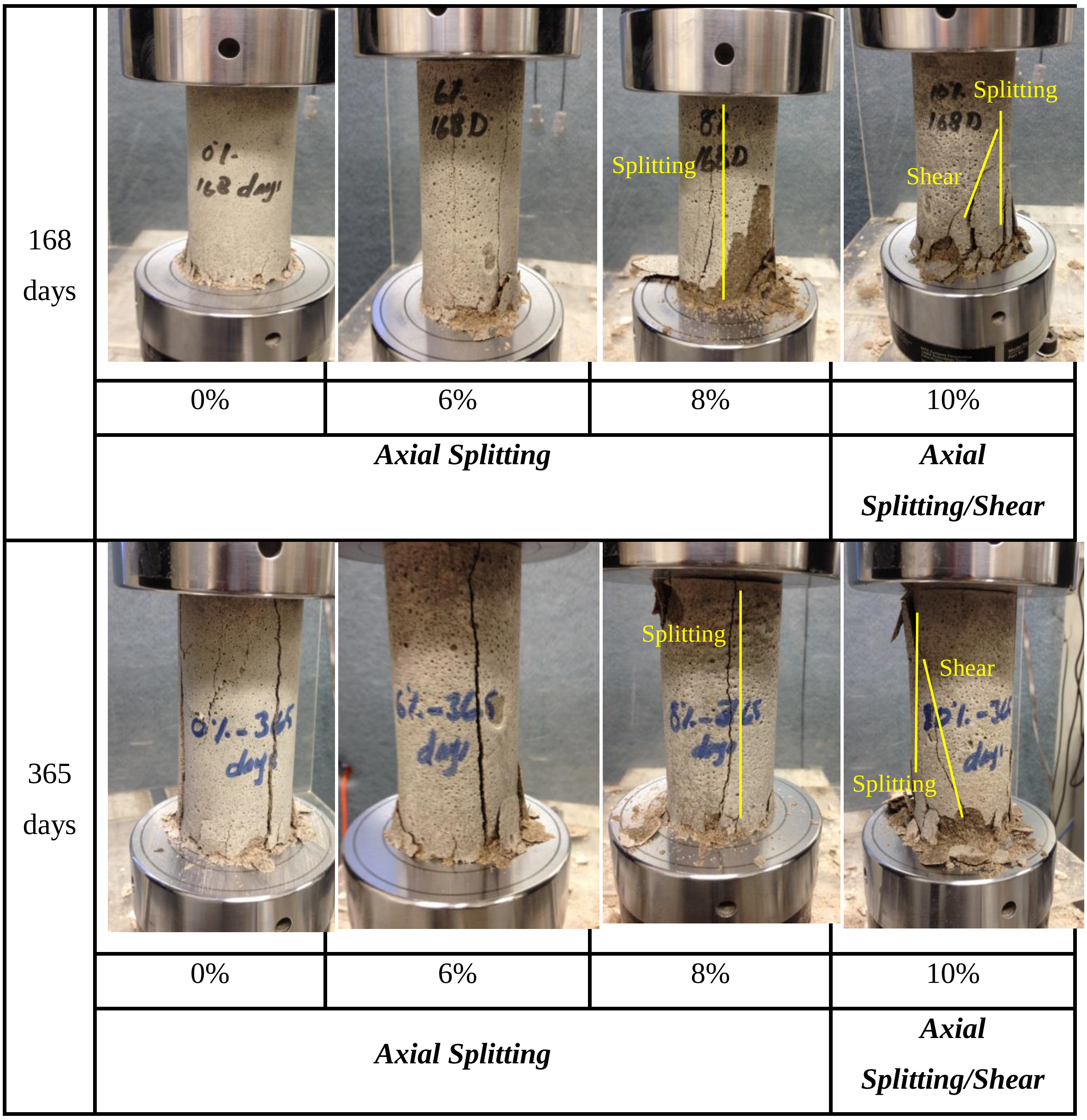


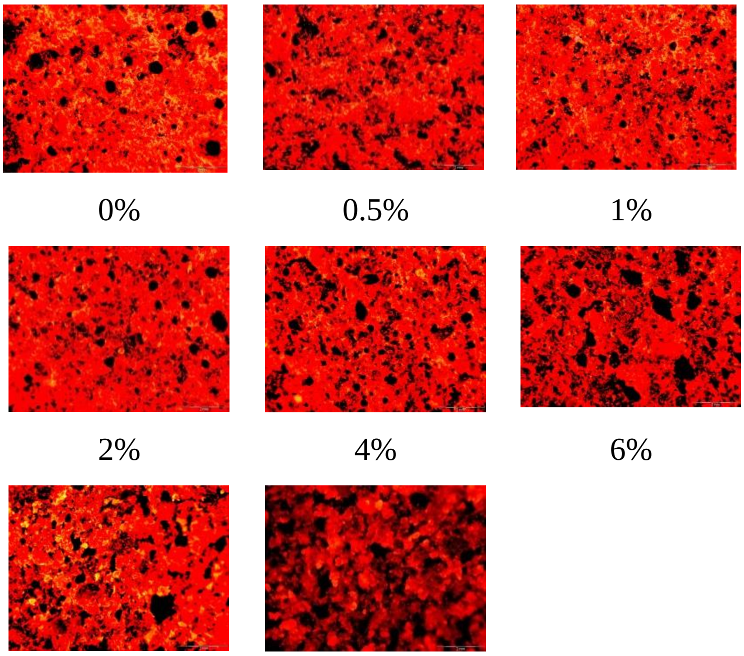
Figure 6.2 Failure mode of different curing ages and different crude oil content

6.3.3 Porosity

The percentages of total porosity of the cement mortar with different light crude oil contamination (0%-10%) at different curing times are listed in Table 6.2. A decrease in the total porosity for all levels of oil contamination can be noticed with the advancement of the hydration period. Similarly, the total porosity increases with an increase in the oil contamination level. Figure 6.3 shows an example image of porosity measurement at different percentages of crude oil contamination

Table 6.2 Average total porosity (%) of the specimen at different ages

days %	7	SD	14	SD	28	SD	56	SD	168	SD	365	SD
0	7.62	0.40	6.92	0.33	4.62	0.52	4.45	0.62	4.36	0.42	4.4	0.25
0.5	10.44	0.35	8.52	0.42	6.23	0.42	6.06	0.58	4.50	0.52	4.42	0.74
1	11.68	0.34	10.26	0.32	8.26	0.70	8.21	0.49	7.48	0.23	6.93	0.42
2	12.52	0.51	10.33	0.25	8.04	0.62	8.08	0.32	7.73	0.45	7.01	0.15
4	13.11	0.22	11.88	0.52	9.28	0.57	9.04	0.22	8.93	0.62	8.51	0.77
6	15.22	0.43	12.86	0.45	10.0	0.54	10.39	0.43	10.12	0.32	10.32	0.74
8	18.33	0.62	15.51	0.62	11.51	0.52	10.53	0.14	10.39	0.41	10.29	0.56
10	23.01	0.44	21.13	0.41	19.52	0.48	18.86	0.25	18.72	0.62	18.26	0.62



0% 0.5% 1%

2% 4% 6%

8% 10%

Figure 6.3 Shows an example of the images used to measure the porosity of different percentages of crude oil contamination

6.4 Discussion

6.4.1 Strength development during 365 days

Figure 6.4 shows the percentages of the strength gained by cement mortar with different percentages of light crude oil contamination over time (up to 365 days). The strength gained after 28 days was considered as the benchmark (100% strength). It can be seen that 70% up to 84% of the compressive strength was gained by the cement mortar with 0% to 10% of light crude oil contamination at 7 days, and 81% up to 91% of the strength was gained after 14 days. The strength gain of the cement mortar with 0% to 1% of light crude oil contamination after 28 days was slightly increased, by an average of 4% at 54 days, while after that it remained constant up to 365 days. Thus it can be said that cement mortar with 0% to 2% of light crude oil contamination achieves most of its strength at 28 days. The strength development was slightly increased (6%) at 56 days of specimens with 4% and 8% oil contamination, and hence those specimens achieved most of their strength after 56 days. Increasing the curing time by up to 365 days did not cause a significant strength gain. On the other hand, the specimens with 10% oil contamination achieved most of their compressive strength after 168 days, and only a slight increase (2%) at 365 days. The longer period to gain 100% of strength for higher levels of oil contamination, i.e. 10% compared to the lower contamination levels (0% to 8%), may be due to the slower cement hydration process. From there, the cement mortars did not gain further compressive strength, regardless of the level of light crude oil contamination.

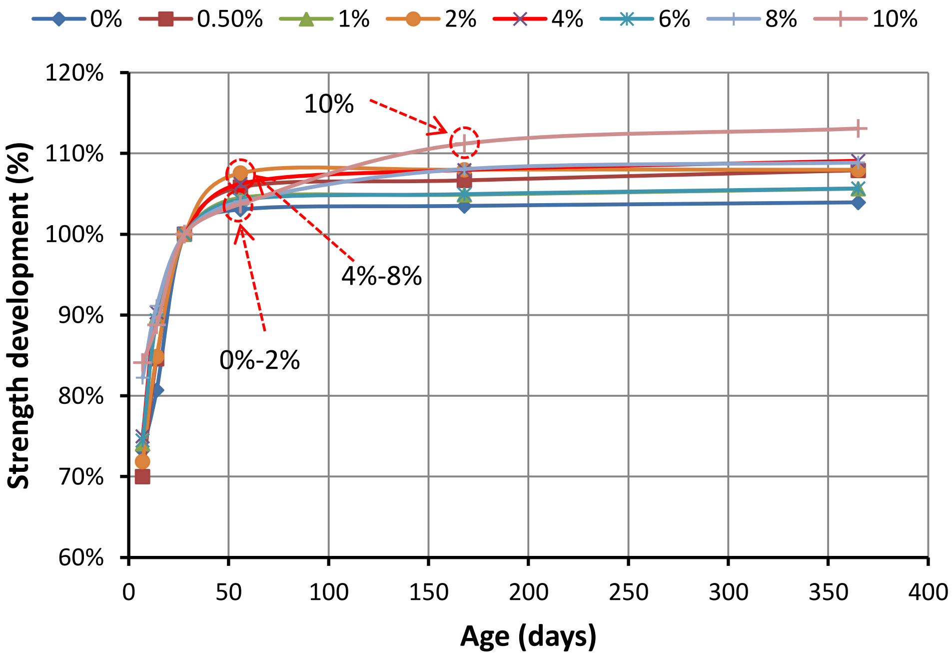
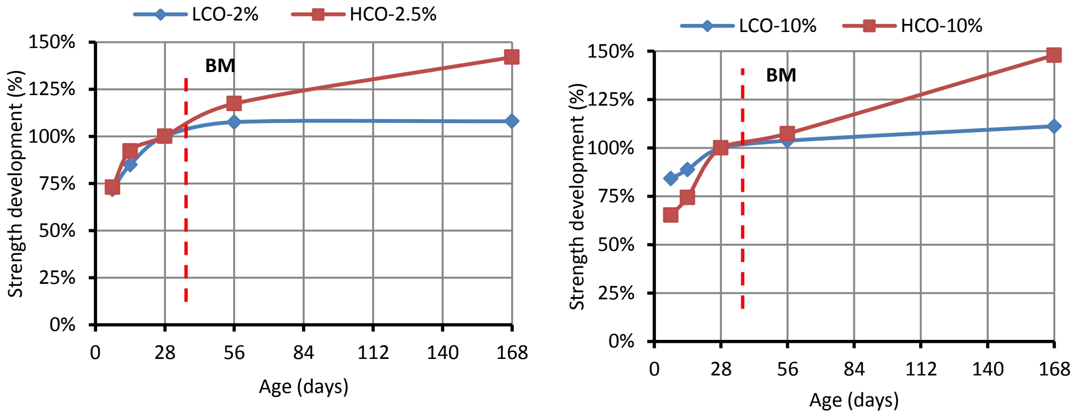


Figure 6.4 Compressive strength development in 365 days

Ajagbe et al. (2012) have investigated the effect of heavy crude oil (API gravity of 11.43, specific gravity of 0.99, density of 62 lbs/cuft, as reported by (Martínez-Palou et al., 2011) contaminated sand on the strength development of concrete, with different percentages of oil contamination (2.5, 5, 10, 15, 20, and 25% by weight of sand). They concluded that the use of contaminated sand has a serious effect on the strength development of concrete. In order to make a comparison between the effect of light crude oil (LCO) and heavy crude oil (HCO) on the strength development, a similar benchmark of 28 days and similar crude oil contamination (2%, 10%) were selected. The percentages of crude oil were 2% and 10%, while the curing ages were 7, 14, 28, 56, and 168 days. As shown in Figure 6.5, the compressive strength gained (approximately 72%) at 7 days, both for HCO and LCO contaminated specimens, was almost the same. At 14 days, the HCO achieved 92% of its compressive strength, with only 85% for LCO. After 56 and 168 days, the strength gained for HCO was 17% and 42% respectively, compared to the 28-day compressive strength, while the LCO gained only 8% after 28 days.



(a) 2% oil contamination (b) 10% oil contamination

Figure 6.5 Comparison between strength development of (HCO (Ajagbe et al., 2012)) and LCO contaminated mortar

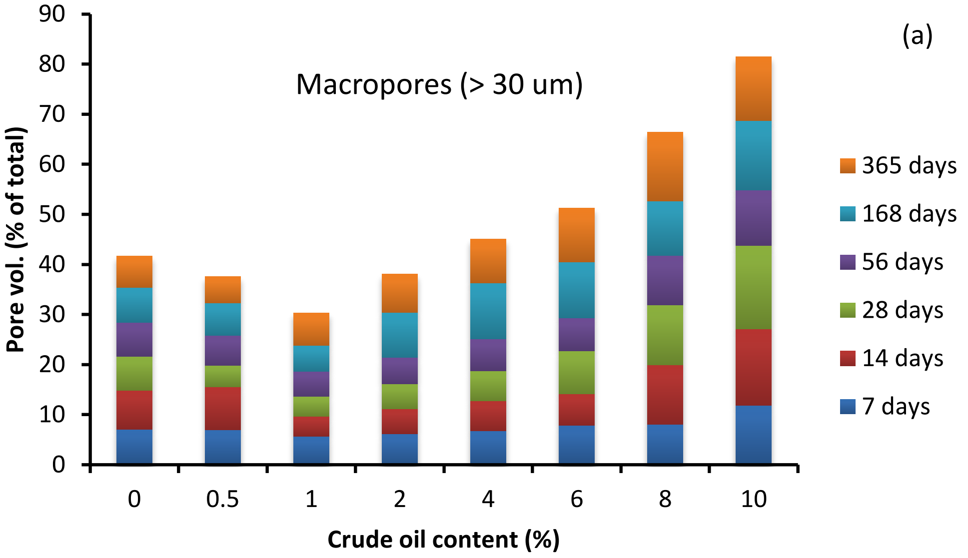
At 10% of crude oil content, the strength gained for HCO contaminated concrete was only 65%, while the LCO was 84% after 7 days. At 14 days curing, the strength gained by HCO and LCO was 74% and 89%, respectively. After 56 days, HCO and LCO specimens gained 7% and 4% respectively, compared to the 28-day compressive strength, while the increase of the strength for each specimen after 168 days was 48% and 11%, respectively. These results confirmed that the presence of oil contamination affects the hydration of cement and hinders the strength development of the produced concrete. On the other hand, the faster development of strength in mortar with light crude oil contaminated sand, compared to concrete with heavy crude oil, is due to the different properties of these crude oils, as highlighted by (Fine et al., 1997, Nudelman et al., 2002, Tuncan and Pamukcu, 1992). The light crude oil has low viscosity, low specific gravity and high API gravity, due to the presence of a high proportion of light hydrocarbon fractions. However, it is likely that oil filled pores still create zones of weakening and therefore lower compressive strength. Moreover, Fingas (2013) has stated that light crude oil changes very dramatically from fluid to viscous, which is not the case with heavy oil because it is so thick and it becomes solid-like. These solid-like particles in the heavy crude oil are asphaltenes (Strassner, 1968, Shetty et al., 1992, Taylor, 1992), which may surround the cement particles and decrease the contact between the cement and water. As a result, the hydration process is retarded and the strength development is delayed.

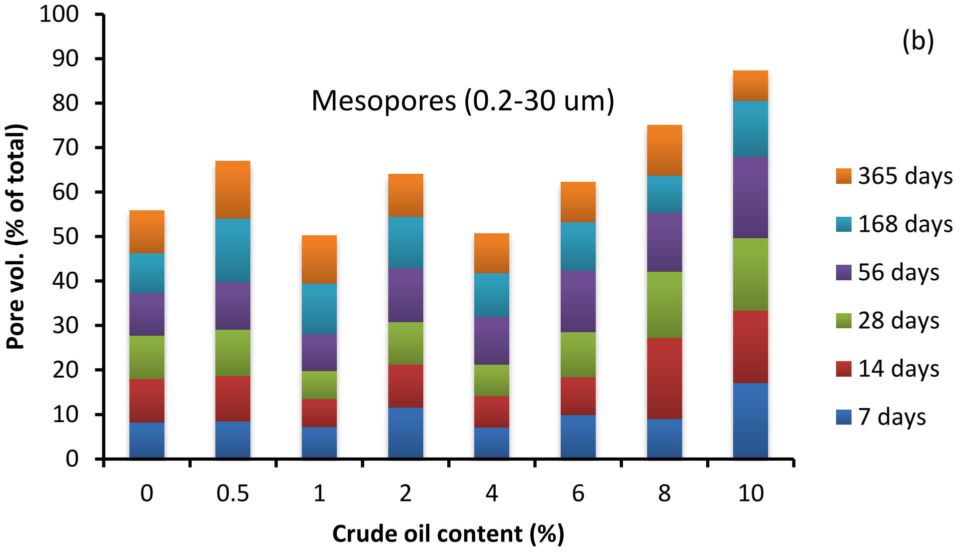
Based on the results from this study, the strength development of cement mortar is not affected at low percentages of the crude oil contamination (0.5% to 2%). The compressive strength developed by the cement mortar with lower crude oil content is higher than the uncontaminated samples, and the rate of reaction is greater because the surface of the sand particles is already dampened with oil. Lea (1970) stated that the overall rate of cement hydration is dependent on the hydration of individual components, and it may be accelerated by increasing the water-to-solid ratio. Thus, in this case it was expected that adding 0.5%, 1% and 2% of light crude oil to the dry sand would cause an increase in the water-to-solids ratio because the sand particles were partially dampened by the crude oil. As a result, all the added water reacted with cement, which enhanced the hydration process resulting in a better compressive strength than the uncontaminated samples.

The cement mortar with high levels of light crude oil (4% to 10%) developed its compressive strength at a very slow rate, as shown in Figure 6.5. This can be attributed to two factors. First, there was an increase in the w/c + oil ratio, and second, there was an increase in the levels of some organic compounds present in the crude oil, which hindered the adequate development of the cementitious matrix. These organic contaminants include aromatics, alkenes, alkanes, and cycloalkanes (En, 2001), which limited the reaction between the calcium hydrates (that were produced during the hydration of the cement) and the SiO_2 of sand. This reaction was not desirable because the calcium hydrate (portlandite) alone yielded a poor mechanical resistance, whereas its combination with silica yielded a strong tobermorite phase. This tobermorite occurs in hydrated cement paste and can be found in nature as alteration mineral in metamorphosed limestone and in skarn. Paria and Yuet (2006) have stated that organic compounds are generally nonpolar and hydrophobic; they do not react with non-organic binders and may interfere with the hydration reactions of cement or pozzolanic materials, inhibiting the setting of cement. Furthermore, almost all organic compounds are retarders in cement setting, and many organic acids that strongly chelate calcium likewise have a strong retarding capability. Similarly, these organic compounds form a protective layer around the cement particles, thus hindering the formation of calcium hydroxide (Chandra and Flodin, 1987, Edmeades and Hewlett, 1998, Sora et al., 2005). In addition, organic compounds such as methanol and phenol form amorphous structures after drying, resulting in a detrimental effect on the compressive strength of cement (Sora et al., 2005). The phenol prevents the formation of calcium hydroxide during the initial period of setting and hardening (Vipulanandan and Krishnan, 1993). As expected, the strength development is much slower for those with higher levels than for those with lower levels of oil contamination. As presented, the cement mortar with 4% and 8% oil contamination achieved most of its strength after 56 days, while the specimens with 10% achieved most of their compressive strength only after 168 days. This may be due to the increase in the percentage of organic compounds, as a result of the increase in the light crude oil contamination.

6.5 Pore structure

Figure 6.6 (a, b, and c) shows the volume and pore diameter (macropores, mesopores and micropores) at different curing times, as a function of different crude oil contaminations. At the age of 7 days of hydration, there were nearly similar percentages of micropores (<0.2 um), under different percentages of crude oil by up to 8%, which was around 84%, while at 10 %, lower percentages of micropores were observed (71%). The volume of the mesopores (0.2-30 um) was high (around 17%) at the highest percentage of crude oil content (10%), compared to the lower percentage of crude oil content, which varied between 7% and 11%. On the other hand, the volume of the macropores pores (> 30 um) decreased slightly at 0% up to 1% of crude oil contamination, and achieved 5.7%, while the highest percentages (11.9%) appeared at the highest percentage of crude oil content (10%).





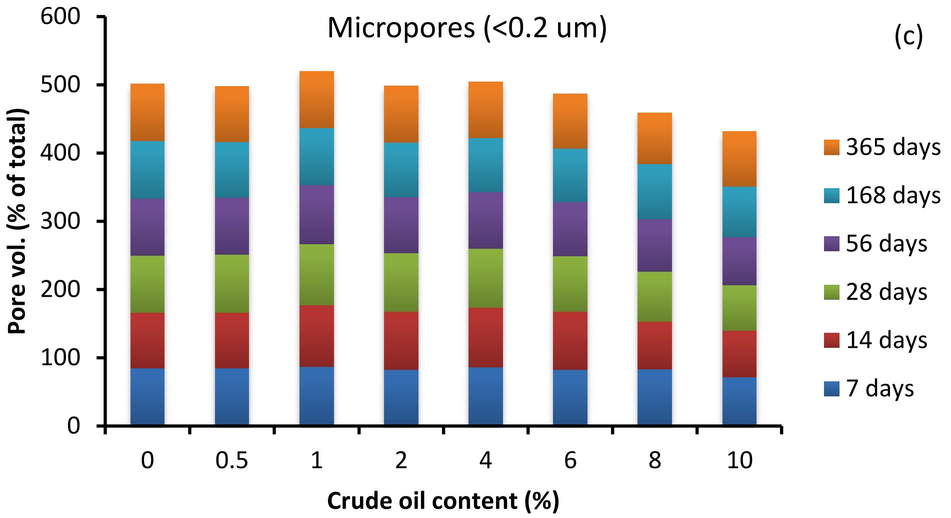
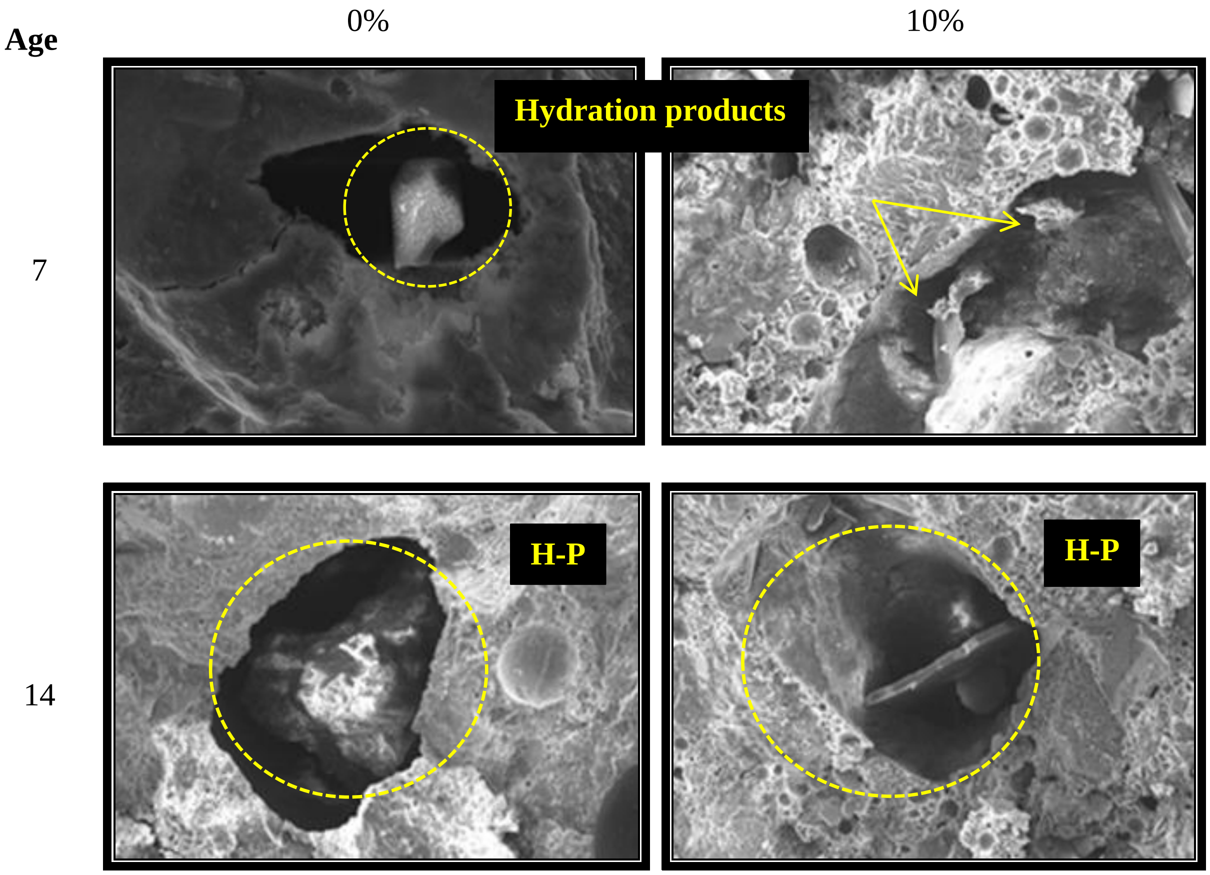


Figure 6.6 Pore size distribution of mortar with light crude oil content

At 14 days, with 0% and 0.5% of crude oil contamination, the percentages of micropores (<0.2 um) were similar to those that appeared at 7 days of curing, while by increasing the crude oil content to 1% and 2%, higher percentages of micropores (by 2.5%) were observed at 14 days curing compared to 7 days curing. By contrast, mesopores and macropores decreased significantly at those percentages up to 3%, compared to 7 days curing, and slightly by 1.5 and 2% respectively, at 4% and 6% of crude oil contaminations. As the hydration advanced, the larger pores were converted into smaller ones by gradually filling the pores with cement hydrate materials such as ettringite, Portlandite, fine crystalline C-S-H, and others, as shown in Figure 6.7. At high percentages of crude oil contaminations, the percentages of large pores (mesopores and macropores) were higher by 4.2% and 3.55%, compared to those observed at 7 days of curing. This is attributed to high levels of crude oil content which prevents further hydration as explained in section 6.4.2.

At 28 days, the trend shows an increment of micropores compared to mesopores and macropores, which indicates that the large pores converted to smaller pores due to the increment in hydration products. This was clearly seen in up to 4% of crude oil contaminations. The micropores (<0.2 um) increased by 1.5% compared to those observed at 14 days, while mesopores (0.2-30 um) and macropores (> 30 um) were decreased by 1.1% at this age, compared to 14 days. This was expected, due to the hydration products, and hence large pores converted to many smaller pores by the crystalline network of CSH (Pandey and Sharma, 2000). On the other hand, at a higher percentage of crude oil level (10%), the micropores (<0.2 um) decreased and the macropores (> 30 um) increased by 10%, compared to that observed at 14 days. This is due to the saturation status achieved at this percentage (10%), as the pores were filled with liquid (crude oil), so it was expected that the oil retarded the hydration product to be created, and by increasing the curing time crude oil may have evaporated. As a consequence, the pores occurred with their sizes and with less hydration product. This led to an increase in large pores at high levels of crude oil content, due to the lower degree of hydration, and this in turn led to higher porosity and a lower amount of C-S-H (Eijk, 2001).



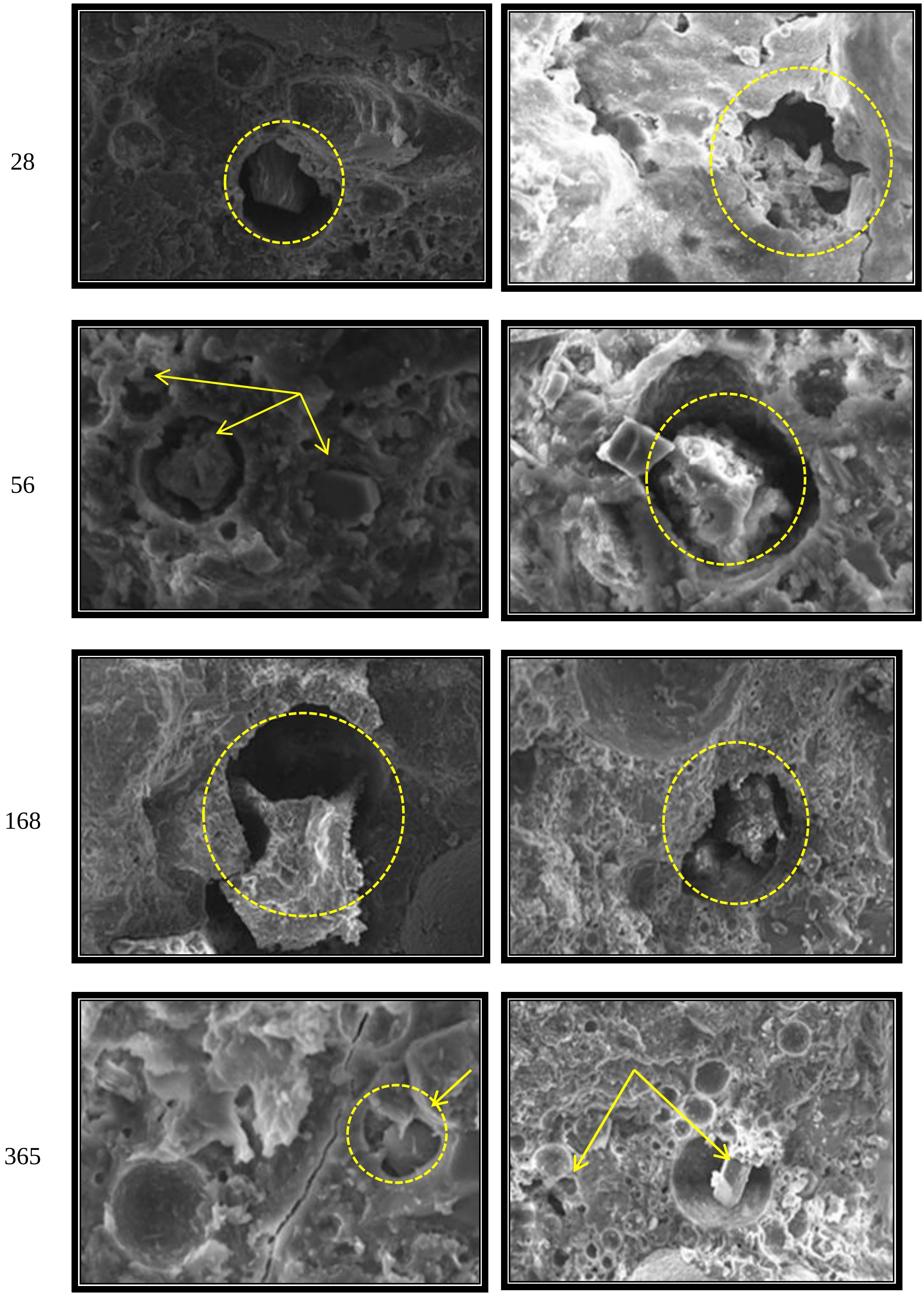


Figure 6.7 Shows hydration products of cementitious material

The interesting observation is that at 56 days of curing, the micropores (<0.2 um) at high levels of crude oil contamination also increased by 3.6%, while the macropores (> 30 um) decreased by 3.8%. This actually supports my previous discussion regarding the case of evaporation that is expected to occur for this type of crude oil: “light crude oil”. Light oils will change very dramatically from fluid to viscous (Fingas, 2013). This indicates that the hydration products were a retardant and were not completely inhabited. Thus, the hydration products with 10% of crude oil contamination were smaller compared to uncontaminated samples, as shown in Figure 6.7. In addition to that, at high levels of crude oil contamination, the large pores were converted to small pores, but at a slower rate and thus more time was needed (56 days). This indicates that strength development is gained at high levels of crude oil contamination, but at a very slow rate, which may depend on the amount of evaporation of the hydrocarbons.

At 6 months (168 days), there was a further decrease in the pore size increasing the percentages of micropores (<0.2 um) and decreasing the percentages of mesopores (0.2-30 um) at a high level of crude oil contamination. This was due to the deposition of slow hydrated products in the large capillaries that were caused by the presence of crude oil at high levels. At lower levels of crude oil contamination (0%-6%) the mesopores (0.2-30 um) increased compared to macropores (> 30 um), while there was no significant variation in the smallest pore diameters of the micropores. This indicates that more large pores, which are classified as macropores, were converted to mesopores, due to the increase in the rate of hydration. However, at one year (365 days), the majority of large pores slightly decreased, while a slight increment was observed in mesopores and micropores, due to the formation of more pozzolanic reaction products.

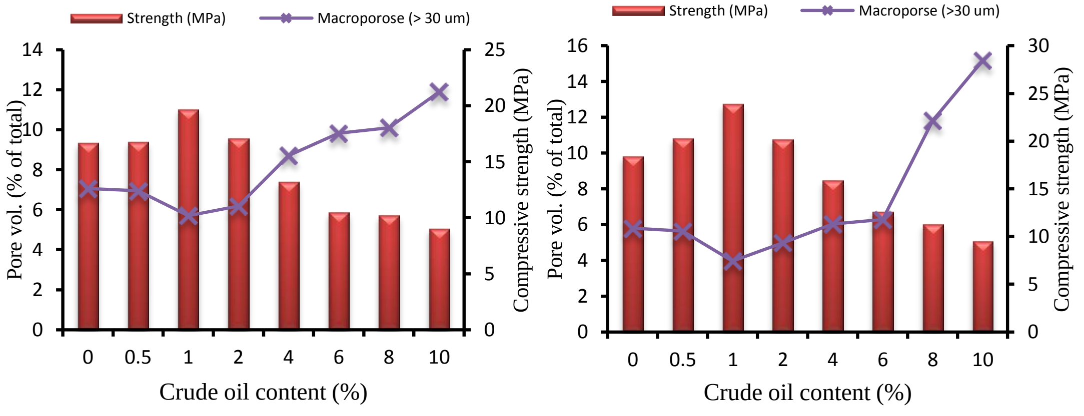
6.6 Relationship between porosity and compressive strength

The effect of porosity on compressive strength was investigated under deferent percentages of light crude oil contaminations. Previous studies (Yudenfreund et al., 1972, Auskern and Horn, 1973, Pantazopoulou and Mills, 1995), have indicated that porosity plays a large role in developed compressive strength. These researchers indicated that the strength of cement mortar is more heavily influenced by the volume and the number of large size pores than by smaller pores. Figure 6.8 shows the pore volume and compressive strength at different ages of mortar (7, 14, 28, 56, 168, and 365 days). The pore size distribution of mortar with high levels of crude oil contamination shifted towards the larger pore size, with an increase in pore diameter at all stages of hydration up to 365 days, causing a decrease in compressive strength and retarded strength development, compared to specimens with lower crude oil content. In general, organic compounds have a strong effect on the microstructure of the cement paste. The structure and nature of the organic molecules are responsible for the microstructure characteristics. For example, the presence of 1-chloronaphthalene in the cement mortar increases its porosity and decreases its mechanical strength, while the effect of 2-chlorophenol is less significant (Cioffi et al., 2001).

In spite of the fact that increasing the crude oil content affects total porosity at different curing ages, the macroporosity (> 30 um) was found to show the largest effect of pores on the compressive strength, as shown in Figure 6.8 (a-f). For instance, the strength of mortar at 7 days seemed to be influenced by the volume of macropores (> 30 um) that appeared at a high level of crude oil contamination (above 6%) as can be observed in Figure 6.8(a). The greater the volume of pores (> 30 um), the lower the compressive strength, at 7 days. Light crude oil content from 4% to 10 % showed a decrease in strength at an early age, as shown in Figure 6.6, due to the presence of a large number of such pores. By contrast, the strength of specimens with lower crude oil content (0% to 2%) was not significantly affected, and because of the high percentage of their pore volume, micropores or mesopores were much higher than macropores, as shown in Figure 6.6.

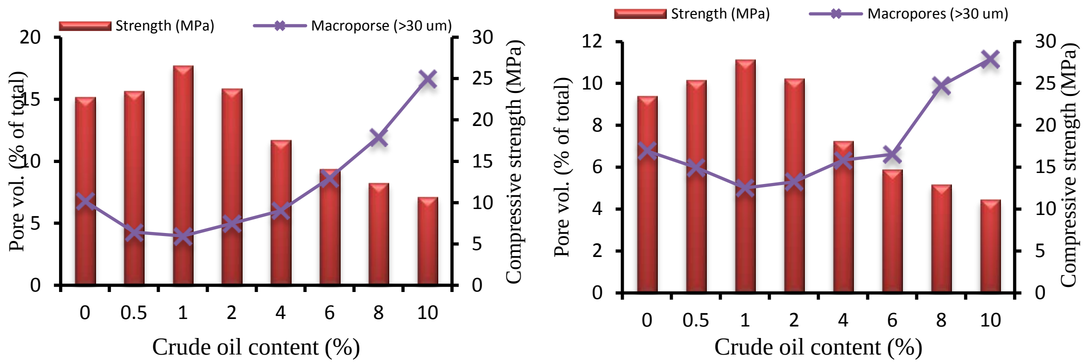
The strength at 14 days (Figure 6.8(b)) seems to be related to the pore volume of (> 30 um). With the advancement of hydration, the volume of large pores at a low level of crude oil (0%-1%) decreased and the volume of the smaller pores increased. On the other hand, the large pores (> 30 um) increased significantly at high levels of crude oil contamination (2% and 10%), while the small pores decreased, as shown in Figure 6.6. Thus, a lower strength was obtained at high levels of crude oil content. Similar results were obtained at 28 days (Figure 6.8(c)), and as the curing period increased, the large pores decreased at low crude oil content (0% to 1%) due to the hydration products, as explained earlier. Nevertheless, the macropores started to increase as the amount of crude oil increased from 2% to 10%, and hence lower compressive strength was obtained.

At 56 days (Figure 6.8(d)), the large pores macropores (> 30 um) slightly decreased at high levels of crude oil content (8% and 10%), compared to 28 days. This indicates that a longer curing period is needed for mortar with higher levels of oil contamination in order to complete the hydration process. As a consequence, the amount of large pores was reduced, leading to an enhanced compressive strength. By contrast, at an age of 168 and 365 days (Figure 6.8(e) & (f)), the large pores slightly decreased, which indicates that the hydration products were still created but at a very low rate. Several studies (Al-Harthi et al., 1999, Price et al., 1994) have indicated that compressive strength depends upon the amount of macroporosity and pore structure. Luping (1986) found that a material with low porosity, but with more large pores, may have a lower strength than a material with a higher porosity and less large pores. As shown in Figure 6.8 (a-f), as the amount of crude oil content increased towards 1% of light crude oil, the total macroporosity decreased, while by increasing the crude oil content from 2% up to 10%, the total macropores increased. This aligned with the compressive strength obtained (and discussed) in section 6.5.



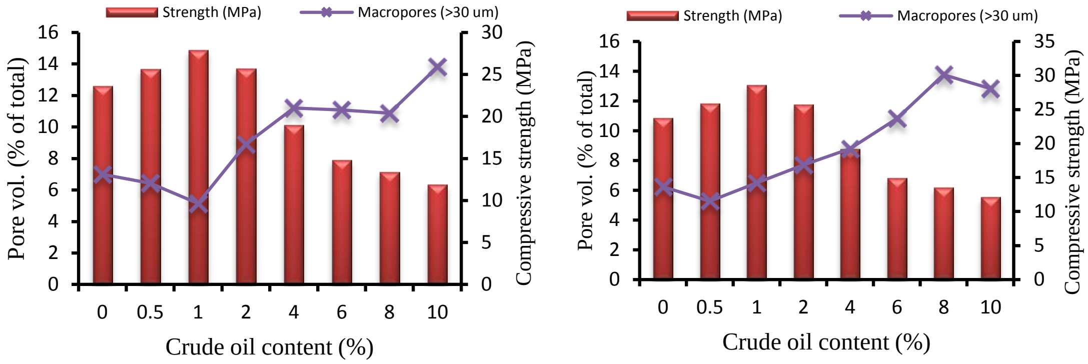
(a) 7 days curing

(b) 14 days curing



(c) 28 days curing

(d) 56 days curing



(e) 168 days curing

(f) 365 days curing

Figure 6.8 Comparison of the pore volume with compressive strength at different curing ages

6.7 Conclusion

This study has investigated the effect of light crude oil contamination on the strength development of mortar. Based on the results, the following conclusions were drawn:

- The contamination of sand with light crude oil has no effect on the strength development of cement mortar containing fine sand with lower levels of oil contamination, but it has a significant effect at higher levels of oil contamination. The cement mortar with 0% to 2% of light crude oil contamination achieved most of its strength after 28 days. On the other hand, the cement mortar with high levels of light crude oil (4% to 10%) developed its compressive strength at a very slow rate. The cement mortar with 4% and 6% of light crude oil contamination achieved most of its compressive strength after 56 days, while the cement mortar with 8% and 10% of oil contamination achieved most of its strength only after 112 days.

- The failure modes were strongly affected by curing time. At an early curing age (7 and 14 days), the dominant failure mode was axial splitting for up to 4% of oil contamination, and a combination of axial splitting and shear failure for specimens with 6% to 10% oil contamination. As the curing time increased (28 to 365 days), most of the specimens failed due to axial splitting.

- The total porosity in the cement mortar decreased from the early age of the hydration period for low levels of crude oil contamination (0.5% to 4%). This is due to the gradual filling of large pores by hydration products of cementitious material, resulting in the development of compressive strength of the cement mortar. On the other hand, the amount of macropores (> 30 um) started to decrease for the cement mortar with 8% and 10% light crude contamination only after 56 days of curing. This indicates that a longer curing period is needed for mortar with higher levels than those with lower levels of oil contamination in order to complete the hydration process.

- The microstructure and the strength development of cement mortar with and without crude oil content (0% and 10%) has been carried out using SEM analysis. It can be clearly seen that the hydration products increase with curing and fill the pores resulting in the decrease in the total porosity. Furthermore, the presence of 10% light crude oil did not inhibit the hydration products; however, the growth of the hydration products at this percentage (10%) of light crude oil contamination was retarded. At all curing ages, the volume of the hydration products in mortar with oil contaminated sand were smaller in size, compared to uncontaminated samples.

These results show that up to a certain amount of crude oil achieved most of its strength after 28 days, which indicates that the strength development was not affected. However, a longer period is needed to gain 100% of strength for higher levels of oil contamination. Based on these results, it can be seen that using fine sand contaminated with light crude oil up to a certain level enhanced the properties of cement mortar. In the next Chapter, mechanical properties of geopolymer mortar with light crude oil contaminated sand are presented.

Chapter 7

Properties of Geopolymer Mortar with Light Crude Oil Contaminated Sand

7.1 Introduction

The results of the previous chapters demonstrate the high potential of mixing fine sand contaminated with light crude oil and Ordinary Portland Cement (OPC). This material combination can produce a cement mortar with reasonable physical and mechanical properties suitable for building and construction. Based on these findings, it was concluded that stabilising oil contaminated sand with cement could offer a cheaper alternative to existing remediation methods and has high potential to solve many economic and environmental issues of sand contamination in oil. However, it is also well-known that cost is an important factor in considering the effectiveness of new remediation methods for oil contaminated sand. While OPC has been found as a suitable binder for oil contaminated sand, geopolymer is a cheaper alternative binder and has emerged as a novel engineering material in the construction industry. The price of the fly ash used in geopolymer is between 10% and 30% less than that of Portland cement due to the very high supply of fly ash. Even if the price of the activating chemicals needed to create geopolymer concrete is considered, it is estimated that enough sodium silicate solution and sodium hydroxide to convert 1 ton of fly ash to 2.5 cubic meters of geopolymer concrete can be purchased for about US $55 (Kambic and Hammaker, 2012, Hardjito and Rangan, 2005). This is the main reason why geopolymer is considered as an environment-friendly construction material with great potential for sustainable development. Apart from the environmental advantages, pastes and concrete made of geopolymer can exhibit many excellent properties, for example, high early-age strength, low creep and shrinkage, high resistance to chemical attack, and good fire resistance (Palomo et al., 2004, Jiménez and Palomo, 2005).

Geopolymer has many advantages over OPC and has been of great research interest as an ideal material for sustainable development. Different raw materials, which provide the source of silica and alumina, have been used to produce geopolymer. Research has shown that the presence of calcium compounds in the raw material can improve the mechanical properties of geopolymer products due to the coexistence of the geopolymer gel and the calcium silicate hydrate (CSH) and calcium aluminium hydrate (CAH) gels (Yip et al., 2005, Zhang et al., 2010, Zhang et al., 2012, Temuujin et al., 2009). However, there is still a lack of research activities conducted on recycling waste concrete via geopolymerisation.

Results of some early studies suggest the positive effect of adding some waste materials to geopolymer concrete. Yang et al. (2009) produced geopolymer concrete by using recycled aggregates as partial replacement for the fresh ones, and a mixture of waste concrete powder and metakaolin, along with silica fume, as the source materials for the geopolymeric binder. Their study indicated that the content of metakaolin and silica fume, and the increase in alkalinity, lead to high compressive strength geopolymer concrete. The silica fume offered active SiO_2, which was profitable for geopolymer production. Thus, the addition of silica also improved the mechanical properties of mortar and made the structure much denser. Allahverdi and Kani (2009) investigated the geopolymerisation of a mixture of finely ground waste brick and concrete in different mix proportions. They demonstrated that higher brick content and alkalinity results in stronger geopolymeric binder and the final setting time is reduced with higher alkalinity. This proves that the calcinated aluminosilicate content of waste brick is more suitable for geopolymerisation reactions. However, no studies have reported on the effect of crude oil waste on the properties of geopolymer concrete, which is the main focus of this Chapter. A comparison between geopolymer mortar and cement mortar, in terms of porosity, hydration and compressive strength, is also conducted and presented.

7.2 Materials and method

7.2.1 Materials

Sand

The dry sand used is similar to that used in previous chapters. The physical and mechanical properties of the fine sand are reported in Section 3.2.1.

Fly ash

Class F (low calcium) fly ash of approximately 15 µm was used in this study. This was sourced from Pozzolanic Millmerran in Queensland, Australia. The chemical composition of the fly ash is provided in Table 7.1. The density of fly ash is 1100 kg/m^3.

Table 7.1 Chemical composition of fly ash (%)

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Percentage (%)	51.8	24.4	9.62	4.37	1.5	0.34	1.41	0.26

Alkaline solution

A combination of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) solutions was used as the alkaline liquid.

Sodium silicate solution

The sodium silicate solution was obtained from PQ Australia. This solution is recommended for use as a detergent ingredient, adhesive, binder, feedstock silica source or industrial raw material. Some of its important properties are shown in Table 7.2.

Table 7.2 Properties of sodium silicate solution

Properties		Value
Composition	Sodium oxide, (Na_2O)	14.7 (%)
	Silicon dioxide, (SiO_2)	29.4 (%)

	Water	55.9 (%)
Specific gravity of solution		1.52
PH value		11 to 13
Solubility in water		Completely soluble

Sodium hydroxide solution

The sodium hydroxide solution was prepared in the laboratory by dissolving sodium hydroxide pellets in water. Its specific gravity depended on its concentration expressed by the term molar (M). Generally, the concentration for making geopolymer concrete varies from 8M to 16M. A previous study, conducted by Hardjito and Rangan (2005), measured the mass of the NaOH solid by using a different concentration. Based on their investigation, an 8M solution contains 262g of NaOH solid per kg of solution while 10M, 12M, 14M, and 16M contain 314g, 361g, 404g, and 444g, respectively. Thus, the specific gravity of the NaOH solution can be calculated; for instance, the actual weight of a 1 litre, 12M solution is (12×40×1000)/361 = 1329.6 g, where 40 is the molecular weight of the NaOH, and its specific gravity is 1329.6/1000 = 1.10. In this study, a 10M solution was prepared. This molarity was selected based on initial trials comparing 10M and 13M, where a 30% higher compressive strength was achieved for 10M than 13 M. The properties of the Sodium hydroxide (NaOH) are given in Table 7.3

Table 7.3 Properties of sodium hydroxide solution

Properties		**Value**
Compositions (10 molar solution)	Sodium hydroxide (NaOH) solid	36.1 (%)
	Water	63.9 (%)
Specific gravity, (10 molar solution)		1.10

7.2.2 Sample preparation

Preparation of oil contaminated sand

The preparation of oil contaminated sand was presented in Section 3.2.2, and the proportion was similar to that conducted in the previous Chapters "One part of fly ash and three parts of sand (by mass)". The alkaline solution to fly ash ratio was 0.5, which is similar to the optimum w/c ratio that was selected in Chapter 5. In this Chapter, three percentages of light crude oil contamination (0%, 1%, and 10% by the weight of sand) were used to evaluate the effect of curing methods. These percentages represent the optimum strength (1%), lowest strength (10%) and control samples (uncontaminated samples 0%). On the other hand eight different percentages (0%, 0.5%, 1%, 2%, 4%, 6%, 8% and 10 %) were considered to examine the mechanical properties and pH. In this Chapter, fine sand with 15% and 20% light crude oil contamination were excluded, as recommended in Chapter 5, as their strength has been significantly affected due to the saturated status of the contaminated sand at those levels.

The effect of saturated surface dry (SSD) condition has been considered and investigated in this study based on the recommendations by (Lokuge et al., 2013, Rangan et al., 2005). These researchers suggested using sand in the SSD condition to minimise absorption of chemicals, or contributing more water to the mix. A comparison between the mortars produced using sand in SSD condition, and with different percentages of light crude oil contamination, was done.

Pre-preparations

The mixing was performed manually in the laboratory using Kitchenaid mini mixer (mono phase 5lt). The crude oil content varied from 0% up to 10% of light crude oil contamination. The mixing procedure was as follows.

- Oil contaminated sand was mixed at least 72 hours before and kept in plastic containers with lids, to avoid any vaporisation of the crude oil before mixing day, in order to meet the homogeneous condition to mimic the real contaminated sand on site.
- Alkaline solutions were prepared by mixing the sodium hydroxide and sodium silicate solutions at least one day before mortar mixing.

- Based on the recommended mixing method in Chapter 4, the alkaline solution was gradually added to the fly ash and mixed for two minutes. Oil contaminated sand of proper proportion was then added to the mix.

Casting

The fresh mortar was cast and compacted following the method described in Section 4.2.1. Plastic moulds (50mm diameter and 100mm high) were used to avoid using any agent or grease to release the specimens that may affect the properties of the hardened geopolymer mortar. This also prevented any crude oil leaching from the mix. The fly ash-based geopolymer mortar was cohesive and dark in colour. The specimens were compacted as shown in Figure. 7.1.

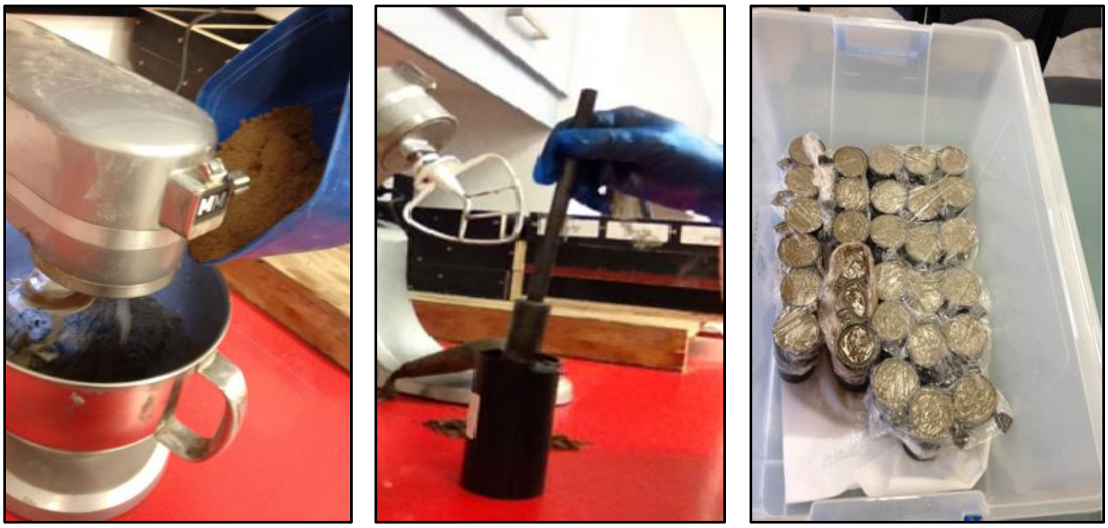


Figure 7.1 Mixing and compaction of fresh geopolymer mortar in plastic moulds

Curing

As mentioned earlier only mortar with 0%, 1% and 10% oil contamination levels were considered in this part of study. The mortars were cured under two different conditions, i.e. ambient curing in air (AC) and heat curing (HC). The HC was considered based on previous studies (Hardjito et al., 2005a, Hardjito et al., 2004, Hardjito et al., 2005b) whilst the AC curing of geopolymer concrete at ambient temperatures had already been carried out by other previous studies (Memon et al., 2011, Lloyd and Rangan, 2010). In this study, AC was considered to investigate if ambient curing would be enough to achieve suitable strength with the presence of crude oil. The AC specimens were left in open air to cure until testing at 28 days.

The room temperature was around 22ºC with a humidity of 60% during the time of curing. HC specimens were kept in an oven under 60ºC for 24 hr and afterwards they were kept in a similar condition in ambient (AC) to cure until testing at 28 days.

Specimen details

A summary of the different specimens investigated in this chapter are provided in Table 7.4.

Table 7.4 Details of the experiment and the specimens

Experiment type	Oil content (%)	Test time days	Number of tests	Curing type
Curing	0, 1 and 10%	28	9	HC
			9	AC
Saturated surface dry (SSD)	0 %		6	HC
				AC
Un-saturated surface dry (USSD)	0%		6	HC
				AC
Strength	0, 0.5, 1, 2, 4, 6, 8, 10		24	HC
Total			54	

7.2.3 Testing procedure

Compressive strength test of geopolymer mortar

The cylindrical specimens were surface-grinded before being placed in the testing machine to make the top and bottom surfaces smooth, ensuring a uniform load distribution as shown in Figure 7.2. Three 50×100 mm size cylinders were tested from every mix which represented crude oil contamination from 0% up to 10%. Testing was conducted according to AS-1012.9 (2014). The load was applied using a 100 kN MTS machine at a constant cross head speed of 1mm/min. The compressive strength was calculated by dividing the load by the cross section area of the specimens. The failure mechanisms of each specimen were also observed and recorded.

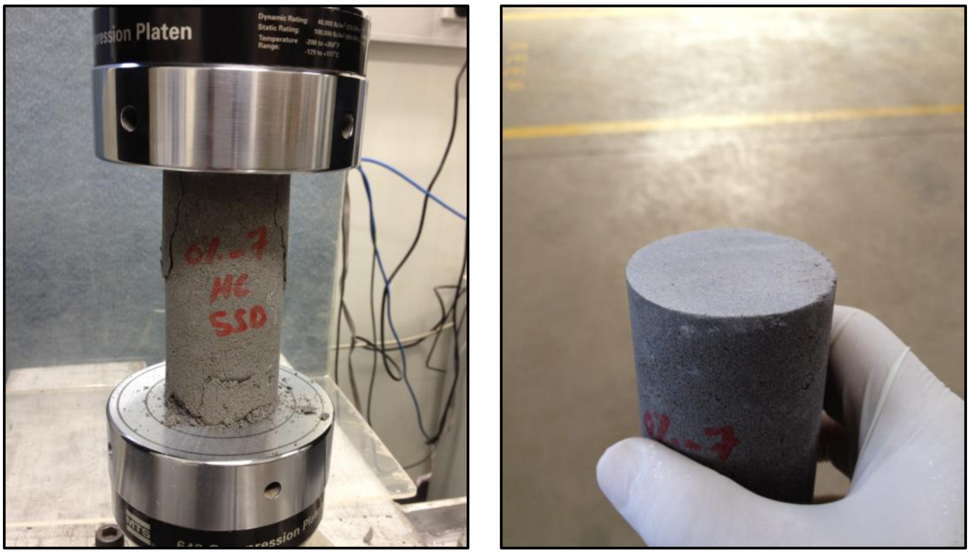
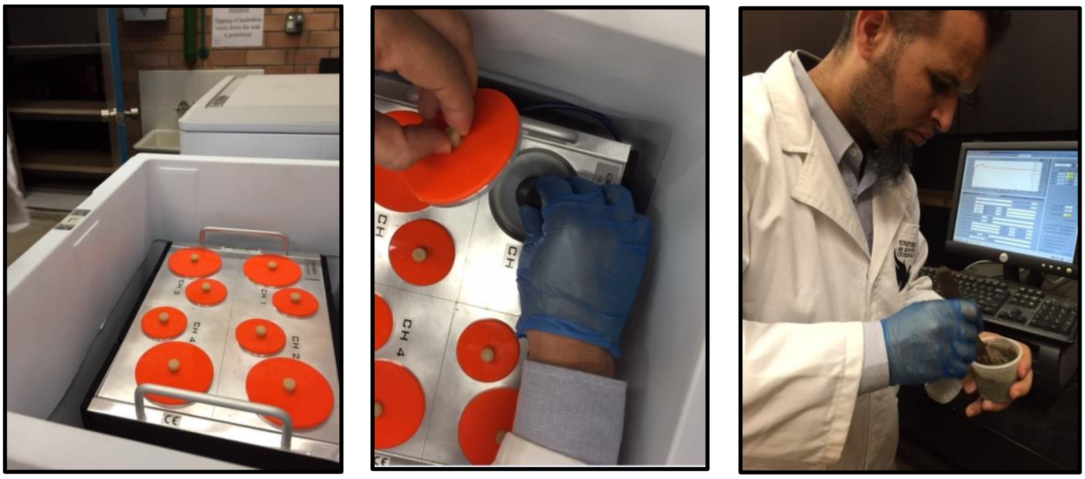


Figure 7.2 Compressive strength machine

Isothermal Calorimetry

Isothermal calorimetry is a useful technique to study the hydration of a cementitious system (Wadsö, 2003), particularly during the first 48 hours of hydration. This device has the advantage of being able to test a material at a specific temperature. Typically, isothermal calorimetry is used to investigate the major thermal peak that occurs during the acceleration phase of the hydration process, as shown in Chapter 4. The experiments were carried out based on ASTM-C1679 (2014). Sodium hydroxide (NaOH) was mixed in water and allowed to cool to ambient temperatures. It was then mixed with a sodium silicate solution to form the activator. The pastes were mixed externally and loaded into the isothermal calorimeter, as shown in Figure 7.3. The time elapsed between the instant the activating solution was added to the powder, and the past loaded into the calorimeter, was around 2 minutes. This method of mixing was employed to avoid the large instantaneous heat release associated with alkali dissolution in water. In this investigation the tests were run for 48 hour.



Isothermal Calorimetry Installing the sample Sample preparation

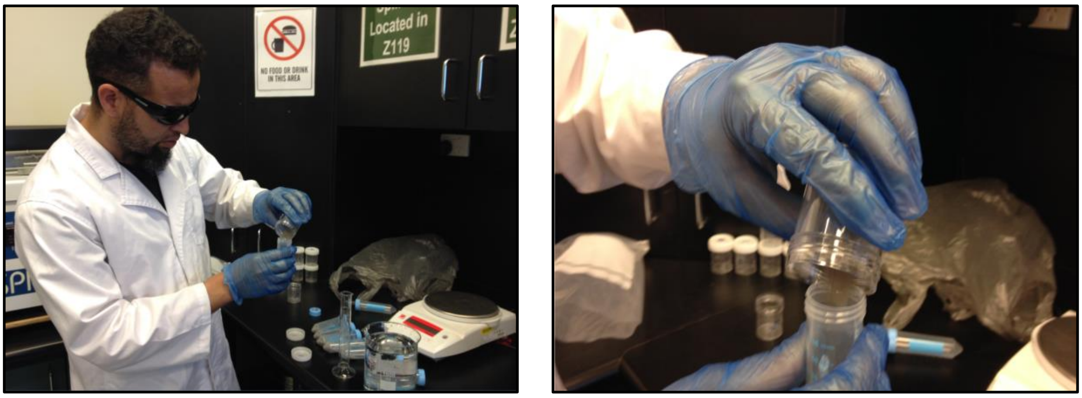
Figure 7.3 Isothermal calorimetry, sample preparation steps.

pH measurement

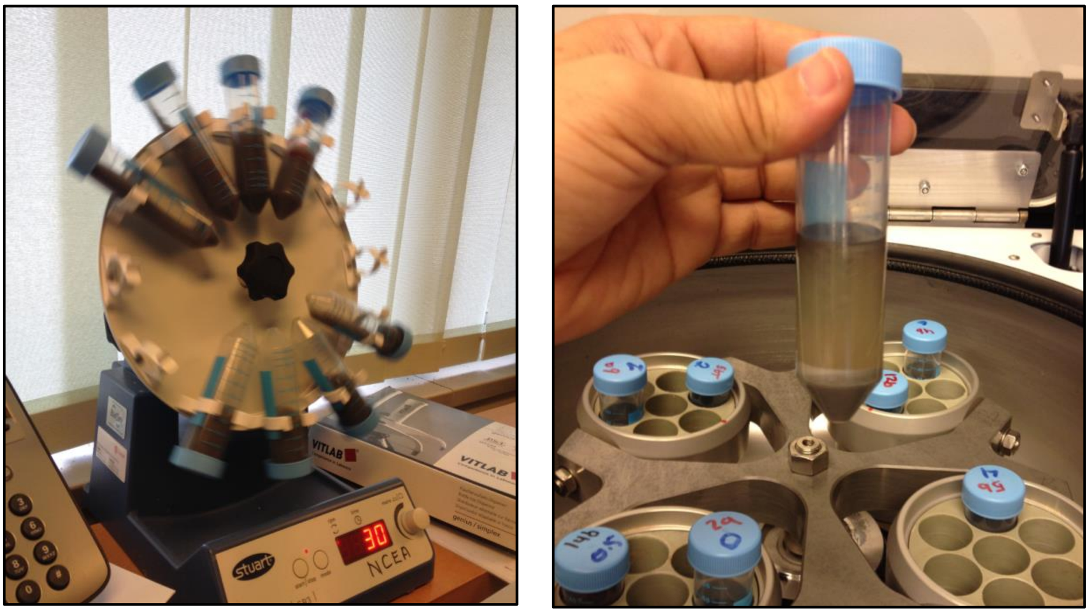
The pH was measured by grinding the geopolymer mortar into a less than 2 mm fraction and preparing a 1:5 (grinded concrete: water) solution according to ASTM D4972 - 13. The solution was prepared according to the following procedure:

1. Add 25 mL of deionized water into a centrifuge tube containing 5 g of grinded geopolymer mortar;
2. Shake the tube in a rotary shaker for 1 hour and then centrifuge at 3000 rpm for 5 minutes;
3. Remove the supernatant and store in a clean tube for analysis;
4. Use the grinded geopolymer residue from the water extraction to prepare 1:5 (grinded geopolymer: 1M NH_4Cl) extract with a procedure that is exactly the same as the water extraction, except that 25 mL of 1M NH_4Cl solution is used to replace deionized water as an extracting agent.

The above steps of pH measurements are shown in Figure 7.4.

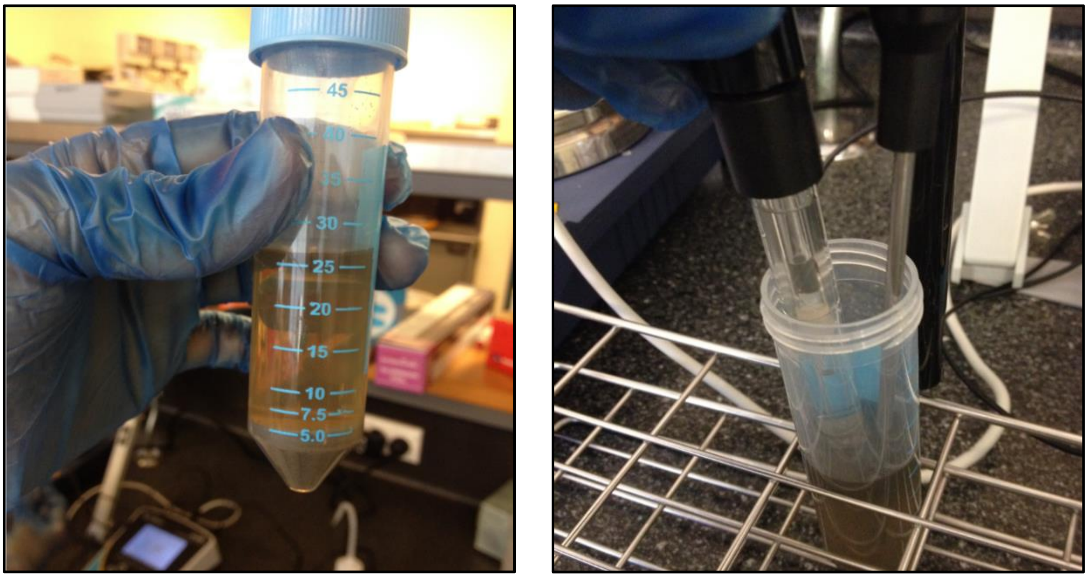


Mixing



Rotary shaker

Centrifuge



pH meter

Figure 7.4 Steps of pH measurements

Heat transfer

Two conditions were investigated with the fine sand at the SSD condition and with 2% of light crude oil contamination. The 2% was considered as it was found in Chapter 3 that fine sand will start not to absorb any water in this condition. In these experiments, two thermocouples were used to measure the temperature in each sample: T_1 represented the temperature in the surface of the specimen, while T_2 represented the heat at the centre of the specimen. In addition, T_3 measured the environmental temperature “inside the oven”, as shown in Figure 7.5. Both samples were placed in the oven at 60ºC and the temperature was recorded every minute, until the T_2 of both specimens reached 60 ºC. Three replications of each sample were conducted and the average value was recorded.

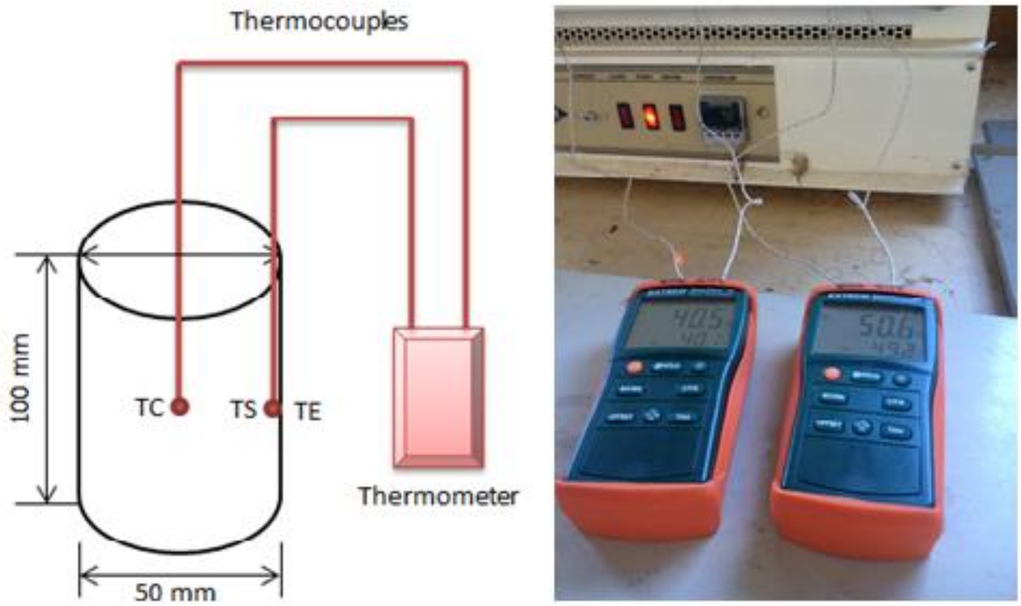


Figure 7.5 Heat transfer test

Scanning Electron Microscope (SEM) images

The microstructure of all geopolymer mortar samples was observed using a scanning electron microscope (SEM) (JEOL JCM-6000, Tokyo, Japan), following the procedures described in Section 4.2.6.

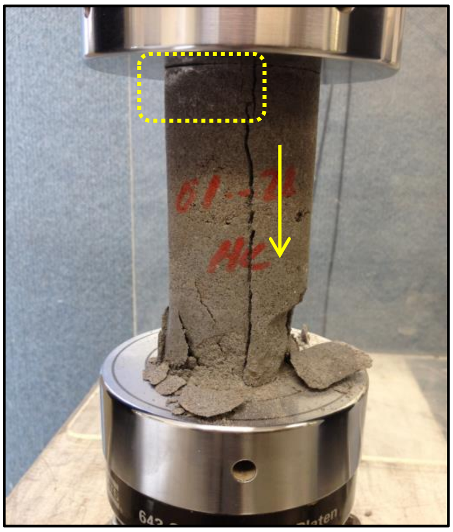
7.3 Results and Observation

The compaction of the geopolymer mortar was not as easy as the cement mortar and hence, higher porosity was observed with geopolymer mortar, compared to cement mortar in total porosity, as well as in the mesopores and macropores. The compressive strength, type of failure, and pH values of all specimens are shown in Figure 7.5.

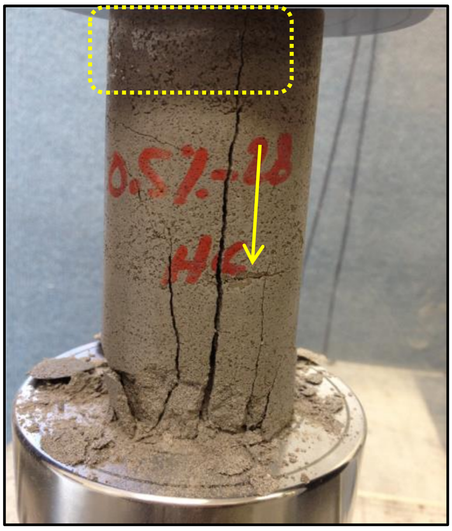
Table 7.5 Failure strength, failure type and pH values of geopolymer mortar with different crude oil contamination

Crude oil content (%)	Failure strength MPa	Standard deviation	Type of failure	pH
0	16.8	1.001	Axial splitting	11.45
0.5	18.6	1.569		11.45
1	24.1	1.443		11.42
2	20.2	1.067		11.3
4	17.0	0.975		11.19
6	14.0	0.982	Shear failure	11.12
8	12.1	1.116		10.95
10	11.3	1.123		10.79

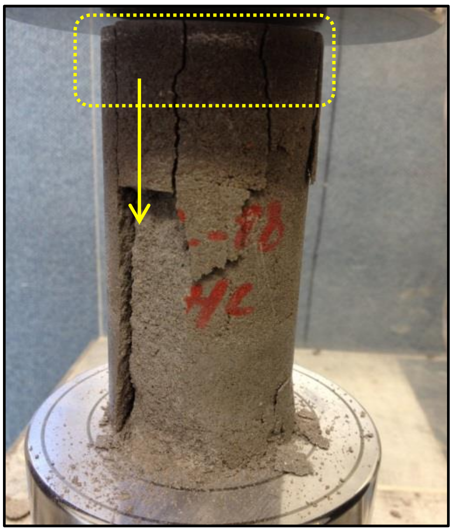
Figure 7.6 shows the typical failure modes of geopolymer mortar cylinders with oil contaminated sand under compression. Two different failure modes were observed, i.e. axial splitting (columnar fracture), and shear failure. The specimens containing crude oil from 0% up to 4% all failed due to “axial splitting”, as shown in Figure 7.6. On the other hand, the dominant failure mode for the mortar with a crude oil content from 6%-10% was a shear failure. Furthermore, Figure 6.7 shows the visible formation of efflorescence on the surface of geopolymer mortar with up to 2% of crude oil contamination. However, the efflorescence products are not observable with the naked eye on specimens containing 4% or more crude oil. The observation that the presences of light crude oil at high levels can reduce the efflorescence product, is an interesting area of investigation for future research as this issue is increasingly becoming a concern to concrete researchers.



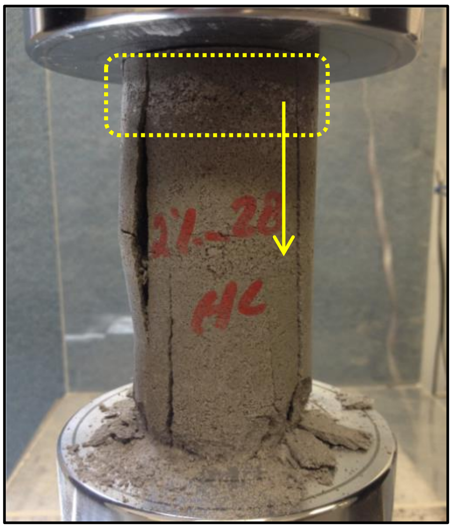
0%- axial splitting



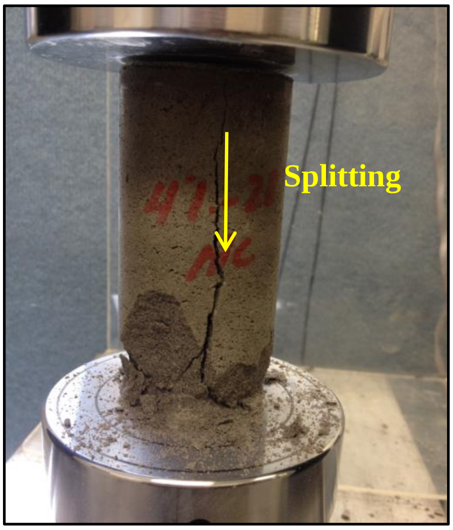
0.5%- axial splitting



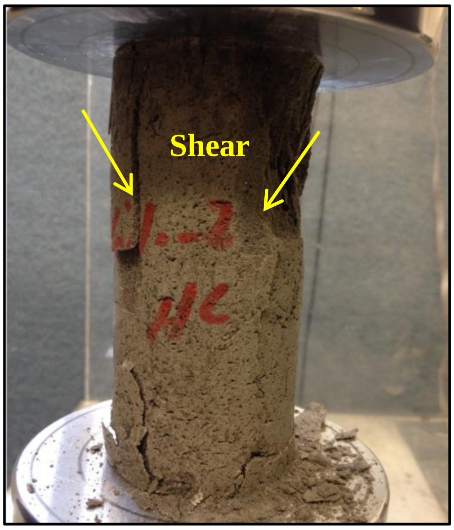
1%- axial splitting



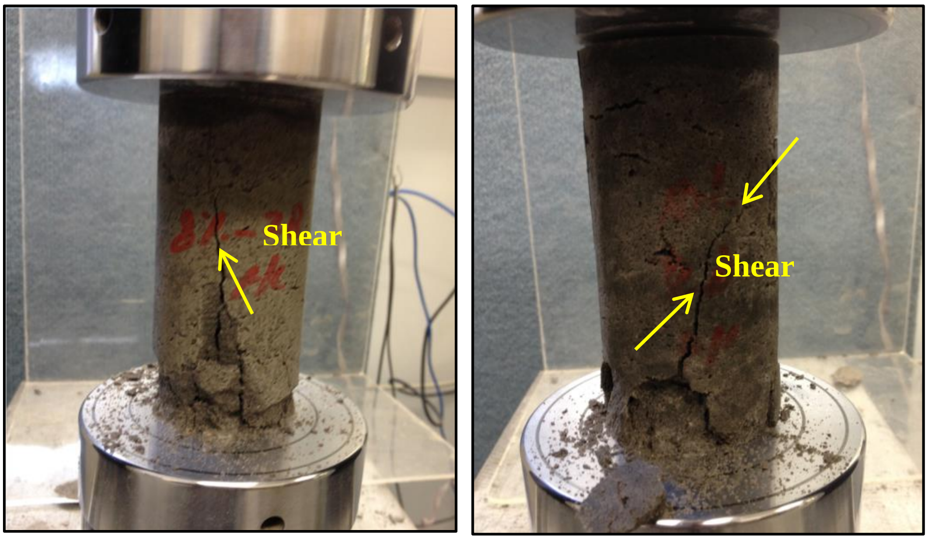
2%- axial splitting



4%- axial splitting



6%- shear failure



8%- shear failure 10%- shear failure

Figure 7.6 Failure modes of specimen

Table 7.6 shows the measured pH values of fly ash geopolymer mortar, containing different percentages of light crude oil contamination (0%, 0.5%, 1%, 2%, 4%, 6%, 8%, and 10%). In general, increasing the crude oil content decreases the pH values. The mortar with 10% crude oil contamination had a pH of around 10.8 while the uncontaminated sample had a pH of 11.4. The pH values of geopolymer mortar with 0% up to 1% of light crude oil contamination decreased slightly, while by increasing the crude oil from 2% to 10%, the pH values gradually decreased.

7.4 Discussion

7.4.1 Effect of curing methods on the strength of geopolymer

Figure 7.7 shows the comparison of the compressive strength at 28 days between the geopolymer mortar with 0%, 1% and 10% of oil contaminated sand, and that cured by heat curing (HC) and air curing (AC). It was observed that the HC specimens exhibited an almost 2.5 times higher compressive strength than AC specimens for the three levels of light crude oil contamination. This is due to the high temperature (60 ºC) during curing which enhances the geopolymerisation process. This is expected as Hardjito et al. (2005a) reported that curing temperature plays an important role in the geopolymerisation process of fly ash based geopolymer mortar. Similarly, Vijai et al. (2013) found that the compressive strength development of geopolymer concrete occurred quite rapidly when oven curing was implemented. Moreover, the more than twice the strength achieved for HC geopolymer mortar with oil contaminated sand reinforced the findings by Patil et al. (2014). These authors found that the strength of geopolymer mortar at 28 days was enhanced by 2.1 times when heat cured compared to ambient cured. Furthermore, K. Vijai et al. (2010) concluded that the compressive strength of heat cured concrete is around 47% higher than that of ambient cured concrete. These findings suggest that heat curing is an effective method to produce a geopolymer mortar containing oil contaminated sand with good compressive strength.

The higher strength of HC geopolymer mortar with oil contaminated sand, compared to AC mortar, can be also explained by the increase in the kinetic energy and degree of reaction at high temperatures, which subsequently increase the density of the pore system in the mortar as indicated by (Olivia and Nikraz, 2012). It is also believed that a higher temperature activates alumina-silicate phases in the fly ash (FA), so they are generally cured at 60 ºC – 90 ºC (Memon et al., 2011). Therefore, disregarding the results obtained with different crude oil content, the amount of strength gained when heat curing was used compared to air curing was similar to previous studies (Hardjito and Rangan, 2005, Vijai et al., 2013, Patil et al., 2014). This indicates that a similar result was observed in terms of the effect of curing methods when oil contaminated sand is used in a geopolymer concrete mix. On the other hand, the low compressive strength, developed by the geopolymer mortar with oil contamination at ambient temperatures, is due to the slow reaction and setting of FA- based geopolymeric materials as indicated by (Olivia and Nikraz, 2012).

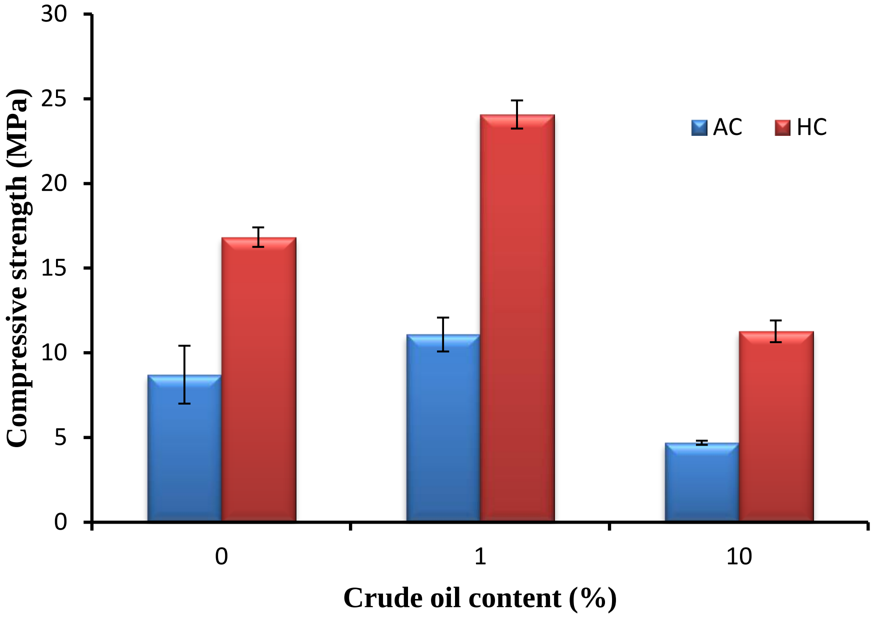


Figure 7.7 Compressive strength as a function of crude oil content

7.4.2 Effect of surface condition of fine sand on the strength of geopolymer mortar

The effect of the surface condition of the fine sand particles on the compressive strength of the geopolymer mortar, cured under HC and AC methods, is shown in Figure 7.8. In general, the compressive strength of mortars produced with fine sand in the SSD condition is higher compared to mortar with fine sand in the unsaturated surface dry condition (USSD). For instance, the compressive strength of HC-SSD is 10.5% higher than that of HC-USSD. A similar trend was observed for AC-SSD, which exhibited a 42% higher compressive strength compared to AC-USSD, as shown in Figure 7.8. This indicated that the SSD condition plays a large potential role in enhancing the compressive strength. For USSD, the dry sand absorbs water in the concrete mix which severely disrupts the ratio of water to geopolymer solids and creates uncontrollable and non-calculable changes to the mix, as indicated by Black (2012). This aligns with the finding in section 6.4.1 in which a higher compressive strength was obtained at 1%, compared to the uncontaminated sample (0%), due to the degree of wettability on the surface of the sand particles. In this condition, where contaminated sand is used, the condition of SSD can be achieved at a certain contamination level after which it will change the SSD to a fully saturated state where a high percentage of crude oil may affect the compressive strength of geopolymer mortar.

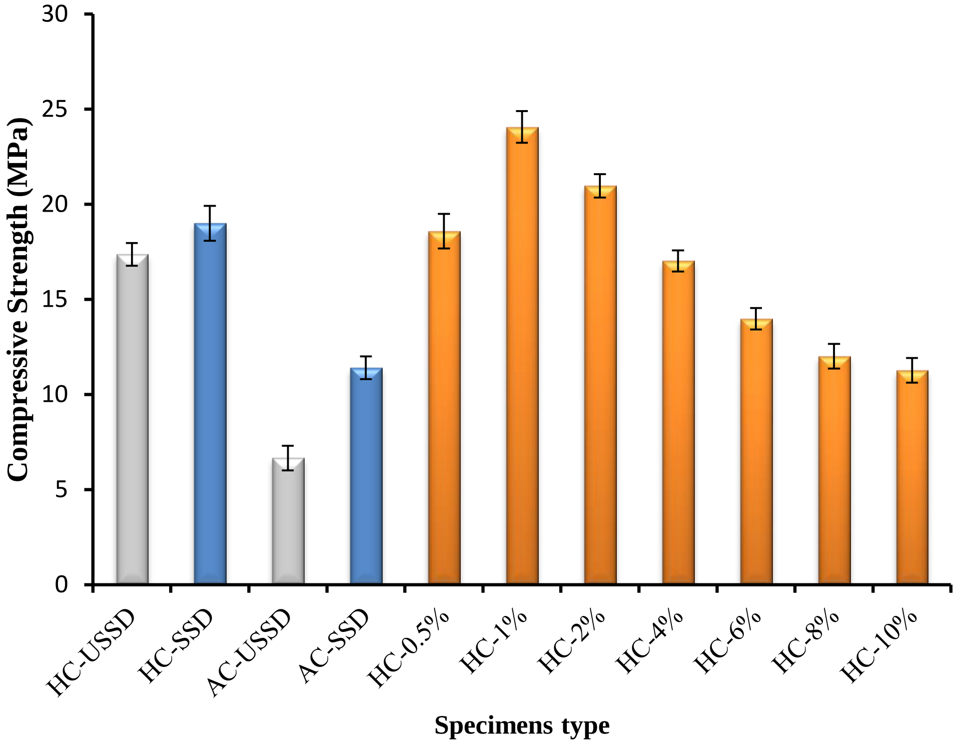


Figure 7.8

Figure 7.8 Effect of surface condition of the fine sand on the compressive strength

The comparison of the compressive strength between the geopolymer mortar containing fine sand in the SSD condition, and those containing fine sand contaminated with light crude oil, is also shown in Figure 7.8. It is interesting to note that the mortar with 0.5% of light crude oil has a compressive strength similar to that of the HC-SSD condition (~19.0 MPa), and when the crude oil content was increased to 1% (HC-1%), a 20.8% higher compressive strength than HC-SSD was observed compared to uncontaminated samples (HC-USSD). Similarly, the mortar with 2% oil contamination had at least an 8% higher compressive strength than HC-SSD. This higher compressive strength for mortar with oil contaminated fine sand is due to the degree of wetness caused by the crude oil, which replicates the SSD condition of sand. In Chapter 3, it was found that uncontaminated sand had the highest percentage of water absorption and as the amount of crude oil increased the absorption percentage decreased. At 0.5% the absorption was 2.35%, and at 1% the absorption was decreased up to 0.8%, while at 2% water absorption became 0%, as the sand started to become changed from a partially saturated condition to a fully saturated status. This indicates that the alkalinity was not diluted at these percentages, due to the unavailability of free water in order to achieve the SSD condition, as the sand particles were already coated by the crude oil. Increase in alkalinity leads to a high compressive strength geopolymer concrete, as found by (Rakhimova and Rakhimov, 2015, Nasvi et al., 2014, Zhuang et al., 2016).

Hardjito et al. (2004) have stated that the concentration of alkaline solution is the most significant factor for geopolymerisation and that a higher concentration of NaOH yields a higher compressive strength. Thus, the higher compressive strength of the geopolymer mortar with 1% and 2% of oil contamination, rather than the mortar with fine sand in the SSD condition, was due to the high alkalinity of the solution, which dissolved and activated the amorphous, reactive silica and alumina during the geopolymerisation process, leading to generation of more geopolymeric binder. As the sand particles were coated with light crude oil, the concentration of the alkaline solution was not affected, while an additional 29 g of water was available for fine sand with SSD condition. This amount of water may have diluted the alkaline solution, and hence affected the rate and extent of geopolymerisation reactions, which then resulted in a lower compressive strength than the mortar with oil contaminated sand. Furthermore, the enhancement of the compressive strength at HC-1% and HC-2%, compared to HC-SSD, may have been due to the higher thermal conductivity of oil compared to water. The heat transfer (HT) tests conducted confirmed that heat transfer in mortars with crude oil (2%) was higher than that for SSD specimens, as shown in Figure 7.9. The heat transfers from the surface to the centre of the specimens containing crude oil were faster by 124 minutes, indicating a faster polymerisation process. Khale and Chaudhary (2007) have indicated that curing time improves the polymerization process, resulting in higher compressive strength. This result also explains the higher compressive strength of the HC mortar compared to that of AC mortar, as shown in Section 7.4.1.

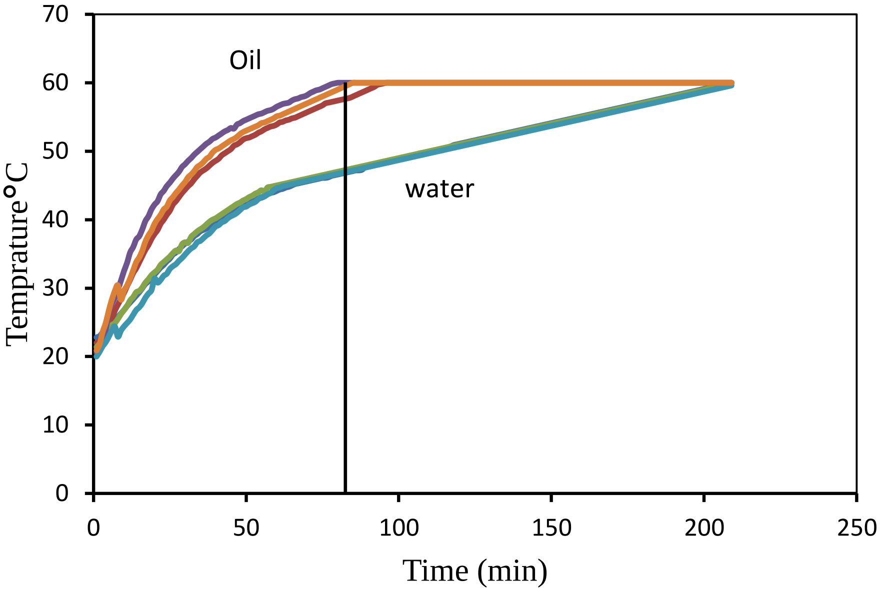


Figure 7.9

Figure 7.9 Heat transfer curve (HTC)

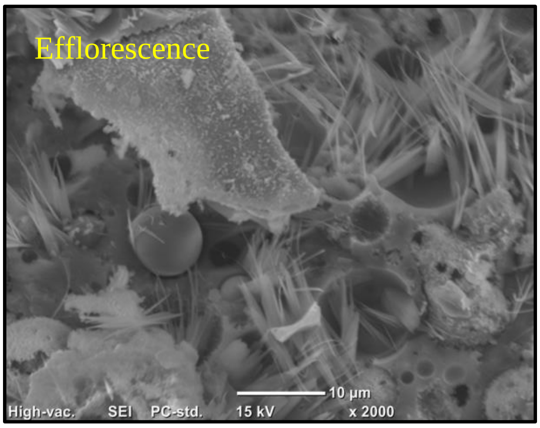
7.4.3 Effect of oil contamination level on the strength of geopolymer

As clearly shown in Figure 7.8, the sample with 1% of light crude oil produced the maximum compressive strength (24.0 MPa) compared to others. Meanwhile, the minimum compressive strength was obtained with 10% of crude oil contamination (11.0 MPa). The increment of the strength at 1% of crude oil contamination can be attributed to two main reasons: firstly, it was due to the increase in the cohesion between sand particles, as described in Chapter 3. The second reason may be that the crude oil and the fly ash acted as the emulsifying agents. Jackson and Dhir (1989) have stated that emulsions are comparatively stable systems of small globules of binder, dispersed in water, and kept in permanent suspensions by means of an emulsifier. Furthermore, the emulsion binders and the water are generally referred to as anionic or cationic, depending on the type of the emulsifier used. Previous studies (Bechhold et al., 1921, Jain and Srivastava, 1969) have used the finely divided solids as emulsifiers, and they found that the formation of emulsion depends upon: (i) the grain size of the powder - the smaller the grain the better the emulsion, until an optimum is reached, after which smaller grains have inferior emulsifying properties; and (ii) The quantity of powder - the more powder there is available the more globules can be covered, providing the powder is sufficiently fine (Bechhold et al., 1921, Menon and Wasan, 1988). Thus, it is expected that the fly ash with crude oil worked as an emulsifying agent whereby the fly ash distributed in crude oil and created the emulsion. When this emulsion is mixed with the aggregate, it creates a thin layer, with the water evaporating to leave a coating of the original binders on the surface (Jackson and Dhir, 1989). This may be the reason behind the enhancement of the compressive strength, with up to the 4% of crude oil contamination, whereby it showed higher compressive strength compared to uncontaminated samples.

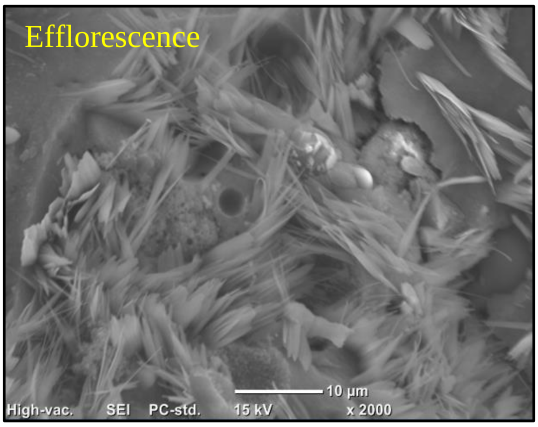
Increasing the crude oil content from 4% to 10% caused a significant reduction in compressive strength due to the saturation of the sand particles with oil. By increasing the crude oil content, the ratio of alkaline liquid -to- fly ash will be increased, because the sand and the fly ash will be saturated with crude oil. Black (2012) has stated that when the alkaline liquid to fly ash ratio (AL: FA) ratio is increased above a certain level, the compressive strength will actually decrease. This reduction in strength may be due to fly ash particles, with a finite surface area, not being fully saturated with alkaline liquids, because the sand is already saturated by the crude oil, and hence, at a certain point, any more alkaline liquid is simply wasted within the mix. This excess alkaline liquid then effectively becomes extra water, diluting the mix and affecting the bonding between aggregate and binder.

The SEM analysis in Figure 7.10 showed that the microstructure of each mixture tends to change too dramatically as the crude oil content is increased up to 2%, which aligns with the visual observation in Figure 7.6. It can be observed that the efflorescence of the product was clearly seen up to 2% of crude oil contamination, whereas increasing the crude oil content above 2% decreased or rather inhibited the efflorescence. It seems, judging from these images, that the higher percentages of light crude oil hindered the rapid efflorescence products. This is in contrast to the common understanding that a porous structure provides more channels for the transport of water and alkali cations, which is expected to lead to efflorescence (Zhang et al., 2014). The presence of crude oil at high percentages may play a great role in retarding the efflorescence that is created as the porosity start to be filled by the crude oil.

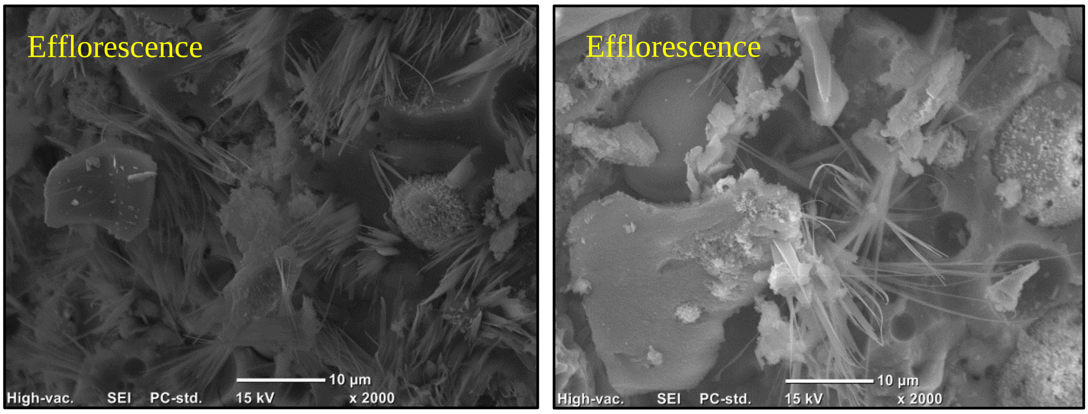
Geopolymer, contain much higher soluble alkali metal concentrations than conventional cement; could be a significant issue when effloresce products are exposed to humid air or come in contact with water (Škvára et al., 2009, Zhang et al., 2013). Merrigan (1986) stated that the appearance of the efflorescence comes through the travel of alkali sulphates through the pores to the surface. If the natural pores in the concrete can be reduced, it becomes harder for the salts to migrate through to the surface. Therefore, it appears that the presences of light crude oil at high level (4%-10%) filled the pores and hence, retarded the travel of alkali sulphates through the pores of the hardened mortar to the surface. Furthermore, Najafi Kani et al. (2012) have elaborated that when a concrete column comes in contact with damp sand at its base, so that water moves upwards through the concrete by capillary action and evaporates from its surface, it leaves the surface enriched in the alkali cations which were present in the pore solution. The deposited alkalis can then react with atmospheric CO_2, results in the formation of the white carbonate surface deposits known as efflorescence. Based on results in Chapter 3, the fine sand contaminated by 4% of light crude oil is already hydrophobic. This prevents them to be contact with moisture as well as the atmospheric CO_2, thus inhabits the formation of the efflorescence products. On the other hand, the presence of efflorescence in geopolymer mortar with 2% or less light crude oil did not affect the compressive strength due to the small macropores present in these samples.



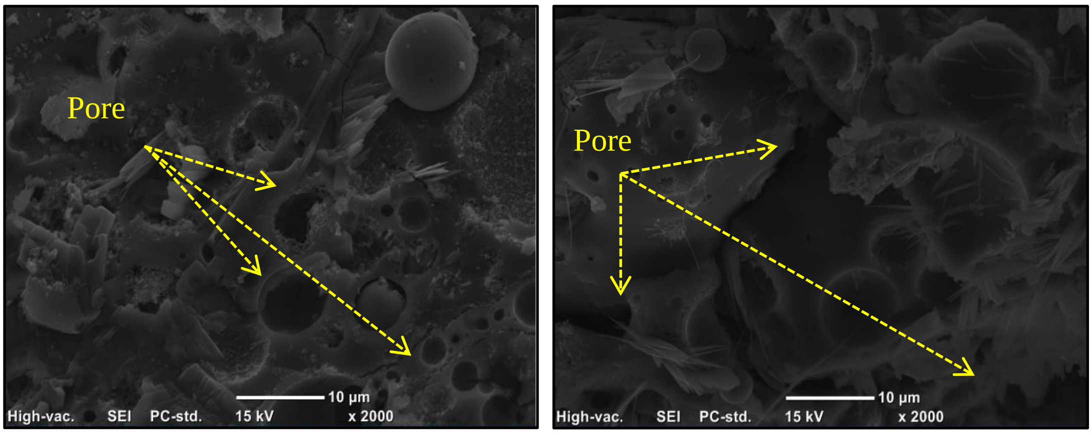
Crude oil content 0%



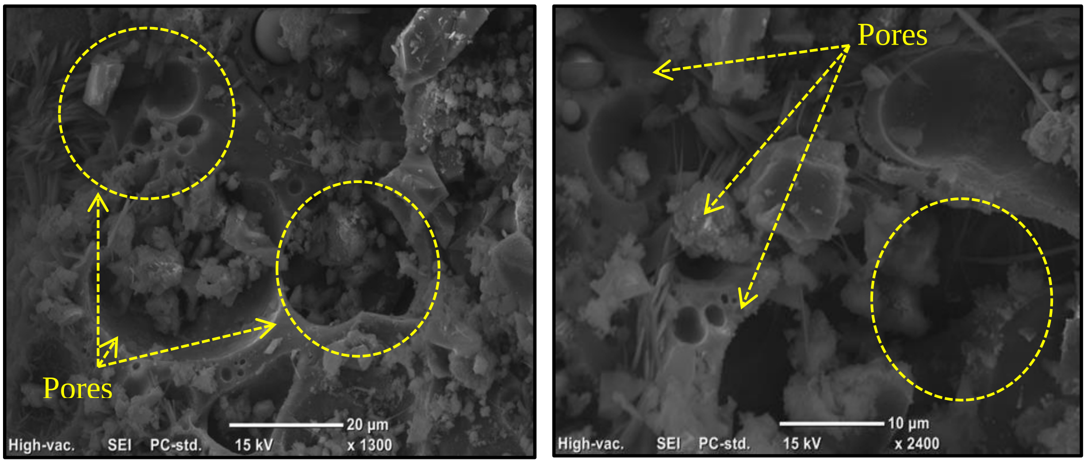
Crude oil content 0.5%



Crude oil content 1% Crude oil content 2%



Crude oil content 4% Crude oil content 6%



Crude oil content 8% Crude oil content 10%

Figure 7.10 SEM images of geopolymer mortar with different levels of crude oil content

7.4.4 Compressive strength of geopolymer and cement mortar

Figure 7.11 shows the percentage change of the compressive strength of geopolymer and cement mortar with respect to uncontaminated samples (0%). The above x axis represents the increase in compressive strength, while the below x axis indicates a decrease in compressive strength. In general, a higher gain in strength was observed for geopolymer mortar than for OPC mortar. At 0.5% of light crude oil contamination, the compressive strength of the geopolymer mortar was 10% higher than uncontaminated samples, while the OPC mortar is similar to the uncontaminated sample. At 1% oil contamination, the strength gain of geopolymer mortar was 22% higher than that of OPC mortar. On the other hand, a more significant decrease in the compressive strength of OPC mortar was observed than for geopolymer mortar when the oil contamination was 44% and higher. This may be related to the curing method used with the geopolymer, which is heat curing, because HC increases the kinetic energy and degree of reaction, which causes an increment of the density of the pore system and improves the mechanical properties of the resulting composite.

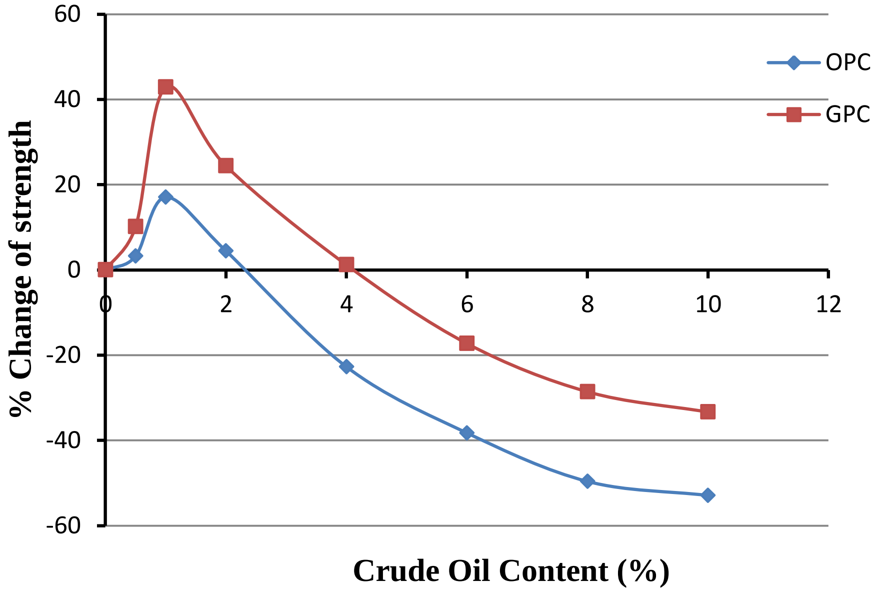
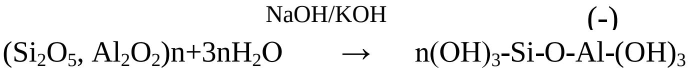


Figure 7.11 Normalized compressive strength between geopolymer and OPC

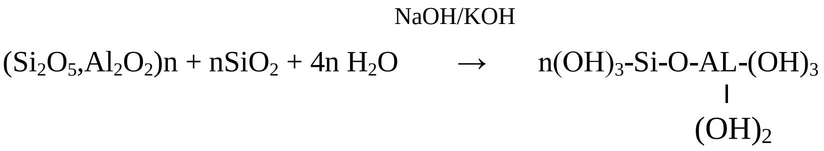
7.4.5 Effect of pH on the strength of geopolymer

The pH of the geopolymer mortar had an effect on the developed compressive strength. Adding light crude oil up to 1% did not show a significant variation, but as the crude oil increased, the pH value deceased. This could be attributed to the organic acids available in crude oil. The ionic H^+ from the organic acids present in the light crude oil started to combine with OH^- from the NaOH as shown in equations

7.1 and 7.2, and created the H_2O. The creation of water in the mix diluted the alkaline solution and decreased the alkalinity and level of pH. As expected, the amount of additional water created due to this process increased as the amount of crude oil increased. With a decrease in pH for high level of oil contamination, the amount of soluble aluminium to react with calcium decreases and hinders the geopolymerisation process (Phair and Van Deventer, 2001, Phair et al., 2000, Duxson et al., 2005).



$$(Si_2O_5, Al_2O_2)n+3nH_2O \xrightarrow{NaOH/KOH} n(OH)_3\text{-Si-O-}\overset{(-)}{\text{Al}}\text{-}(OH)_3 \qquad (7.1)$$



$$(Si_2O_5,Al_2O_2)n + nSiO_2 + 4n\ H_2O \xrightarrow{NaOH/KOH} n(OH)_3\text{-Si-O-}\underset{(OH)_2}{\text{AL}}\text{-}(OH)_3 \qquad (7.2)$$

Figure 7.12 shows a comparison between the pH values of geopolymer and cement mortar as a function of different crude oil contaminations. It can be seen that the pH values of cement mortar containing light crude oil at 0% was 12.54, and increasing the crude oil content from 0.5% to 6% did not show a significant variation. However, when the crude oil increased to 8% and 10%, the pH values decreased. The drop in pH of concrete was caused by a chemical replacement reaction within the cement paste that is usually thought to replace the hydroxide anion in calcium hydroxide with a carbonate anion to form calcium carbonate. This chemical process is called carbonation. The model of carbonation that is most widely accepted takes place in dissolved phases (Ishida and Maekawa, 2000, Engelsen et al., 2005). The dissolution theory of carbonation is a series of complex reactions that replace the hydroxide anions in calcium hydroxide with a carbonate anion. The following equations summarize the main chemical reactions in the carbonate system

$$CO_2(g) + 2H_2O(l) \leftrightarrow H_2CO_3(aq) \qquad (7.3)$$

$$H_2CO_3(aq) \leftrightarrow H + (aq) + HCO_3 - (aq),\ pKa = 6.35 \qquad (7.4)$$

$$HCO_3\text{-}(aq) \leftrightarrow H\text{+}(aq) + CO_3{}^{2-}(aq),\ pKa = 10.33 \qquad (7.5)$$

As the reactions continue, with the addition of carbon dioxide, more calcium hydroxide will dissolve in order to maintain equilibrium of the system, allowing more calcium carbonate to form until essentially all of the calcium hydroxide is converted to calcium carbonate (Engelsen et al., 2005, Pan et al., 2012, Kwon and Na, 2011). The rate at which carbonation occurs in traditional concrete depends on the moisture content of the concrete, the relative humidity in the ambient air, the partial pressure of carbon dioxide in the atmosphere, the depth of the specimen, and the surface area of the concrete specimen (Neville, 1981, Masters and Ela, 2008, Pade and Guimaraes, 2007). Furthermore, Šavija and Luković (2016) indicated that the carbon dioxide from the atmosphere can react with hydrated cement in presence of moisture. Increasing the crude oil content increases the amount of free water as the aggregates are already saturated with crude oil, and hence, the carbonation rate increases with higher porosity, resulting in lower compressive strength.

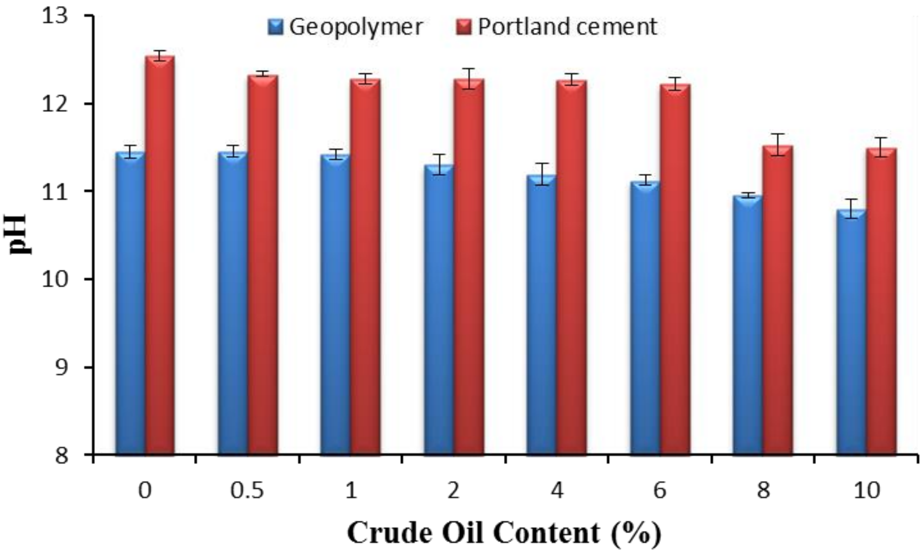


Figure 7.12 pH values of geopolymer and cement mortar as a function of different crude oil content (%).

7.4.6 Effect of porosity on the strength of geopolymer mortar

Figure 7.13 shows the results of total porosity (%), micropores (<0.2 um), mesopores (0.2-30 um), and macropores (>30 um) of geopolymer specimens, compared to OPC as a function of different percentages of light crude oil contamination. In general, it can be seen that in the overall trend of total porosity, micropores and macropores were similar in geopolymer and OPC. For instance, increasing the crude oil content increased the total porosity (%) in both geopolymer and OPC dramatically. However, the total porosity of the geopolymer was higher by around 2.3 times compared to the porosity of the OPC. The increment was clearly seen. The increment of the total porosity and the pores size in geopolymer, compared to cement mortar, can be explained by the geopolymer mortar containing a lot of air voids, some compaction voids, and tiny curved microcracks, which were not seen in the cement mortar as shown in Figure 7.14. A large part of the air voids is related to hollow fly ash particles (Valcke et al., 2012).

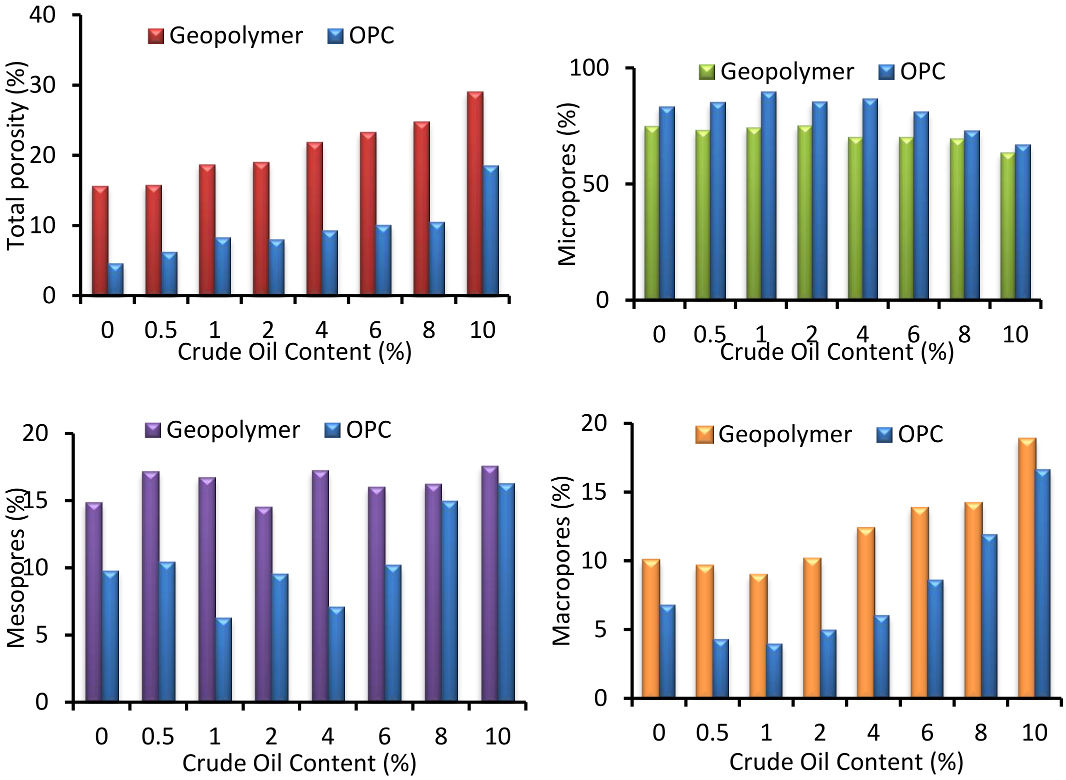
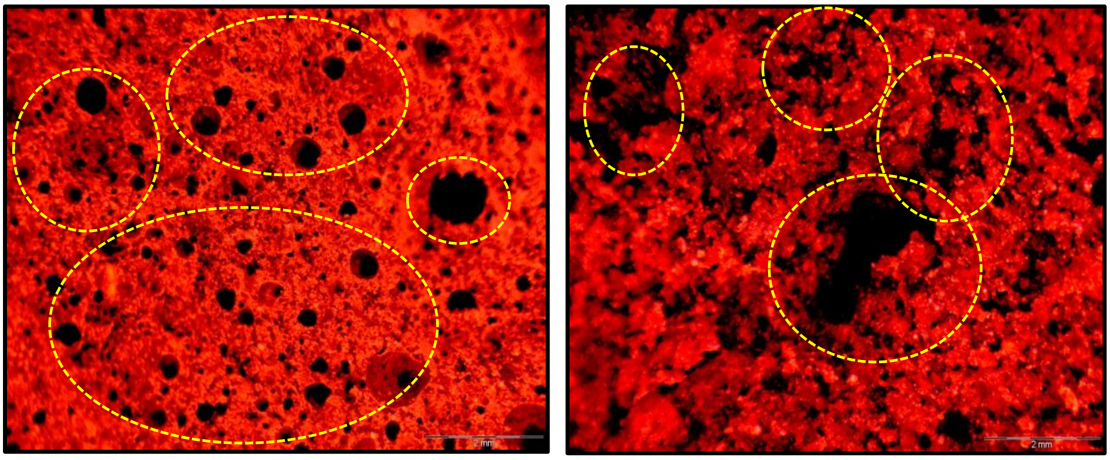


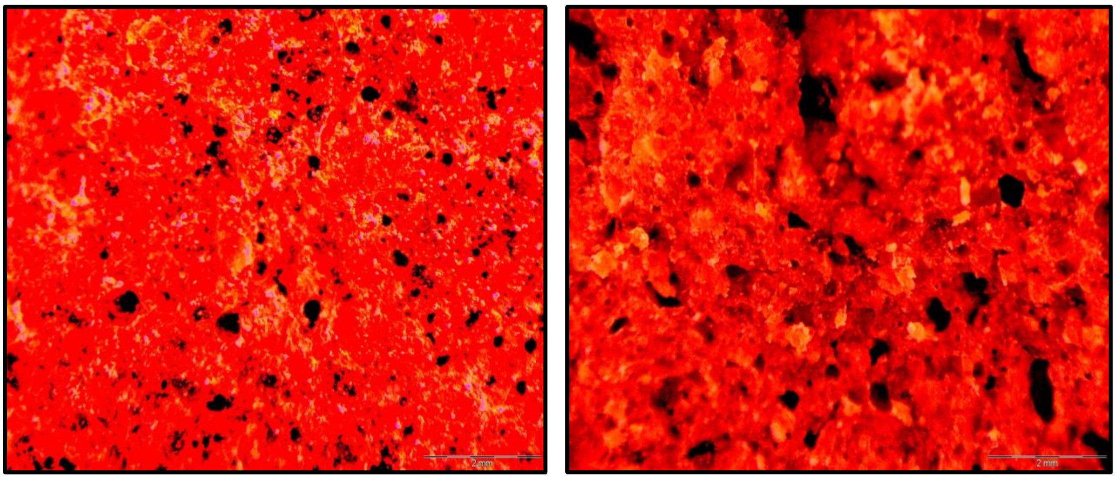
Figure 7.13 Relationship between porosity of geopolymer and cement mortar with different crude oil contamination (%)

Looking more in detail at similar magnifications, local variations in pore structure of geopolymer mortar can be seen. In both percentages of crude oil content the number of the pores, and the pore sizes, were higher with geopolymer compared to cement mortar, and a more open pore structure can be seen in Figure 14 (0%-Geopolymer mortar and10%-Geopolymer mortar). Many small micro-cracks can be seen in geopolymer with 10% of crude oil contaminations, as shown in Figure 7.15. Some of these micro-cracks show an open space appearing where few reaction products have developed. The overall structure looks denser, and fewer micro-cracks and less open space occur with hardened cement mortar, compared to geopolymer mortar. Based on the visual observations this may be due to lower workability observed with geopolymer mortar compared to cement mortar. The alkaline solution to fly ash ratio was made 0.5, which is similar to the optimum w/c ratio that was selected in Chapter 5 to make a workable consistency, which may have been affected if a different ratio had been used. However, percentages of micropores were higher with cement mortar compared to geopolymer mortar, which indicates that the large air voids were removed by the compaction when the cement mortar was used.



0%-Geopolymer mortar (magnification of 2mm)

10%-Geopolymer mortar (magnification of 2mm)



0%-Cement mortar (magnification of 2mm)

10%-Cement mortar (magnification of 2mm)

Figure 7.14 Microscopic images of the pore size distribution in geopolymer and cement mortar with and without crude oil contamination

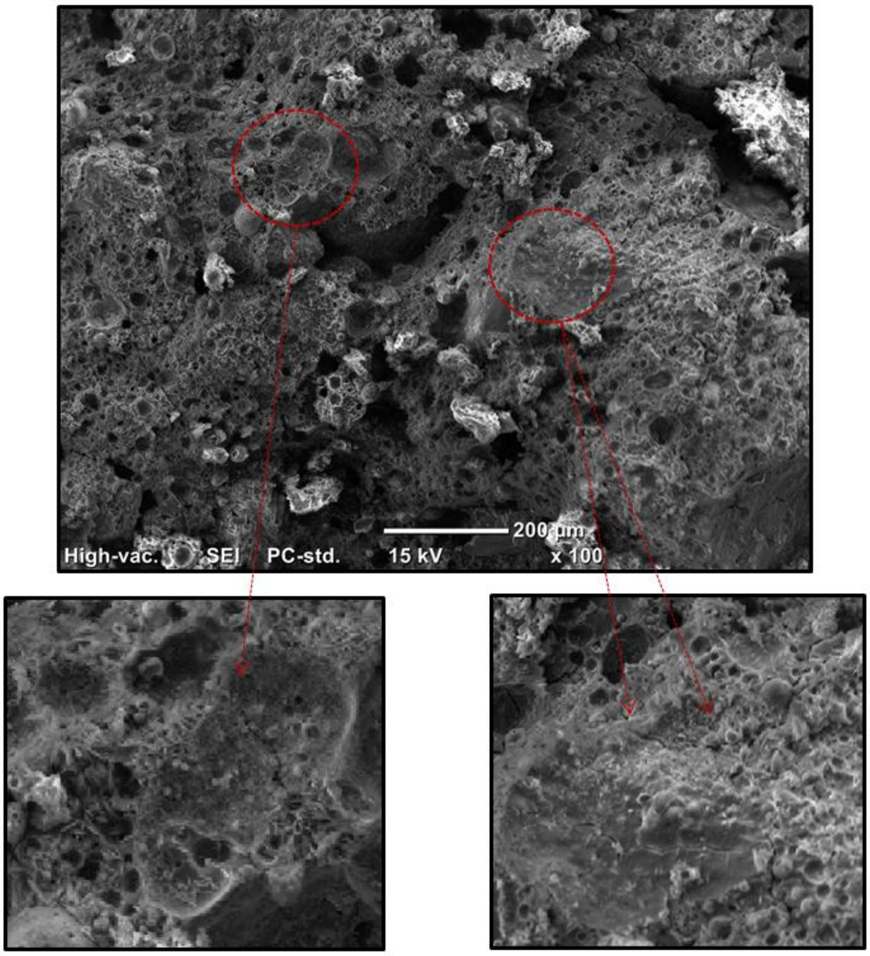


Figure 7.15 Micro-cracks at geopolymer mortar with 10% of crude oil contaminations

7.4.7 Influence of temperature on the hydration of activated fly ash

The influence of temperature on the reaction of fly ash, cement, and their blends, is elucidated in this section using the calorimetry tests, conducted on geopolymer mortar and cement mortar, containing 0% and 10% of light crude oil contaminations at 25 °C. Figure 7.16 shows the heat release response of activated fly ash while the OPC mortar was presented in Chapter 4 Figure 4.15 for comparison. Instead of the two-peak system observed for the cement mortar, as shown in Figure 4.15 (Chapter 4), the geopolymer mortar shows only one large peak that is generally observed within the first 1-2 hrs. The general single peak trend in geopolymer mortar mixture is due to the fact that the dissolution of some of the initial materials happens early, along with some gelation, to form reaction products, but no additional reaction products of exothermic kinetics are formed until much later. It is anticipated that when the later reactions take place, the heat release rate is in all probability slow and low.

For the fly ash activated pastes, an increase in crude oil content from 0% to 10% resulted in insignificant changes in the calorimetric response. The dissolution of the geopolymer mortar, with and without crude oil, was taking place simultaneously as indicated by the single peak response. The significant increase in peak intensity at 0% of crude oil indicated an increased amount of reaction products during the early stages. This resulted in the further diffusion-controlled reaction being slowed down, consequently influencing the rate of property development in such a system. A similar trend and similar temporal location of the acceleration peak, but with a lower rate by around 10%, were observed when 10% of crude oil contaminations was used compared to uncontaminated samples. However, adding 10% of light crude oil to OPC resulted in significant changes in the calorimetric response, especially with respect to the temporal location of the acceleration peak. Such a drastic change was not noticed for the fly ash activated paste, while the effect of light crude oil on the hydration process was discussed in detail in Chapter 4 section 4.5.4.

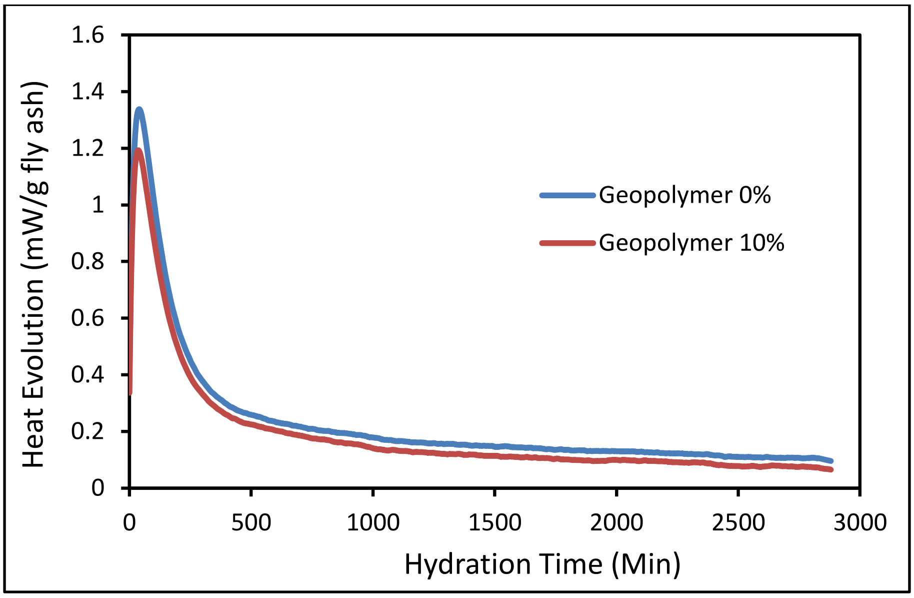


Figure 7.16 Influence of light crude oil on the calorimetric response of geopolymer mortar

Figure 7.17, shows that the increase in crude oil content decreased the cumulative heat values after 48 hrs, in geopolymer mortar, while the OPC mortar is presented in Figure 4.15 Chapter 4. The cumulative heat release values for geopolymer mortar were lower than those for cement mortar. The maximum cumulative heat releases (at 0% and 10%), after 48 hrs for geopolymer mortar, were found to be 196 J/g and 17.96 J/g, respectively. However, the maximum cumulative heat releases (at 0% and 10%), after 48 hrs for cement mortar, were found to be 243 J/g and 196.4 J/g, respectively. The reduction of cumulative heat evolution in both of geopolymer mortar and cement mortar provided evidence that the cumulative heat evolution was affected by the presence of light crude oil (Figure 7.17). The reaction of the alkaline solution with the fly ash was highly affected by the presence of 10% of light crude oil. The cumulative heat, evolved from specimens containing 10% of crude oil content, showed a significant reduction compared to uncontaminated samples, and it reached 91% in 2880 minutes. This shows the effect of light crude oil on the activation of NaOH activated fly ash mortar. This may be due to the influence of the light crude oil in the fly ash blend, which is more pronounced, and thus the difference in the cumulative heat flow curves are much larger for fly ash when compared to cement mortar (Chithiraputhiran, 2012).

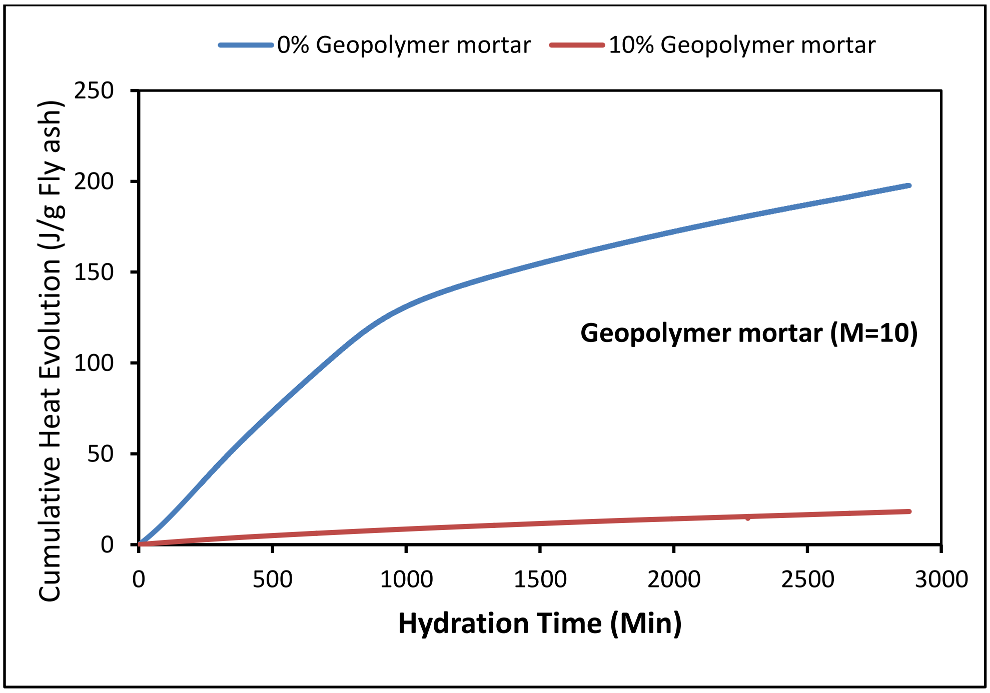


Figure 7.17 The isothermal calorimeter results of geopolymer mortar with 0% and 10% of light crude oil

7.5 Conclusion

This chapter has investigated the effect of light crude oil contamination on the physical, mechanical and microstructure of geopolymer mortar. Based on the results, the following conclusions were drawn:

- The geopolymer mortar containing oil contaminated fine sand, and cured under heat curing (HC), exhibited higher strength than those cured under ambient curing (AC) conditions. The HC mortars reached double the strength of AC mortars, indicating that heat curing is an effective method to produce a geopolymer mortar containing oil contaminated sand.

- The surface condition of the fine sand significantly affected the compressive strength of the geopolymer mortar. The compressive strength of the HC mortar with fine sand in the SSD condition was 10% higher than that of the HC mortar containing dry fine sand (both in an uncontaminated situation). However, it was generally lower than, or equal to, the HC mortars with oil-saturated sand, ranging from 0.5% to 4%, which could be attributed to three main reasons. Firstly, unlike oil, additional water to achieve the SSD condition reduced the alkalinity of the solution. Secondly, the thermal conductivity of oil is higher than that of the water. Thirdly, the sand reached optimum cohesion as a result of oil acting as a binding agent for the sand particles; hence, the mortar with oil achieved faster thermal equilibrium status than the mortar with water.

- Higher compressive strength was obtained at HC-1% and HC-2%, compared to HC-0%-SSD. This attributed to the higher thermal conductivity of oil than water. The heat transfers from the surface to the centre of the specimens containing crude oil were faster by 124 minutes when HC-2% was used compared to HC-0%-SSD. This indicates that the equilibrium thermal status of specimens containing crude oil was faster, as the thermal conductivity of oil is higher than water. Thus, a shorter time of thermal balance status was achieved with specimens containing crude oil, which improved the polymerisation process, resulting in higher compressive strength.

- Increasing the crude oil content by more than 1% reduced the compressive strength of the HC mortar, owing to two factors. First, the presence of a large amount of organic acids in crude oil induced the chemical reaction $H^+ + OH^-$ (H^+ comes from organic acids while OH^- originates from NaOH), which produced water (H_2O) in the mix that diluted the alkaline solution, thereby reducing the degree of polymerisation process. Second, the higher the crude oil content, the higher the total porosity, resulting in lower compressive strength.

- The efflorescence was observed for specimens with crude oil content from 0% to 2% both by the naked eye as well as on the SEM images but was not seen for mortar with 4% to 10% of light crude oil contamination. This indicates that increasing the crude oil content from 4% decreases or inhibits the efflorescence due to the filling up of the pores by the crude oil, and hence, this retarded the migratory paths for the salt solution in travelling through to the surface. However, the efflorescence did not affect the compressive strength due to low amount of macropores in geopolymer mortar with low percentages of oil contamination.

- Although the total porosity of the geopolymer was higher by around 2.3 times, compared to the porosity of the OPC, higher gain in strength was observed for geopolymer mortar than for OPC mortar. This may be related to the curing method used with the geopolymer, which is heat curing. This is because HC increases the kinetic energy and degree of reaction, which causes an increment in the density of the pore system, improving the mechanical properties of the resulting composite. Furthermore, the reaction of the alkaline solution, with the fly ash at 10% of crude oil contamination, was extremely high compared to cement mortar. This may be due to the influence of the light crude oil for fly ash blend, which is more pronounced, and thus the difference in the cumulative heat flow curves is much larger for the fly ash when compared to cement mortar.

These results demonstrated that the cement and geopolymer mortar containing fine sand contaminated with light crude oil has the potential of creating a new engineering material utilising waste materials that affect significantly the environment. Hence, in order to evaluate further the proper end use application of this waste material, an investigation of the properties of concrete containing fine sand contaminated with light crude oil is an important next step. Therefore, next Chapter the properties of concrete containing fine sand contaminated with light crude oil is presented.

Chapter 8

Properties of Concrete Containing Fine Sand Contaminated with Light Crude Oil

8.1 Introduction

The fundamental properties of cement mortar containing oil contaminated fine sand have been extensively investigated in the previous chapters. The results of these investigations have provided information on the proper mixing, curing, and effective water cement ratio to produce a cement mortar with optimal mechanical properties. In addition, a detailed understanding of how oil contamination impedes the hydration process, delays the strength development, and affects the mechanical properties of hardened mortar was gained. More importantly, these results point towards the high potential and beneficial use of oil contaminated sand in civil engineering and construction. This Chapter further explores the usage of oil contaminated sand in concrete and investigates how light crude oil contamination affects the important physical and mechanical properties of concrete.

It is well known that the successful use of waste materials in concrete depends on the developed mechanical properties of the end product. While some studies have investigated the effects of oil contamination on concrete, these studies have focussed only on heavy crude oil and engine oil (Ajagbe et al., 2012; Ahad and Ramzi, 2000; Hamad et al., 2003) as well as hydrocarbons (Hebatpuria et al., 1999; Cullinane et al., 1987; Hamad et al., 2003). More recently, Almabrok et al. (2013) have investigated the effect of incorporated mineral oil on the cement solidification process, and its consequent effect on the fresh and hardened properties of mortar. Almabrok et al. (2011) they further investigated oil solidification using a direct immobilization method. It is clear that the previous studies focussed only on medium to heavy crude oil, but no one has considered light crude oil (API > 31.1). Light crude oil is a typical oil contamination in oil producing countries such as Libya. This type of crude oil causes more adverse environmental effects than medium and heavy crude oil, as it easily penetrates and migrates through the sand particles. Moreover, most studies have focused only on the characterisation of the compressive strength of the produced concrete and none has evaluated the microstructure of concrete containing oil contaminated sand. Hence, this Chapter reports on an extensive investigation that was conducted to evaluate the effects of light crude oil on the mechanical properties of concrete, including compressive and tensile strength. In addition, microscopic observations were conducted to examine the porosity and microstructure of concrete. Data analysis and modelling was also applied to develop simplified equations to describe the mechanical properties of a concrete mix containing fine sand contaminated with light crude oil.

8.2 Materials and methods

8.2.1 Materials

The cement used for the investigation was Ordinary Portland Cement based on the Australian Standard (AS-1012.2, 2014). Clean potable water was used. The coarse aggregates had a maximum size of 10 mm, the particle size distribution of coarse aggregates is presented in Table 8.1, while the grain size of fine aggregates (fine sand) was less than 2.36 mm. The coarse aggregates were in SSD condition while the fine aggregate was mixed with different levels of light crude oil (0, 1, 2, 6, 10 and 20%). The main reason beyond choosing these percentages because these percentages represent the critical change point based on the results obtained from the previous Chapters. The preparation of oil contaminated sand is described in Section 4.2.1.

Table 8.1: Sieve analysis of coarse aggregates

Sieve size	% Weight retain	Cumulative %	% Passing
19 mm	0	0	100
9.5 mm	4.19	4.19	95.81
4.75 mm	91.34	95.53	4.47
2.36 mm	3.53	99.06	0.94
1.18 mm	0.52	99.58	0.42
600 μm	0.11	99.69	0.31
300 μm	0.06	99.75	0.25

150 µm	0.06	99.81	0.19
75 µm	0.12	99.93	0.07
Pan	0.07	100	0

8.2.2 Preparing and casting of concrete

Based on the appropriate mixing method determined in Chapter 4, the concrete was prepared following the recommendations by AS 1012.2 (1991), with mix proportions of 1 part of cement to 3 parts of fine sand and 3 parts of coarse gravel (10mm), and with a water cement ratio (w/c) of 0.5. The programs base concrete mix per batch was conducted based on the concrete mix proportions as shown in 8.2. Plastic moulds (100 mm diameter and 200mm high) were used to avoid any contamination and for easy removal of the cylindrical specimens. Concrete was prepared at a room temperature of around 22ºC, while the curing took place in a fog room set at 25 ºC and 85% humidity for 28 days.

Mixing De-moulding Curing in fog room

Figure 8.1 Shows the preparation steps of concrete containing different percentages of light crude oil

Table 8.2 Materials for mix design

Material	*Quantity (kg)*
OPC	5.32
Water	2.66
Fine Aggregate	15.97
Course Aggregate	15.97

8.2.3 Compression strength test

Compressive strength tests of concrete cylinders with different levels of crude oil contamination were conducted following the procedures prescribed in AS-1012.9 (2014). The specimens were tested to failure using a 2000 kN SANS hydraulic compression testing machine (Figure 8.2). The load was applied at a rate of 2 mm/min. The maximum load applied to the specimen was then recorded and the type of failure was noted. An average of three samples was taken as representative of the compressive strength of the concrete cylinders.

SANS Machine Compression test

Figure 8.2 SANS machine used for compression

8.2.4 Splitting tensile test

The splitting tensile test was conducted as per AS-1012.10 (2000). The test was carried out by placing a cylindrical specimen horizontally between the load surfaces of a 2000 kN capacity servo hydraulic testing machine. The load was applied at a rate of 2 mm/min until failure of the cylinder was observed (Figure 8.3). The maximum load applied to the specimen was then recorded and the type of failure was noted. An average of three samples was taken as representative of the splitting tensile strength of the concrete cylinders.

Figure 8.3 Splitting tensile test using SANS machine

8.2.5 Porosity and Microstructure observations

Typical normal strength Portland cement concrete usually has a density of approximately 2400 kg/m3 and varies depending on the amount and the density of aggregate, air voids, cement-water ratio, and the maximum size of aggregate used (Dorf, 2004). Thus, prior to conducting the mechanical tests, the density of test specimens was estimated through the measured mass and volume of each specimen. Moreover, visual observation of the pore sizes and distribution was conducted for all specimens. A microscope (Motic SMZ-168 series, Motic China Group Co., Ltd.) was used, as shown in Figure 8.4 (a), to examine the microstructure and a measurement of the pore diameters at the fracture surface of the tested concrete cylinders. The results were compared with the microstructure observed using a scanning electron microscope (SEM) (JEOL JCM-6000, Tokyo, Japan), as shown in Figure 8.4 (b).

Microscope (Motic SMZ-168 series)

Scanning Electron Microscope (SEM)

Figure 8.4 Microscopes and SEM

8.3 Results and observation

8.3.1 Surface voids and density

A number of visual differences were observed for the specimens containing different light crude oil contaminations. For instance, increasing the crude oil content increases the surface voids as well as the wetness of the specimens, as shown in Figure 8.5. The surface voids were clearly observed from 6% of light crude oil contaminations and they became larger in size and more distributed over the surface for 10% and 20%. Similarly, the wetness was more noticeable for specimens with 10% and 20% light crude oil contamination than for the other specimens. In these specimens, dark patches of oil could be clearly seen on the surface. Moreover, the specimens with 20% crude oil contamination were excessively saturated with oil appearing to be dark brown in colour, and the oil smell was strong.

Figure 8.5 Surface voids of concrete with different levels of crude oil contamination

Table 8.3 shows the total bulk density of the concrete with different crude oil contaminations. It can be observed that the crude oil content affects the density of the concrete. As the crude oil content increases, the density of the specimens decreases. The highest density was 2439.5 kg/m^3 (for uncontaminated samples) and the lowest density was 2240.7 kg/m^3 for specimens with 20% crude oil contamination. This can be explained by the surface voids observed in the specimens, which progressively became apparent as the oil contamination increased, resulting in a decrease in the specimen’s density.

Table 8.3 Density of specimens with varied oil content

Density of Specimens (kg/m^3)					
Oil Content	Specimens			Average	Standard Deviation
	1	2	3		
0%	2443.5	2445.9	2429	2439.5	7.4
1%	2429.5	2451.7	2420.9	2434.0	13
2%	2423.2	2426.4	2389.9	2413.2	16.5
6%	2403.9	2391.8	2379.3	2391.7	10
10%	2339	2331.3	2337.9	2336.1	3.4
20%	2248.7	2230.7	2242.6	2240.7	7.5

8.3.2 Compressive behaviour

The compressive strength of concrete was calculated by dividing the maximum failure load by the actual cross sectional area of each sample. Table 8.4 shows the average compressive strength (MPa) of concrete containing fine sand with different levels of light crude oil (0, 1, 2, 6, 10 and 20%). It is to be noted that there were only two specimens for concrete with 2% oil contamination, due to premature failure of one of the cylinders. Regardless, the standard deviation and the coefficient of variation were small, indicating the consistency of the measured compressive strength. It can be observed that the average of the compressive strength at 1% of crude oil contamination was slightly higher compared to uncontaminated samples. However, by considering the SD, 0% and 1% of light crude oil contaminations provided similar results. The highest compressive strength was observed at 1% of crude oil contaminations 25.63MPa, while the concrete cylinder with 20% of light crude oil contamination had the lowest strength of 4.74 MPa.

Table 8.4 Compressive strength of concrete cylinders with different levels of oil contamination

Oil Content	Specimens			Average	Standard Deviation	Coefficient of variation
	1	2	3			
0%	25.29	24.2	24.4	24.63	0.58	0.023
1%	26.67	23.96	26.28	25.63	1.45	0.057
2%	21.38	-	22.6	21.99	0.862	0.039
6%	17.66	18.82	18.42	18.3	0.582	0.032
10%	13.72	14.3	13.59	13.87	0.376	0.027
20%	4.55	4.93	4.8	4.76	0.193	0.04

The failure mechanisms of the compressed concrete provide an indication of the compressive strength of the specimens. Most specimens with 0% to 6% oil contamination displayed a splitting-type failure, as shown in Figure 8.6. This failure mode (splitting failure) occurred from the bottom cap and travelled perpendicular to the load. On the other hand, increasing the level of light crude oil contamination to 10% and 20% resulted in the specimens failing in shear, with crushing at the top. The crushing occurred due to the saturation status of the concrete cylinders with light crude oil contaminations, and resulted in a lower compressive strength.

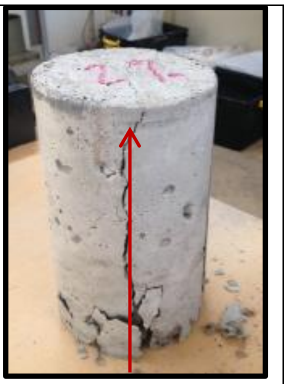
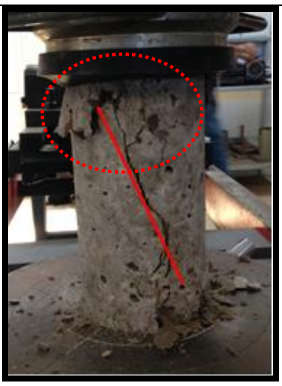
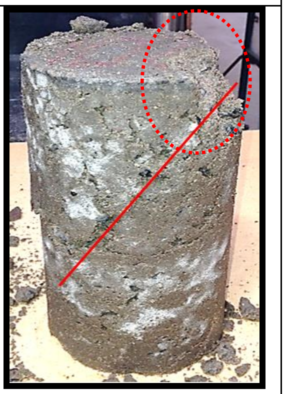
		
Splitting with fracture conically	Splitting failure	
0%	1%	2%
		
Splitting failure	(Shear failure) with fracture conically	
6%	10%	20%

Figure 8.6 Failure modes of specimens containing different crude oil content. (Splitting shear failures with and without fracture)

8.3.3 Splitting tensile behaviour

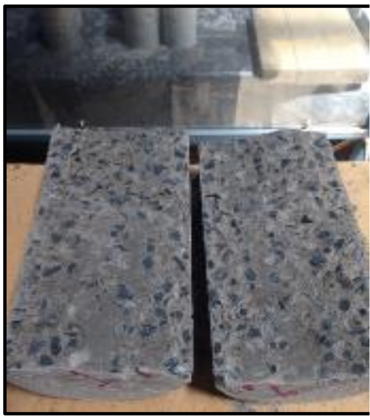
The average values of the splitting tensile strength (MPa) of concrete specimens with different levels of crude oil are presented in Table 8.5. The standard deviation and the coefficient of variation are small, indicating the consistency of the measured tensile strength. The optimum value of the splitting tensile strength of 8.38 MPa was observed for specimens containing 1% of crude oil contamination, while the lowest value of 2.27 MPa was observed for 20%.

Table 8.5 Splitting tensile strength of concrete with oil contamination

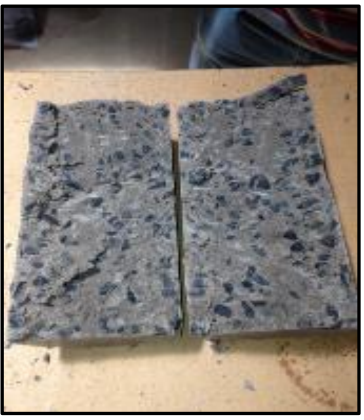
Oil Content	Specimens			Average	Standard Deviation	Coefficient of variation
	1	2	3			
0%	8.46	6.79	8.13	7.79	0.884	0.113
1%	8.26	-	8.51	8.38	0.176	0.021
2%	6.91	5.51	6.34	6.25	0.704	0.112
6%	5.77	5.17	6.79	5.91	0.819	0.138
10%	4.33	4.16	6.97	5.16	1.575	0.305
20%	2.06	2.76	2	2.27	0.422	0.186

Figure 8.7 shows the typical splitting tensile failure modes of the concrete specimens with different crude oil contaminations. Furthermore, the distribution of the coarse aggregates can be clearly seen at the high level of crude oil contamination. This may be due to large percentage of crude oil which increased the workability and hence, it partly segregated and caused the discontinued distribution of solid materials. An initial indication of failure under the splitting tensile test was the audible cracking noises that could be heard during testing. The noise was clearly heard up for up to 6% of crude oil contamination, but decreased for 10% and 20%. Observation inside the specimens clearly showed the crude oil filling the voids of cylinders with 10% and 20% contaminations, but could hardly be noticed in 1% to 4%. The oil appeared in the form of crystallised yellow particles, as shown in Figure 8.7 (crude oil 6%).

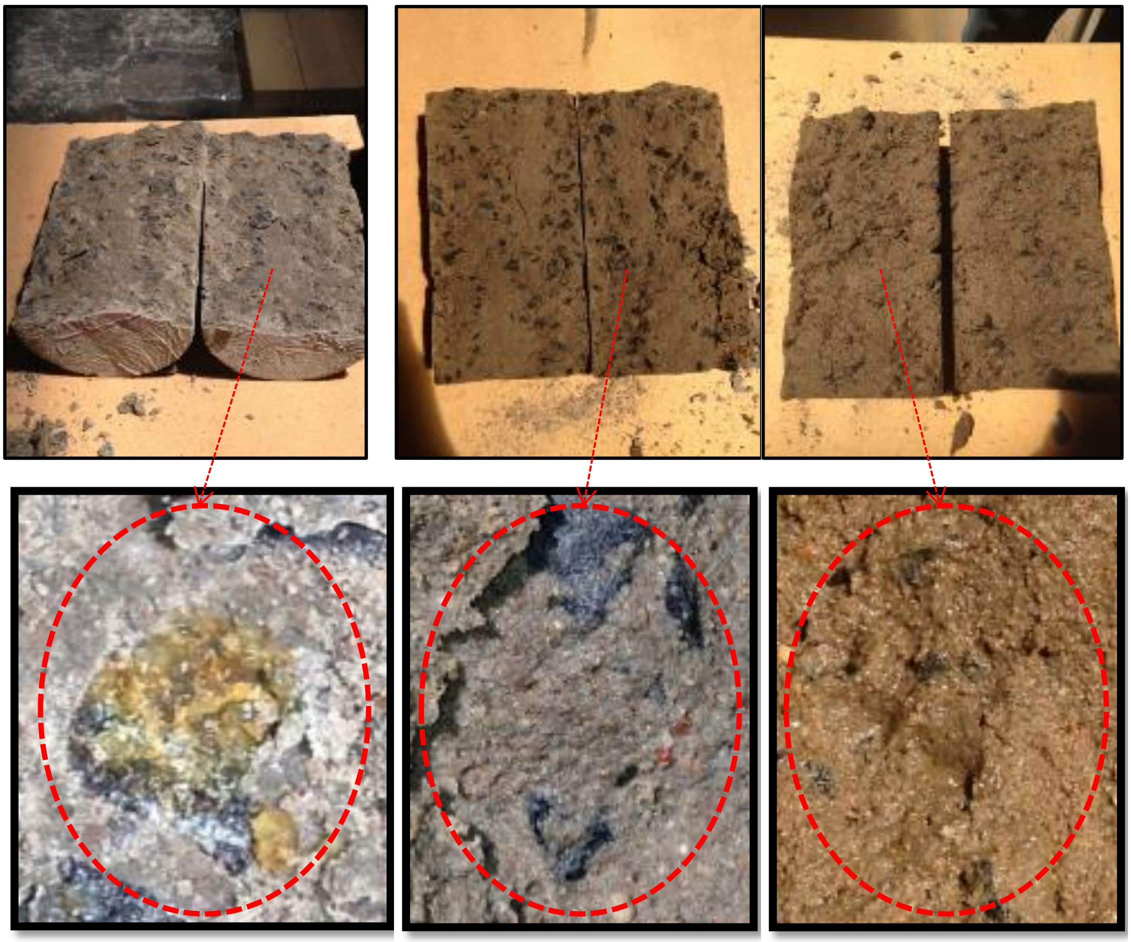
Crude oil 0%



Crude oil 1%



Crude oil 2%



Crude oil 6%   Crude oil 10%   Crude oil 20%

Figure 8.7 Splitting tensile failure modes of concrete with different crude oil content

8.4 Discussion

8.4.1 Effect of crude oil contamination on physical properties

Increasing the crude oil content affected both the concrete porosity and the wetness of the specimens. After 28 days of curing, the samples with 20% oil contamination were excessively porous and saturated, as shown in Figure 8.5. The increment of the porosity at a high level of oil contamination was due to the water seepage during curing. As evidence, water was found in plastic bags, especially for specimens with an oil contamination above 6%. Almabrok et al. (2013) also suspected that the water absorption during curing was prevented due to the saturation status caused by crude oil contamination. As a result, this prolonged the setting time, inhibited the hydration process, and increased the air content.

A study by Madderom and President (1980) demonstrated that water seepage increased the concrete porosity and hence the pores acted as reservoirs that were formed around the aggregates. As a result of over-saturation, air pockets were formed. These authors further indicated that the cement and fine particles carried outwards during seepage weakened the concrete surface by around 20%. Thus, the pores appearing on the surface of the specimens could be due to the vertical water channels and oil seeping from the concrete surface. As result of porosity, density of the hardened concrete decreased as the amount crude oil content increased.

8.4.2 Effect of Oil contamination on Compressive Strength Behaviour

Figure 8.8 shows the average compressive strength of the concrete with different levels of oil contamination. It can be clearly seen that the increase in the level of light crude oil contamination results in decreases in concrete compressive strength. Nevertheless, the compressive strength of concrete with 1% light crude oil contamination is 4.06% higher than the uncontaminated samples. The increase in strength may be due to oil optimising concrete cohesion, without causing water seepage. In Chapter 3, it was found that sand contaminated with 1% of light crude oil achieved an optimum sand cohesion of 10.76 kPa. As a consequence, the total porosity at 1% was less than that at 0%, as shown in Figure 8.10. Above 1%, the sand became saturated with oil, resulting in a reduced compressive strength. This reduction in compressive strength may be due to incompletion of the hydration process at 28 days for concrete with high level of crude oil content. It was found in Chapter 6 that the cement mortar containing fine sand with more than 2% of oil contamination achieved most of its compressive strength only after 56 days of curing. Moreover, increasing the light crude oil from 2% to 20% may have hindered the bond formation between mortar and aggregates, as the oil was coating the sand and the course aggregates. As shown in Figure 8.9, excess oil was present in the space previously occupied by aggregates. When the aggregates exceed the saturated surface dry (SSD) condition, this achieves a damp or wet status where all the pores are completely filled with oil (Neuwald, 2010). Thus the surface area that is able to bond with cement mortar is decreased, leaving the aggregates surrounded by a barrier of oil. Similarly, the formation of oil around the sand particles acts as a cushion preventing inter-particle contact, and the lack of cohesion promotes slippage between the sand particles. After seepage of water, air voids are left and the result is a relatively porous cement paste that has a low internal strength, hence limiting the ultimate compressive strength of concrete.

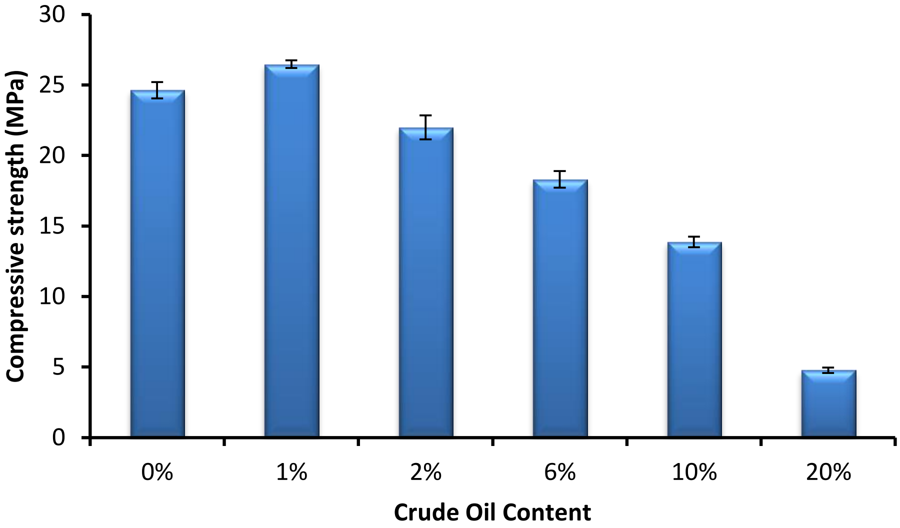
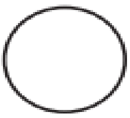
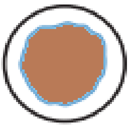
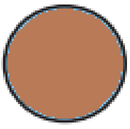


Figure 8.8 Average compressive strength of specimens with different crude oil

State		Total saturation	Crude oil content (%)
Uncontaminated aggregate		None	
			0%
Aggregate partially coated by crude oil		Less than potential absorption	
			0.5%-2%
Aggregate coated by crude oil		Equal to potential absorption	
			4%-6%

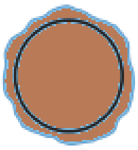
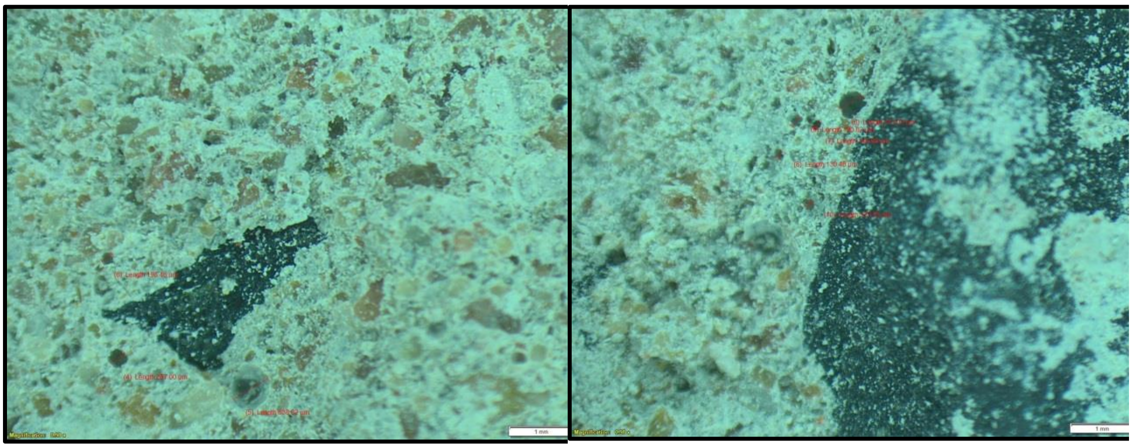
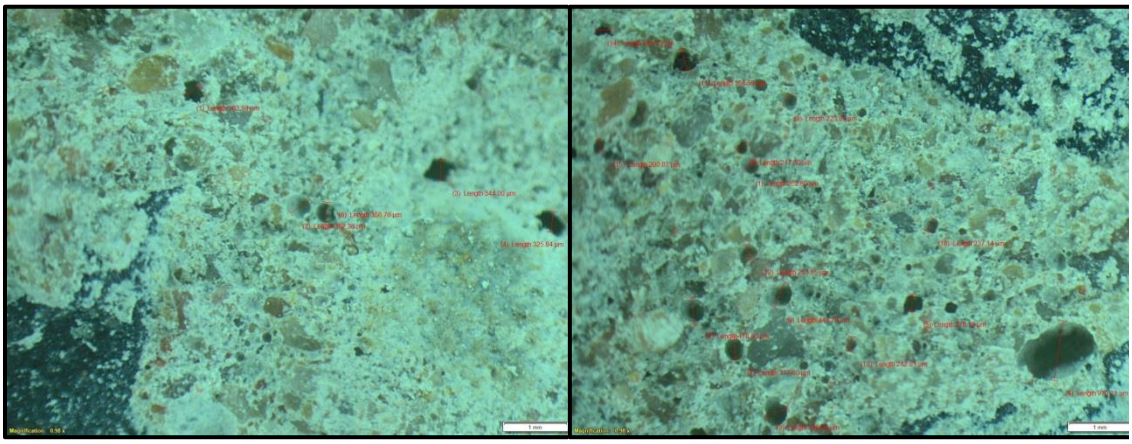
Aggregate saturated by crude oil "Saturation status"		Greater than absorption	
			10%-20%

Figure 8.9 Moisture conditions of aggregate (sand, coarse) compared to that observed at a high level of crude oil content (10% and 20%)

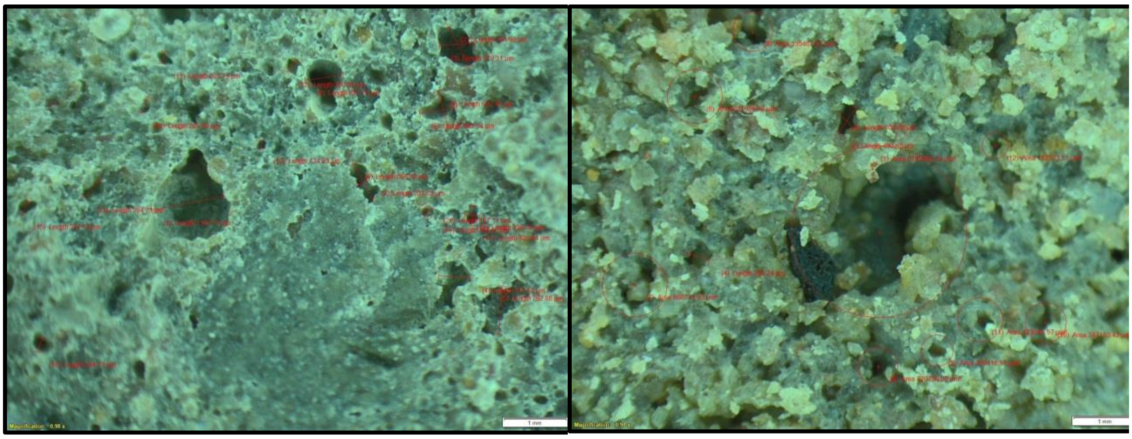
The reduction of compressive strength of concrete containing contaminated fine sand at a high level of light crude oil can be further explained by the increase in the pore sizes. In order to measure the pore sizes, the surfaces of the specimen sections were imaged using TBitmap software as explained in Chapter 4, section 4.2.6. At least 25 images were used for each sample, which represents around 20% of the total surface area. Figure 8.10 shows that with the increase of the crude oil content from 2% to 20% of crude oil contamination, the number and the size of pores increases. This is due to the free water in the concrete mix that was not utilised during the hydration process, creating pores in the concrete mix. These pores transcend even at the surface of the specimens, as shown in Figure 8.6.



(a) 0% (average pore diameter: 454μm)　(b) 1% (average pore diameter: 368μm)



(c) 2% (average pore diameter: 446μm) (d) 6% (average pore diameter: 500μm)



(e)10% (average pore diameter: 720μm) (f) 20% (average pore diameter: 877.95μm)

Figure 8.10 Average pore size diameter of concrete with light crude oil contamination

8.4.3 Comparison between the compressive strength of mortar and concrete

Figure 8.11 shows the comparison between the compressive strength of cement mortar and concrete with different levels of oil contamination. In this figure, the percentage (%) increase or decrease in the compressive strength was calculated, based on the strength of the uncontaminated samples (0%). It is worth noting that the overall trend was similar with a higher value of the compressive strength, as obtained in mortar compared to concrete. This is despite the total volume of light crude oil being less for concrete than for cement mortar, due to the addition of coarse aggregates, even though the mix percentage of oil contamination by weight of sand is the same. At 1% of crude oil contamination, the cement mortar exhibited a 24.4% higher compressive strength than uncontaminated samples, while only an increase of 7.49 % was shown by the concrete. At 2% of crude oil contamination, the mortar still has a 10.5% higher compressive strength than uncontaminated samples, but the compressive strength of concrete decreased by 10%. Up to 9% and 17% lower compressive strength was observed for mortar with 6% and 10% light crude oil contamination, respectively, whereas the decrease in concrete was as much as 25% and 43%, respectively. At 20% light crude oil contamination, the reduction of compressive strength was almost the same for both mortar and concrete, which was around 80%.

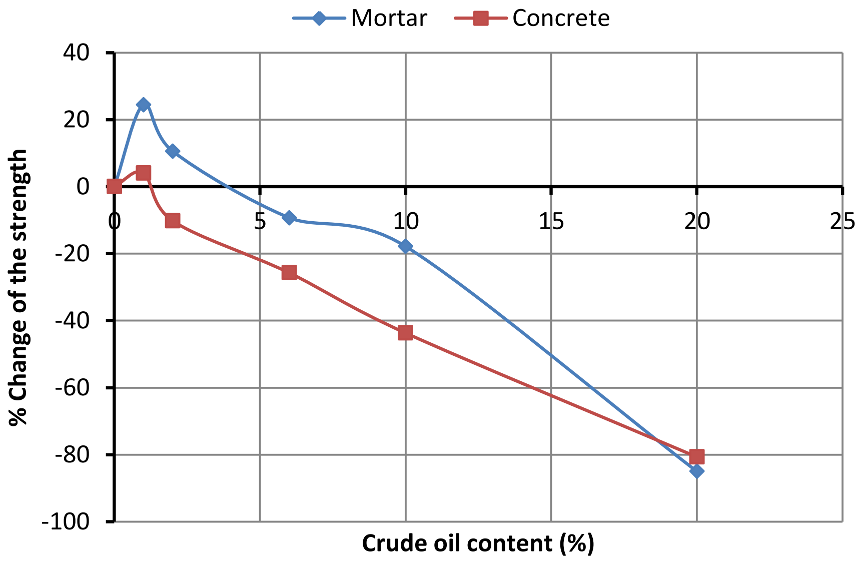
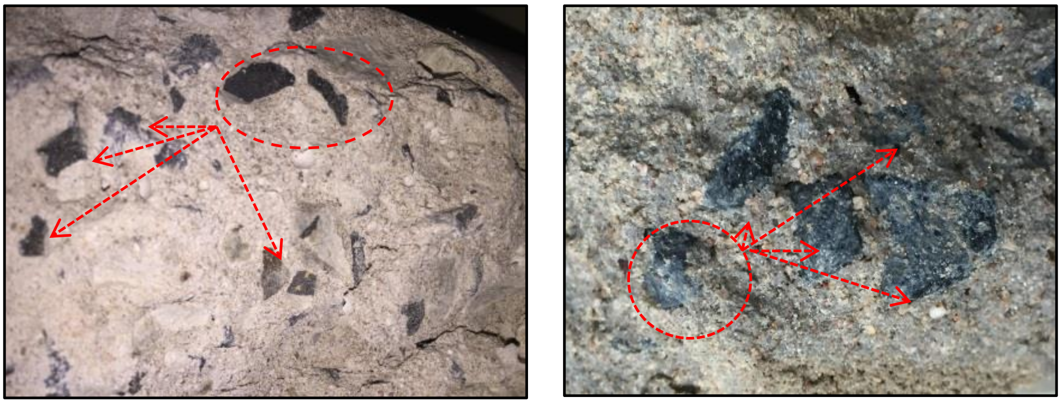


Figure 8.11 Normalized compressive strength between mortar and concrete containing light crude oil contamination

The higher reduction in compressive strength of the concrete with oil contamination, compared to cement mortar, was due to two main reasons: 1) lower cement binder to aggregates ratio (C:A); and 2) bigger aggregates size. Decreasing the amount of binder reduces the ability of the cement to fully cover the aggregates, hence yielding a void structure that forms a path for water permeation. It can be noted that the total volume of the fine sand used with cement mortar was around 75% (1:3), while the combination of fine and coarse aggregates for concrete accounted for almost 85% (1:3:3). This can be related to the internal structure of a pervious concrete, which is relatively less compact due to the insufficient amount of binders which produce the voids (Fu et al. (2014). In addition, the presence of crude oil in high percentages hinders the bond formation between the cement to the large surface area of the coarse aggregates, resulting in more segregation in concrete than in mortar (Osuji and Nwankwo, 2015). As a result, the compressive strength was lower for concrete compared to mortar. Furthermore, as the aggregate size increased, the water permeability of concrete increased. It is worth mentioning here that the connected porosity increased as the aggregate size increased. Previous studies conducted by Fu et al. (2014); Chang et al. (2016) have shown that the compressive and splitting tensile strengths increased as the amount of binder increased, and they decreased with an increase in aggregate size.

The higher strength exhibited by the cement mortar than the concrete, under different percentages of crude oil content, may also be due to an increase in the contaminated surface area of the aggregates. In the concrete mix, the surface area of the coarse aggregate is also coated by crude oil, as shown in Figure 8.12, especially at a high level of crude oil content of 10% and 20%. As a consequence, the total surface area of aggregate achieved damp or wet status (saturation status). Achieving the saturation status of aggregate by crude oil means extra free water will remain in the mix. This hindered the bond formation between cement and the coarse aggregates, resulting in more segregation for concrete than for mortar (Osuji and Nwankwo, 2015). As a result, the compressive strength was lower for concrete compared to mortar.



0% - Uncontaminated aggregates

20%-Coarse aggregate coated by crude oil

Figure 8.12 The surface area of the coarse aggregate under different crude oil contaminations

8.4.4 Splitting tensile strength of concrete with contaminated fine sand

Figure 8.13 shows the relationship between the splitting tensile strength of concrete at 28 days, and the levels of crude oil contamination. The specimens with 1% of crude oil contamination showed a 7.6% higher splitting tensile strength, compared to uncontaminated samples. In contrast, increasing the crude oil contamination to 2%, 6% and 10% decreased the tensile strength by 19%, 24%, and 33%, respectively; while at 20% of light crude oil contamination, a reduction of 70% was observed, compared to uncontaminated samples. These results indicated that the splitting tensile strength of the concrete was enhanced by adding light crude oil content up to 1% but beyond this, the tensile strength decreased. The increase in strength was attributed to the sand reaching optimum cohesion at this level of oil contamination, as a result of oil binding sand particles. On the other hand, increasing the crude oil content above 2% caused the fine sand to exceed the equilibrium condition, and the oil also contaminated the surface of the coarse aggregates. As a consequence, the bond between the cement paste and coarse aggregates was affected, resulting in a decrease in tensile strength. Figure 8.14 shows the failure of the specimens occurred between the cement paste and the surfaces of the largest coarse aggregate particles. This is a bond failure mode.

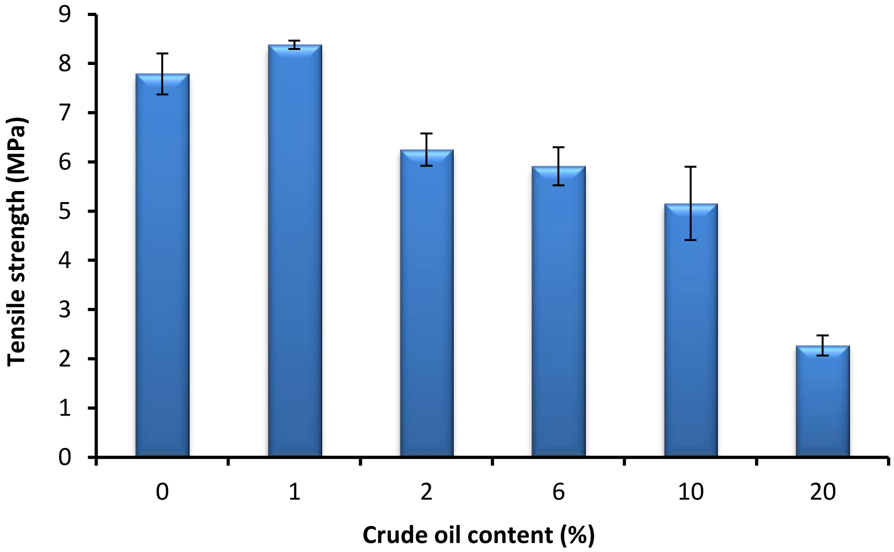
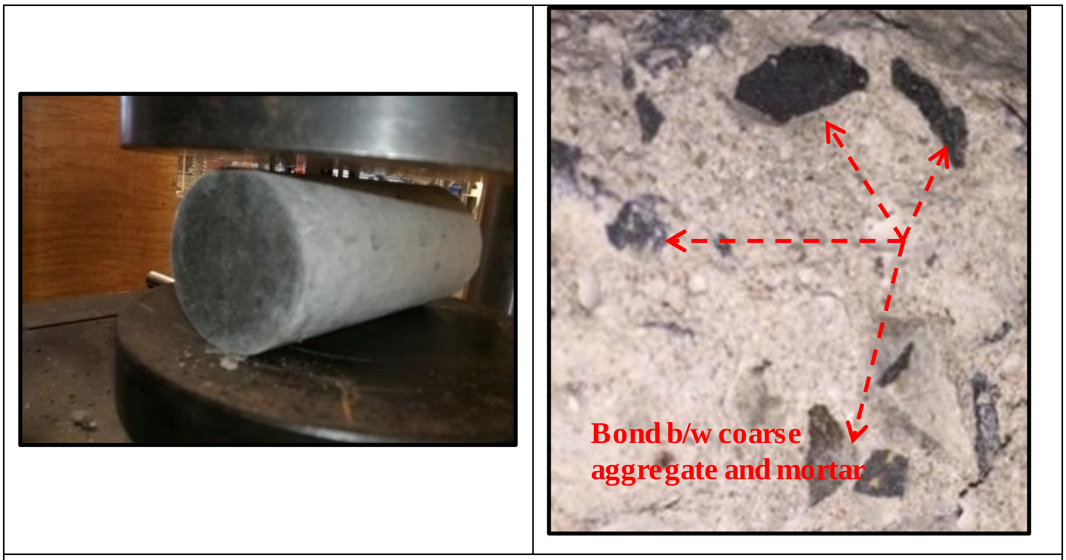


Figure 8.13 Splitting tensile strength test results of oil contaminated concrete

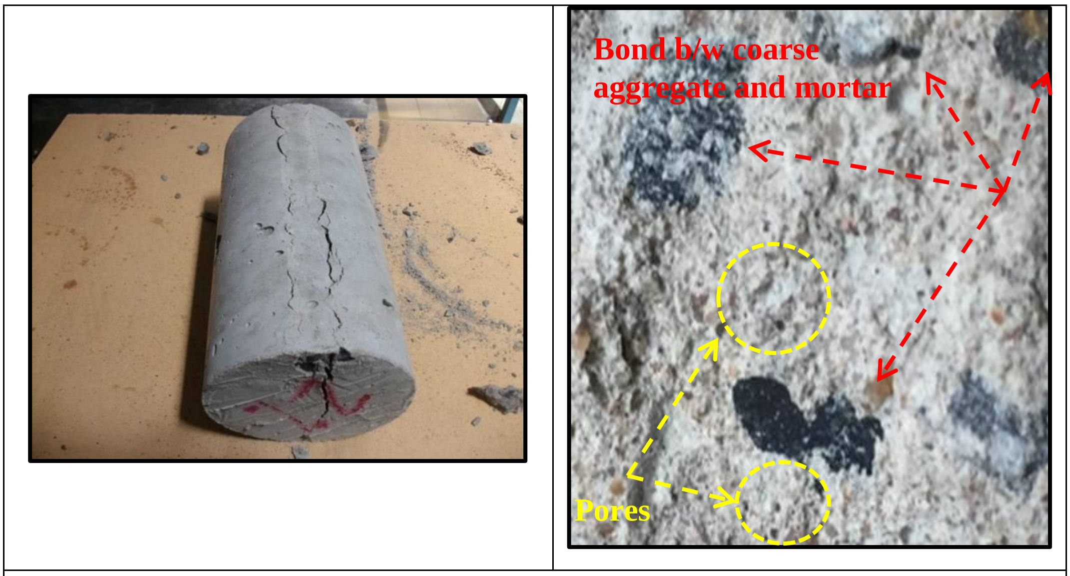
At 6% to 20% oil contamination level, the aggregate particles were expected to be fully covered by oil. This oil creates a thick film over the surface of the aggregates, which decreases their bond with the cement paste, as oil is a hydrophobic material. However, it was observed that emulsion was created at the surface of the aggregates. As was discussed in section 7.4.3, the soft particles of fine sand and cement particles can act as the emulsifying agent because they can work as finely dispersed solids.

Figure 8.14(a-f) shows the cement particles attached to the surface area of the coarse aggregates with up to 10% in crude oil contaminations. However at 20% of crude oil contaminations, the cement particles could not be seen at the surface area of the coarse aggregates, due to the high saturation status of the concrete mix by the crude oil at 20%. As a result, the interaction between the oil/water and the fine particles was far from the surface of the aggregates. Thus, the crude oil worked as an isolator, preventing the bond between the cement paste and the aggregates, and thus resulting in lower compressive strength.

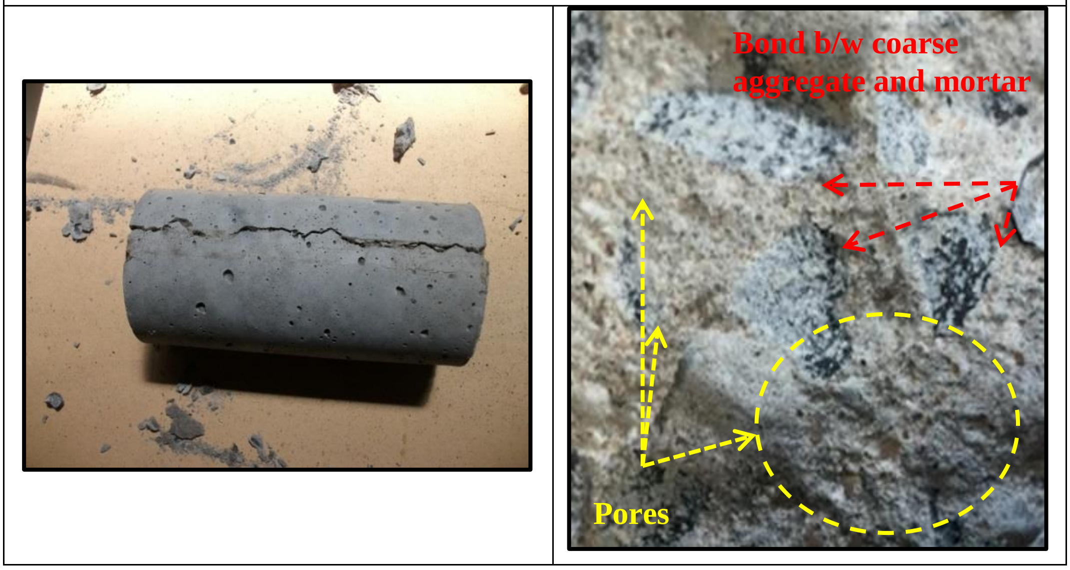


Splitting tensile 0% (a)

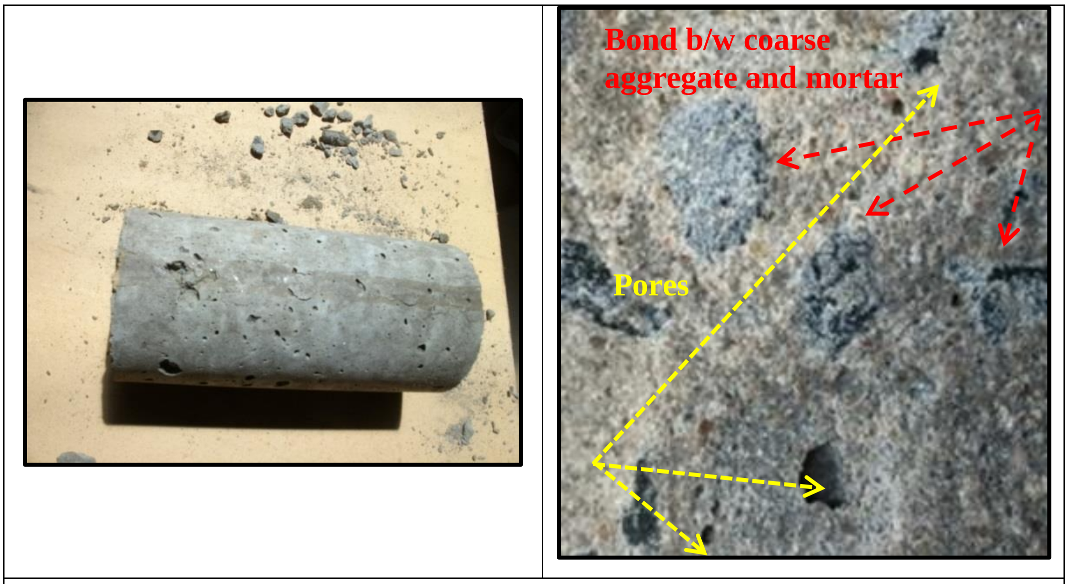
Splitting tensile 1% (b)



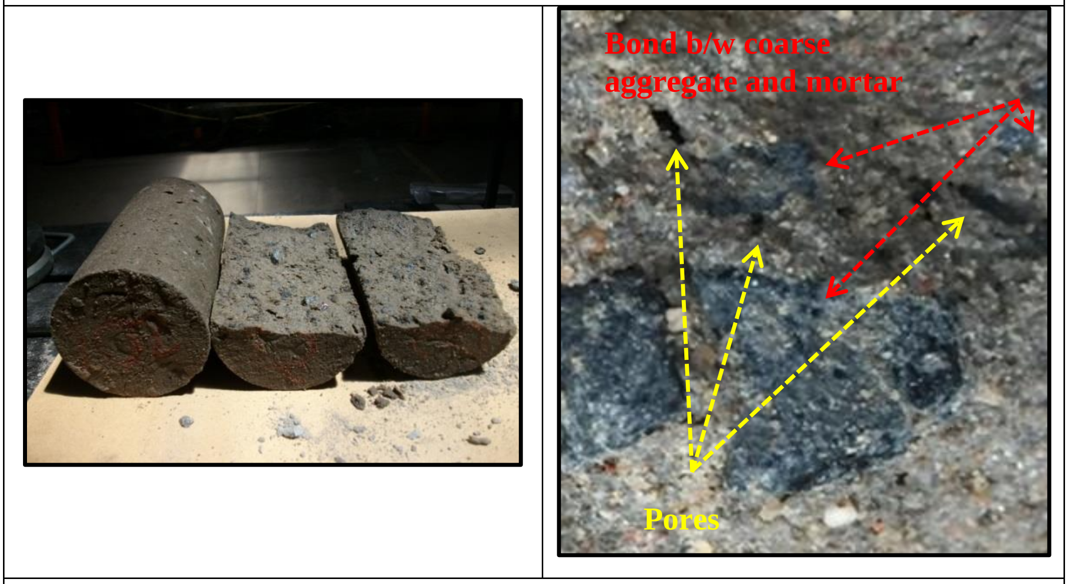
Splitting tensile 2% (c)



Splitting tensile 6% (d)



Splitting tensile 10% (e)



Splitting tensile 20% (f)

Figure 8.14 (a-f) Fracture surface of the concrete with oil contaminated sand

8.4.5 Compressive and tensile strength relationship

Figure 8.15 shows the normalised effect on the compressive strength and splitting tensile strength of concrete containing fine sand with oil contamination. The behaviour of the splitting tensile strength shows a similar pattern to that of compressive strength, but with the percentage of reduction less than for compressive strength. Jasim and Jawad (2010) have attributed this behaviour to the inconsistency of the effect of crude oil contamination between the tensile and compressive properties. Kovler (2012) has indicated that the adding some waste materials, such as superabsorbent polymers (SAP), to concrete can improve the tensile strength to a higher extent than the compressive strength. This can be related to the fact that tensile strength is sensitive to cracking, so any improvement of cracking resistance is expected to be beneficial in terms of tensile properties. This indicates that the viscosity of oil had a significant effect on the splitting tensile strength of concrete, compared to its compressive strength.

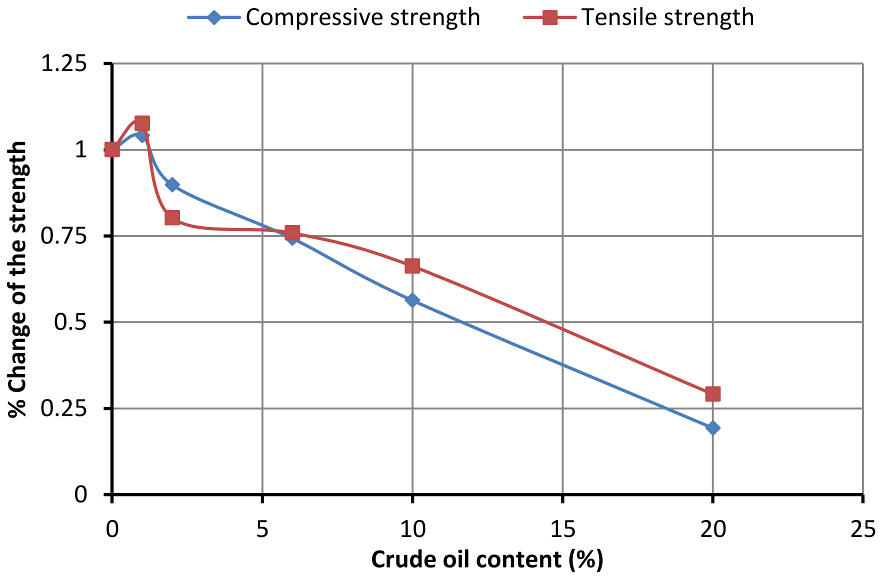
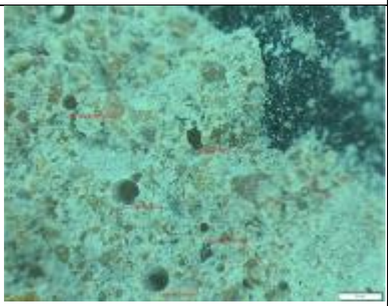
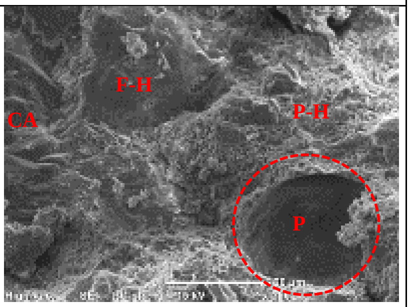
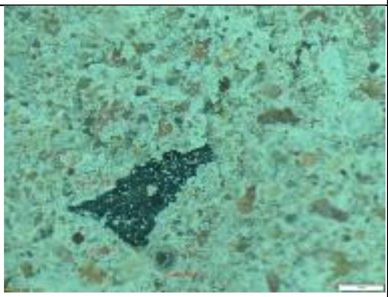
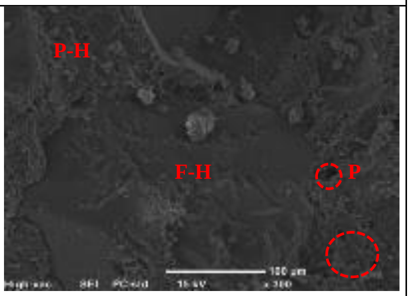


Figure 8.15 Normalized relationships between the tensile compressive strength with different crude oil contaminations

8.4.6 Relationship of porosity, microstructure and compressive strength

The porosity of the specimens with different crude oil content, through visual observation, microscopic images and SEM, is shown in Figure 8.16. Based on the visual observation, the pore size and the pore distribution was found to have decreased slightly for concrete with 1% light crude oil contamination, compared to uncontaminated samples (0%). This was attributed to the sand reaching optimum cohesion as a result of oil binding sand particles, as shown in Chapter 3. Thus, the higher strength of concrete with this level of oil contamination was obtained compared to uncontaminated concrete. In contrast, increasing the crude oil from 2% up to 20% of crude oil contamination increases both the sizes and distributions of the pores. From the microscopic observations, the average pore size in the uncontaminated samples was 454 µm, but only 368 µm for 1% of crude oil contamination. This increased to 446 µm, 500 µm, 720 µm, and 877 µm for 2%, 6%, 10%, and 20% oil of contamination respectively, as shown in Figure 8.10. Furthermore, the interconnection between the large pores, as well as the wettability of the specimens, was high at 20% of crude oil contaminations.

The SEM images in Figure 8.16 can be divided into full hydrated cement (F-H), partially hydrated cement (P-H), pores (P), and the coarse aggregate (CA). In these images, it can be notice that the pore sizes and P-H area were smaller for 1% of crude oil contamination than for uncontaminated samples, which is an indication of an enhanced hydration process. However, as the amount of crude oil increased above 1%, the F-H decreased, while the P-H and pore size increased.

Oil (%)	Surface of the specimens	Microscopic images	SEM images
0			
1			

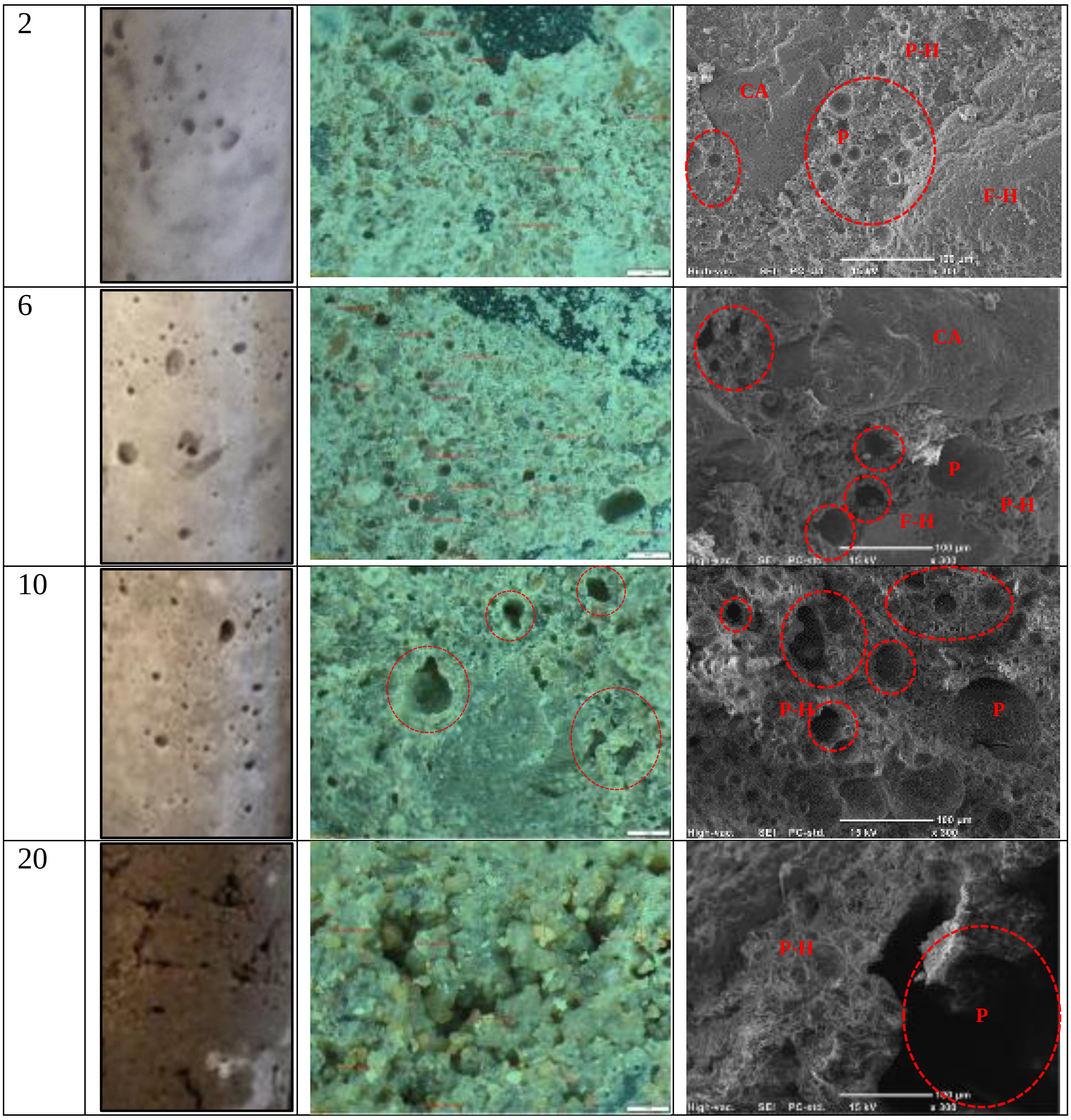


Figure 8.16 Shows the porosity of the specimens with different crude oil content through visual observation, microscopic images and SEM

From the three observation methods used (visual observation, microscopic and SEM) it can be seen that the size and distribution of the pores increased as the amount of crude oil increased (from 2% to 20%). As the oil is hydrophobic, the molecules of oil will bond much more readily with each other than with the water molecules, creating a barrier to the surface of aggregate particles. As a result, this decreases the contact between the cement paste and the aggregates. Moreover, some of the water added to the concrete mix will remain free, creating more and bigger pores compared to uncontaminated samples. Kim et al. (2014) have stated that any excess water can cause segregation of the aggregates and degradation of strength and durability. These authors have further indicated that in a normal concrete mix with the same cement content, hydration can be more easily activated with larger unit water content. Despite this, the consumed water for hydration reaction in the cement paste created more pores, which led to a reduction in compressive strength, even with the same amount of hydration products.

8.4.7 Data Analysis and Modelling

8.4.7.1 Compressive strength of concrete

Data analysis and modelling was conducted to develop simplified prediction equations of the mechanical properties of a concrete mix containing fine sand contaminated with light crude oil. The simulation data was analysed with a one-way repeated Analysis of Variance ANOVA (Miller, 1997) to confirm the significance of light crude oil in the modelling of compressive strength. The ANOVA results are shown in Table 8.6 for *F-statistics and p-values.* Parameters with ($p < 0.01$) were considered to have a significant impact on the compressive strength. The analysis results indicate that compressive strength was affected by each value of light crude oil as p-value 2.19203×10^{-12}.

Table 8.6 ANOVA results for main and interaction effects

Source	Sum of squares	Degree of freedom	Mean squares	F-statistics	p-values
Light crude oil	934.217	5	186.8	326.5	2.19×10^{-12}

The relationship between compressive strength and light crude oil can be established from the ANOVA analysis and Figure 8.8. It was found that there was a polynomial relationship between the compressive strength and the level of light crude oil contamination. The rational model shown in Equation 8.1 was formulated to estimate the compressive strength as a function of crude oil, from a nonlinear regression analysis of the simulation data using MATLAB. The equation also shows the correlation coefficient (R^2) and the Root Mean Squared Error (*RMSE*) of the proposed model.

$$f'_{c(x)} = \begin{cases} f'_{cu} + 1.0x & 0 \leq X \leq 1 \quad \text{Adj. } R^2 = 1, \text{ RMSE} = 1.07 \\ f'_{cu} - 1.03x & 1 < X \leq 20 \quad \text{Adj. } R^2\ 0.99, \text{ RMSE} = 0.87 \end{cases} \qquad (8.1)$$

where $f'_{c(x)}$ is the predicted compressive strength containing fine sand with oil contamination, f'_{cu} is the average compressive strength of uncontaminated concrete, and x is the level of oil contamination in percentage. This model can be used to predict the compressive strength of concrete containing any percentages of light crude oil contamination. This proposed empirical equation was validated with the experimental results. Figure 8.17 shows the resulting (f'_{cp}) scatter point plot of the predicted compressive strength (CS-predicted) against the experimentally measured compressive strength (CS-Experimental). As can be seen in Figure 8.17, the points are located close to the line, which indicates the high accuracy (correlation coefficient of 99%) of the Equation 8.1.

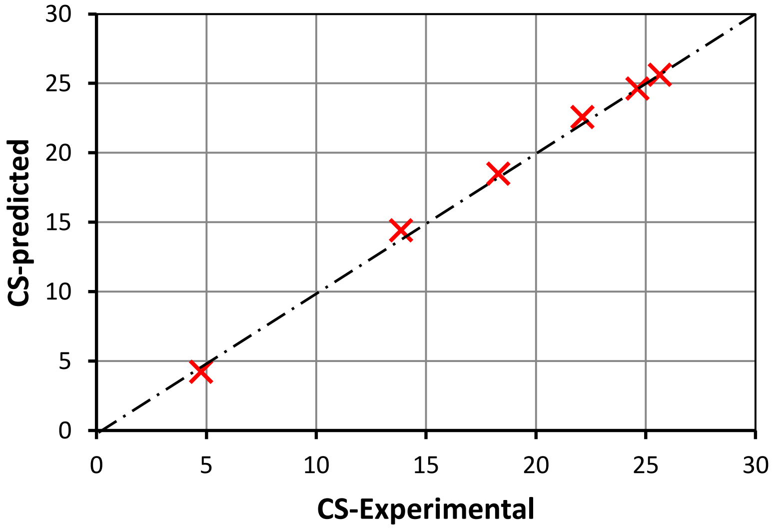


Figure 8.17 Validation of the proposed equation of the compressive strength of concrete containing crude oil with simulation results

8.4.7.2 Compressive strength of mortar

Similar to the concrete, a relationship between the compressive strength of mortar and light crude oil was established in order to correlate the relationship between the cement mortar and the concrete. It was found that there was a polynomial relationship between the compressive strength and the light crude oil. The rational model shown in Equation 8.2 was formulated to estimate the compressive strength as a function of crude oil, with a nonlinear regression analysis of the simulation data using MATLAB.

$$f'_{cm(x)} = \begin{cases} f'_{cmu} + 6.4x & 0 \leq X \leq 1 \quad \text{Adj. } R^2 = 0.96\text{, RMSE} = 0.5715 \\ f'_{cmu} + 6.4 - 1.302x & 1 < X \leq 20 \quad \text{Adj. } R^2\ 0.88\text{, RMSE} = 3.168 \end{cases} \tag{8.2}$$

where $f'_{cm(x)}$ is the predicted compressive strength of mortar containing fine sand with oil contamination, and f'_{cmu} is the compressive strength of uncontaminated cement mortar. These proposed equations were validated from the experimental results and showed a very good correlation, as shown in Figure 8.18.

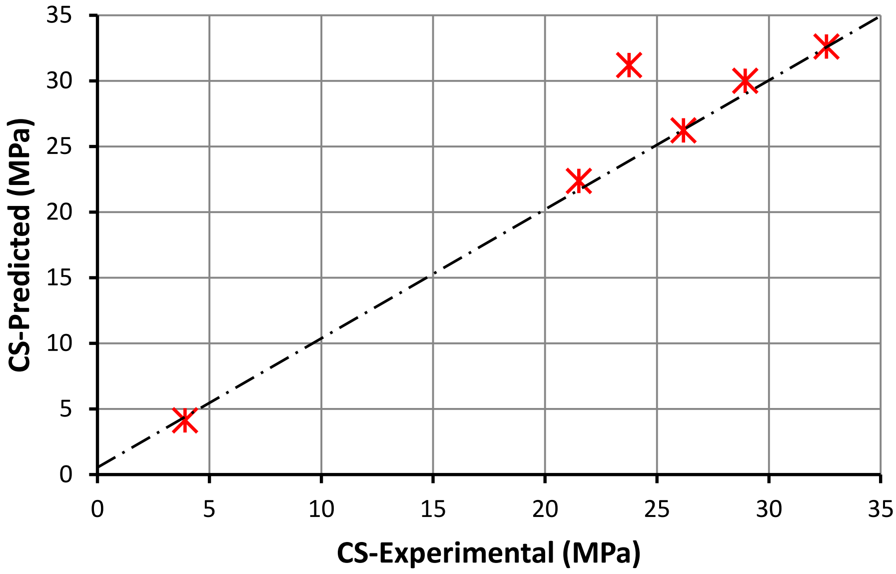


Figure 8.18 Validation of the proposed equation of the compressive strength of mortar containing crude oil with simulation results

8.4.7.3 Relationship between mortar and concrete

The relationship between the compressive strength of mortar and the compressive strength of concrete was estimated to correlate the compressive strength of cement mortar to that of concrete at different levels of oil contamination. A linear interpolation equation was used as shown in Equation 8.3, and the model was designed by using visual basic applications in Microsoft excel. The flowchart of this model is shown in Figure 8.19. Based on the equations (8.2) a new model was established to predict the compressive strength based on mortar as shown in equation 8.3.

$$f'_{c(x)} = f'_{cmu} - D \qquad (8.3)$$

where $f'_{c(x)}$ is the predicted compressive strength, f'_{cmu} is the compressive strength of mortar with uncontaminated sand and D is the differentiation as shown in equation 8.4.

$$D = \begin{cases} 5.39x + 1.56 & 0 \le X \le 1 \quad \text{Adj. } R^2 = 1 \\ 9.98 - 2.67\ln(x) & 1 < X \le 20 \quad \text{Adj. } R^2\ 0.4549 \end{cases} \qquad (8.4)$$

where x is the crude oil content (%)

The model can be used to predict the compressive strength of concrete, from a prediction equation for the strength of the mortar in equation 8.2. The boundaries of this model were based on the crude oil content used in our experiments (0%-20%). Figure 8.20 shows the comparison between the experimental results of the compressive strength of concrete and the predicted values of the compressive strength, using the model. It can be seen that the points of the predicted compressive strength are located close to the experimental results of the compressive strength, which gives an indication of the high accuracy of this model (equation 8.3).

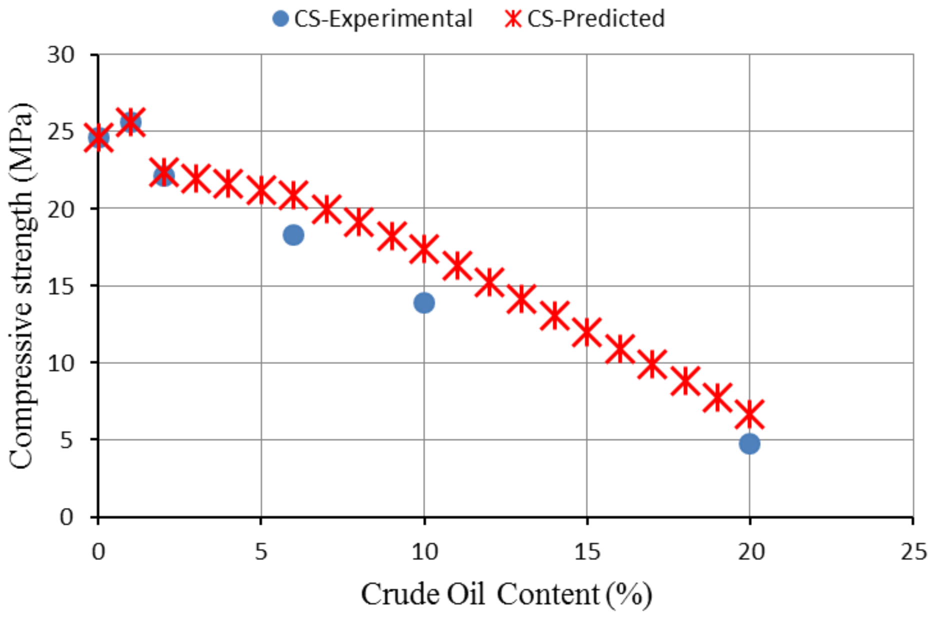


Figure 8.19 Comparisons between the experimental and predicted compressive strength of concrete

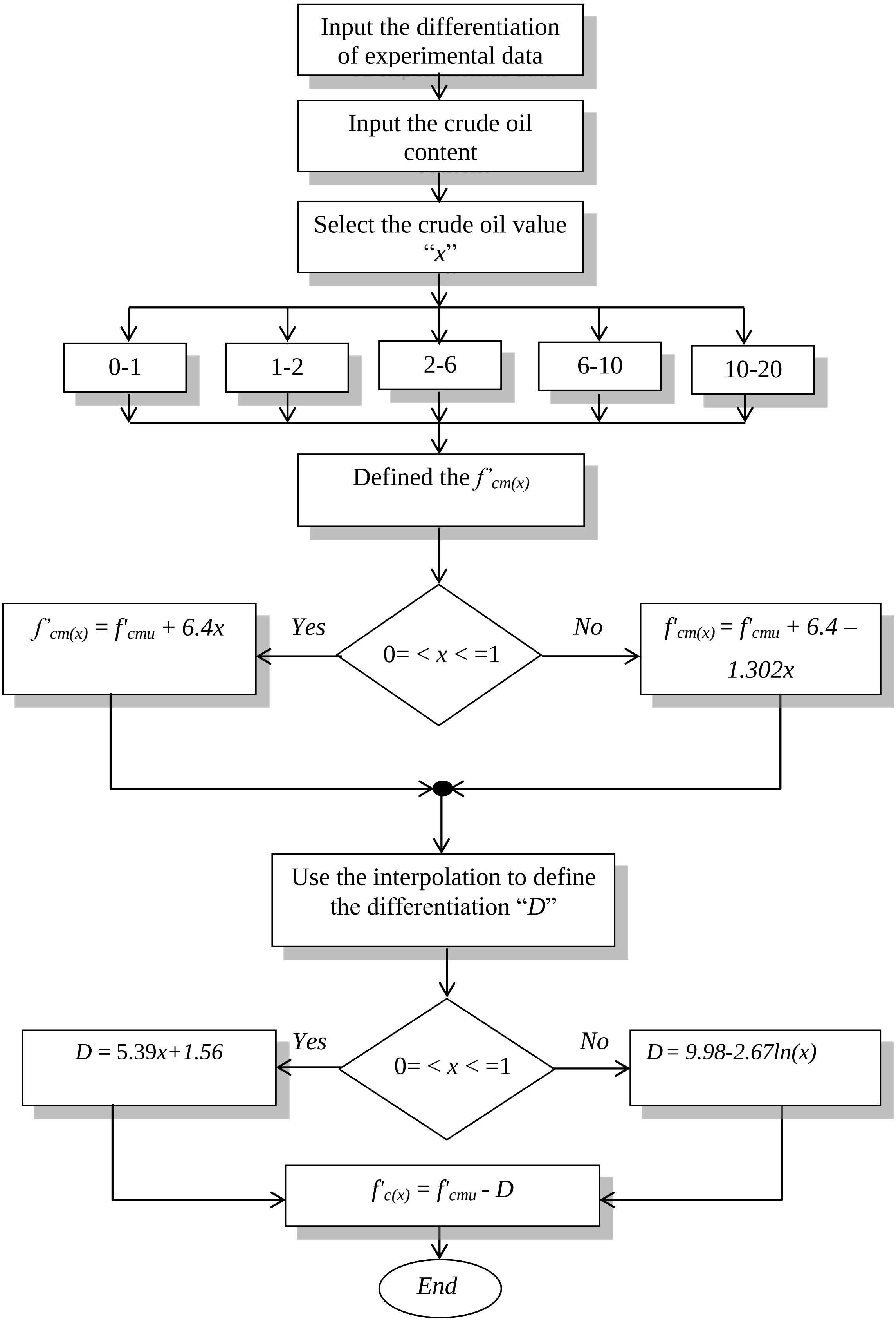


Figure 8.20 Flow Chart model of the predicted compressive strength of concrete

8.5 Conclusion

In this chapter, the effect of light crude oil contamination on the physical and mechanical properties of concrete containing oil contaminated fine sand were investigated. The conclusions drawn from this study are as follows:

- Light crude oil contaminated sand affects the physical properties of concrete at high levels of crude oil contamination. The concrete density was found to decrease as the oil content increases due to an increase in surface porosity. An 8% lower density was measured for concrete containing fine sand with 20% of crude oil contamination compared to uncontaminated samples. The surface wetness of the hardened concrete also increased with increasing levels of oil contamination. At 20% oil contamination, the specimens were excessively saturated and porous with a weakened surface.

- The compressive strength was enhanced by the crude oil up to the certain amount of crude oil level. At 1%, the oil contamination increased by 4.09% compared to the uncontaminated samples. The increase in strength was attributed to the sand reaching optimum cohesion as a result of oil binding sand particles. However, the concrete containing fine sand with 2% to 6% of light crude oil contamination exhibited up to 25% lower compressive strength than uncontaminated samples and failed due to splitting failure. Increasing the crude oil from 10% to 20% resulted in significantly lower strength than the uncontaminated concrete, due to surface saturation of aggregates which decreased the bond formation with the cement paste. The observed failure mode for this concrete was a shear failure.

- The splitting tensile strength of concrete containing fine sand with oil contamination showed a similar behaviour to that of compressive strength. The tensile strength was enhanced by 7% at 1% of crude oil contaminations compared to uncontaminated samples. The increase in tensile strength can be attributed to an increase in cohesion of the fine sand particles. Higher than 1% oil contamination level, the tensile strength decreased as the sand became saturated with oil and the surface of the course aggregates was coated with oil hindering the physical bond formation between cement paste and aggregates. All specimens failed due to splitting tensile failure, but with more audible cracking noises for specimens up to 6% rather than for those with higher levels of light crude oil contamination.

- SEM images showed that the full hydrated area increased while the porosity decreased at 1% crude oil contamination, compared to uncontaminated concrete. As the sand particles were partially coated by the crude oil, the amount of water that the fine sand could absorb decreased, which in turn increased the interaction between the cement and water and resulted in a better hydration. At higher oil contamination levels (2% to 20%), the C-S-H gel decreased due to the higher amount of free water, which created more and bigger pores than the uncontaminated concrete.

- Oil contamination has a more detrimental effect on the mechanical properties of concrete than cement mortar. Up to 7 MPa lower compressive strength was obtained in concrete compared to mortar. This could be attributed to the lower cement binder to aggregates ratio with a concrete mix, compared to mortar. Moreover, the increase in the contaminated area of the coarse aggregates by the light crude oil hinders the bond formation between the cement and the aggregates, and results in more segregation in concrete than in mortar.

- Simple empirical equations to predict the compressive strength of mortar and concrete containing oil contaminations were developed. These prediction equations were a function of the compressive strength of uncontaminated samples and the levels of light oil contamination. Comparison between the experimental results and the predicted values for up to 20% oil contamination gave a 98% accuracy, indicating the reliability of the proposed equations.

Chapter 9

Conclusions

Sand contaminated with crude oil and other hydrocarbons has become a major environmental concern worldwide. This oil contamination adversely affects the ecosystem, including the underground water, and affects the physical and chemical properties of the surrounding sand. The threats posed to humans and the environment by oil contaminated sand has made the assessment and remediation of this waste material very significant. To minimise its adverse effects, a range of remediation methods including sand washing, bio-remediation, electro-kinetic sand remediation, and thermal desorption, have been implemented but they are not cost effective. This cost would be magnified in developing countries where none of the above mentioned remediation methods are available. On this basis there is a definite need to find a better and more cost-effective way of utilising oil contaminated sand.

Mixing the oil contaminated sand with cement and using this as alternative construction material is considered a smart and cost-effective method in reducing its environmental impact. However, a better understanding of the mechanical properties of oil contaminated sand and its produced mortar/concrete is needed, as this is a critical step before this waste material can be considered an emerging and sustainable material. To my knowledge is the first study that investigates the behaviour of fine sand contaminated with light crude oil and the mortar and concrete produced from it Extensive experimental studies were conducted to determine the effects of light crude oil on the geotechnical properties of sand, and the physical, mechanical, and microstructure properties of mortar and concrete containing fine sand contaminated with light crude oil. The conclusions gathered from these studies contributed towards a better understanding of the behaviour of concrete containing light crude oil contamination. Further research is suggested to enhance the adoption of this waste material for building and construction applications.

9.1 Major conclusion from the study

9.1.1 Geotechnical properties of fine sand contaminated with light crude oil

An evaluation of the geotechnical properties of fine grained sand containing different percentages of light crude oil (0.5, 1, 2, 4, 6, 8, 10, 15, and 20%) was conducted as the first step of the study. Important properties related to construction applications such as particle size distribution (PSD), moisture content, water absorption, permeability, contact angle, and shear strength were carefully evaluated and analysed. Based on the results of this study, the following conclusions were drawn:

- The water absorption of fine grained sand (with a maximum particle grain size of 2.36 mm and zero moisture content) was 2.79%. This decreased with an increasing level of light crude oil contamination of up to 2%. Beyond 2%, the fine sand was already coated with crude oil and did not absorb any more water, making it hydrophobic. As a result, the contact angle of oil-contaminated sand increased.

- The permeability of fine sand with 1% light crude oil contamination decreased by 35% compared to uncontaminated sand. However, the permeability increases by as much as 46.9% for 2% to 6% light crude oil contamination, due to the sand particles already coated with crude oil, which resulted in accelerated passage of water. Above a 6% oil contamination level, the permeability decreased as all pores were already filled and saturated with oil.

- The highest value of cohesion was 10.76 kPa and it was observed at 1% of light crude oil contamination. This increase was due to the increased surface wetness of the fine sand particles. However, increasing the crude oil content from 2% up to 20% caused a significant reduction of cohesion value due to the sand particles being fully coated with crude oil, which reduced the interaction between sand particles.

- The frictional angle of fine sand decreased by 7° at 1% oil contamination, compared to uncontaminated samples. This reduction was due to the inter-grain lubrication of the sand particles by the crude oil. Nonetheless, no significant variation in the frictional angle of contaminated sand was observed for samples with oil contamination from 2% to 20%. This was attributed to the fine sand starting to be coated with crude oil.

- The shear strength of fine sand was enhanced by adding light crude oil up to a limited amount. A 10% increment on the shear strength was observed for 1% light crude oil contamination compared to uncontaminated samples. This increase was attributed to the sand reaching optimum cohesion as a result of oil binding sand particles. Above 2% oil contamination, the shear strength decreased due to the sand particles easily slipping or shearing with each other, as the oil was providing lubrication between them. The measured shear strength for fine sand with 20% light crude oil contamination was 14.7% lower shear strength than for uncontaminated sand.

The overall results indicate that some of the physical and mechanical properties of fine sand were adversely affected by light crude oil contamination. However, it was also found that at an optimal level of light crude oil contamination, the physical and mechanical properties of fine sand can be enhanced. This warrants further investigation of the effects of oil contamination on the physical and mechanical properties of cement mortar.

9.1.2 Behaviour of cement mortar containing fine sand contaminated with light crude oil

The evaluation of the physical and mechanical properties of cement mortar containing fine sand contaminated with light crude oil was investigated as the next step in order to gain an understanding of the suitability of this waste material for building and construction. The effects of mixing, curing methods, water-to-cement ratio, and curing duration on the compressive strength, porosity and microstructure of the hardened cement mortar were evaluated. The conclusions related to this study are summarised as follows:

Effects of curing and mixing methods

- An appropriate mixing method is important to produce a cement mortar containing oil contaminated fine sand with a reasonable compressive strength. Mixing cement and water before adding the oil contaminated sand (CWS) yielded up to 19% higher compressive strength compared to the cement mortar prepared by mixing the sand and cement before adding the water (CSW). This was due to the better reaction of cement particles and water during the hydration process, unlike in CSW where the cement particles were coated with oil, preventing them from reacting with water.

- The cement mortars mixed following CWS had a 34% lower total porosity compared to the mortar mixed by CSW. However, as the level of oil contamination increased, the pores of the cement mortar became bigger in size, and more interconnected, compared to the uncontaminated samples and those with low crude oil contamination.

- The pore size distribution was higher for mortar mixed by CSW than by CWS. This influenced the developed compressive strength more significantly than the total porosity. More specifically, the macropores (> 30 μm) had a direct correlation with the compressive strength, as opposed to the micropores and mesopores. CSW yielded up to 45% higher macropores compared to CWS.

- Among the different curing methods, the fog room showed the highest compressive strength at all levels of oil contamination. The cement mortar cured under this condition yielded up to a 45.6% higher compressive strength compared to mortars cured under other curing conditions. This was attributed to enough moisture being available to complete the hydration during the curing process. On the other hand, mortar cured in a sealed plastic bag, especially with 10% oil contaminated sand, exhibited the lowest compressive strength. This was due to the prevention of movement of hydrocarbons in a confined space during the curing process, which hindered the hydration process. Microscopic observations showed that the mortar cured inside the plastic bags was significantly wetter with light crude oil compared to specimens cured under different conditions.

- The total porosity was less and the pore sizes were smaller for the cement mortars cured in the fog room compared to those cured in water, in air, and in plastic bags. The cement mortars cured in the fog room at different percentages of crude oil content (0, 2 and 10%) only had 2.86, 4.42 and 10.52% total porosity, which was significantly lower than the cement mortar cured in other curing conditions. This lower porosity was due to more moisture being available to complete the cement hydration process.

- SEM observations showed fewer long thin crystals in the cement mortar cured in a fog room (FR), rather than under water (W), in air (A) and in plastic bags (PB). Similarly, the cement mortar cured under FR conditions, rather than W, A and PB, had smaller capillary pores, and was partly bridged by a hydration product growing hydrating cement particles. Moreover, the calcium silicate hydrate was much denser and most pores were filled under FR, rather than the under other curing methods.

Effects of water-to-cement (w/c) ratio

- The compressive strength of mortar containing fine sand contaminated with light crude oil was significantly affected by water-to-cement (w/c) ratios. The cement mortar with a w/c ratio of 0.5 yielded up to 35.6% higher compressive strength compared to that with a w/c of 0.4 and 0.6. The higher compressive strength may have attributed to smaller air and less interconnected pores of the samples.

- The w/c ratio and the levels of oil contamination affected the total porosity of the cement mortar. The cement mortars with a w/c ratio of 0.4 had a total porosity of 55% and 47% higher than 0.5 and 0.6, respectively. On the other hand, the total porosity of mortars with a w/c ratio of 0.5 and 0.6 was similar at a low level of crude oil contaminations (0%-2%). At a high level of crude oil contaminations (4% to 10%), the total porosity for cement mortar with a w/c ratio of 0.6 was up to 40% higher compared to a w/c ratio of 0.5.

- The cement mortars with a w/c ratio of 0.5 had the lowest macroporosity, which produced its high compressive strength. The observed macroporosity from these mortars were 29% and 20% lower than the cement mortar with a w/c ratio of 0.4 and 0.6, respectively.

- The SEM observations revealed a larger area of C-S-H gel and lower porosity for cement mortar with a w/c ratio of 0.5 compared to mortar with a w/c ratio of 0.4 and 0.6. On the other hand, a larger area of partially hydrated (P-H) cement was observed for mortar with a w/c ratio of 0.4 and 0.6, compared to 0.5.

Effects of curing duration

- The strength development up to 365 days of cement mortar containing fine sand with up to 2% of light crude oil contamination was very similar to the cement mortar with uncontaminated sand. These cement mortars achieved most of their compressive strength after 28 days. On the other hand, the cement mortar with 4% and 6% of light crude oil contamination achieved most of its compressive strength after 56 days, while the cement mortar with 8% and 10% of oil contamination achieved most of its strength only after 112 days. This indicates that cement mortar with high levels of light crude oil contamination (4% to 10%) developed its compressive strength at a very slow rate.

- The total porosity decreased by up to 35.7% at an early age of the hydration period for low levels of crude oil contamination (0.5% to 4%). This was attributed to the filling of large pores by hydration products of cementitious material, resulting in the development of compressive strength of the cement mortar. In contrast, the amount of macropores (> 30 um) decreased by 17.2% and 32.9% for the cement mortar with 8% and 10% light crude contamination only after 56 days of curing. This indicates that a longer curing period was needed for mortar with higher levels than that with lower levels of oil contamination in order to complete the hydration process.

- The SEM observation revealed that the presence of light crude oil did not affect the hydration products of uncontaminated samples (0%) but retarded the growth of the hydration products at 10% light crude oil contamination. At all curing ages, the volume of the hydration products in mortar with oil contaminated sand were smaller in size, compared to uncontaminated samples.

These results demonstrated that proper mixing and curing methods, w/c ratio, and reasonable curing time was important for cement mortar containing oil contaminated fine sand to achieve reasonable physical and mechanical properties for building and construction. The effects of these parameters were then investigated for mortar utilising geopolymer binder, to achieve a more cost effective remediation method for oil contaminated sand.

9.1.3 Behaviour of geopolymer mortar containing fine sand contaminated with light crude oil

The effect of different percentages of light crude oil contamination on the physical, mechanical, and microstructure properties of geopolymer mortar were investigated. In addition, the effects of curing method and saturated surface condition of the sand particles were evaluated. The following conclusions could be drawn from these studies:

- Curing method significantly affected the compressive strength of the geopolymer mortar containing fine sand contaminated with light crude oil. Heat curing yielded up to 54% higher strength compared to ambient curing. This was due to the increase in the kinetic energy and degree of reaction at high temperatures, which subsequently increased the density of the pore system in the geopolymer mortar. Heat curing also helped the activation of the alumina-silicate phases in the fly ash.

- The level of oil contamination affected the compressive strength of geopolymer mortar. A 21% higher compressive strength was measured for mortar with 1% of crude oil contamination than for uncontaminated samples, but a 42% lower compressive strength was obtained for 10% crude oil contamination. The increment of the strength at 1% of crude oil contamination could be attributed to an increase in the cohesion between sand particles. However, the significant reduction of the compressive strength at a high level of crude oil contamination was due to the saturation of the sand particles with oil and the increase in the alkaline liquid-to-fly ash ratio.

- Geopolymer mortar with 0.5% of light crude oil contamination achieved a similar compressive strength (~19.0 MPa) to uncontaminated samples containing sand with a saturated surface dry condition. When the crude oil contamination was at 1% and 2%, a 20.8% and 8% higher compressive strength, respectively, was obtained compared to uncontaminated samples. The higher compressive strength of the geopolymer mortar with 1% and 2% of oil contamination, rather than uncontaminated geopolymer mortar, was due to the high alkalinity of the solution, which dissolved and activated the amorphous, reactive silica and alumina during the geopolymerisation process, leading to the generation of more geopolymeric binder. As the sand particles were coated with light crude oil, the concentration of the alkaline solution was not affected, while an additional 29 g of water was available for fine sand with a saturated surface dry condition.

- The alkalinity (pH) of the cement mortar decreased with increasing oil contamination levels. This reduction in pH value was due to the creation of water in the mix diluting the alkaline solution and decreasing the alkalinity, resulting in lower compressive strength. The additional water created was due to a reaction of the ionic H^+ from the organic acids in the light crude oil with OH^- from the NaOH.

- The efflorescence, which is considered an issue when the products are exposed to humid air or contact with water, was observed for specimens with crude oil content from 0% to 2% by the naked eye as well as in the SEM images. As the amount of crude oil increased from 4% to 10%, the efflorescence products were not visible. This indicates that increasing crude oil content from 4% inhibited the formation of efflorescence due to light crude oil filling up the pores, hence retarding the migratory paths for the salt solution to travel through to the surface. On the other hand, the efflorescence observed from geopolymer mortar with up to 2% oil contamination did not affect the compressive strength, due to low macroporosity in the samples.

- The compressive strength of the geopolymer mortar containing the same level of oil contamination was lower than that of cement mortar due to its higher porosity. This could also be due to the lower heat evolution of the geopolymer mortar compared with the cement mortar during the 48 hours of the calorimetric response.

These results demonstrated that the cement and geopolymer mortar containing fine sand contaminated with light crude oil had the potential of creating a new engineering material utilising waste materials that significantly affected the environment. Hence, in order to further evaluate the proper end use application of this waste material, an investigation of the properties of concrete containing fine sand contaminated with light crude oil was an important next step.

9.1.4 Behaviour of concrete containing fine sand contaminated with light crude oil

Intensive experimental work was conducted on concrete containing fine sand contaminated with light crude oil, with different levels of light crude oil (0, 1, 2, 6, 10 and 20%). The effect of crude oil on the physical and mechanical properties, including compressive and tensile strength, porosity and microstructure, were evaluated. A simple prediction equation was also established to determine the approximate compressive strength at any crude oil content from 0% to 20%. The following are the conclusions from this study:

- The density of concrete deceased as the amount of crude oil increased. This can be explained by the surface voids observed in the specimens, which progressively became apparent as the oil contamination increased.

- The compressive strength of concrete is affected by light crude oil contamination. A 4% higher compressive strength was obtained for concrete with 1% of light crude oil contamination, when compared to the uncontaminated samples. The increase in strength may be due to oil optimising concrete cohesion, without causing water seepage. Above 1% oil contamination, the sand became saturated with oil, resulting in a reduced compressive strength. This reduction in compressive strength may be due to incompletion of the hydration process at 28 days for concrete with a high level of crude oil.

- The optimum value of the splitting tensile was also observed at 1% of crude oil contamination, which was 7% higher compared to uncontaminated samples. On the other hand, increasing the crude oil content above 2% caused the fine sand to exceed the equilibrium condition, and the oil also contaminated the surface of the coarse aggregates. As a consequence, the bond between the cement paste and coarse aggregates was affected, resulting in a decrease in tensile strength.

- SEM observations revealed an enhanced hydration process and increased C-S-H gel formation for concrete with 1% of crude oil contamination. In addition, the pore size and the pore distribution of concrete with this level of oil contamination was smaller than for the uncontaminated samples. The average pore size in the uncontaminated samples was 454 μm, while it was only 368 μm for 1% of crude oil contamination. However, as the amount of crude oil increased, the average pore size increased, and the highest value was 877 μm for concrete with a 20% crude oil contamination.

- A lower compressive strength was observed for concrete than for mortar containing fine sand contaminated with light crude oil. This was due to the lower cement binder to aggregates ratio and the bigger aggregates size in concrete than in mortar. The low amount of binder in concrete reduced the ability of the cement to fully cover the aggregates. Moreover, the bond formation between cement and the coarse aggregates decreased because the interaction area between the cement paste and the aggregates increased, resulting in more segregation for concrete than for mortar.

- Simplified prediction equations were developed to estimate the mechanical properties of a mortar and concrete mix containing fine sand contaminated with light crude oil. These prediction equations were a function of the compressive strength of uncontaminated samples and the levels of light oil contamination.

9.2 Summary

The investigated properties such as cohesion and shear strength, of sand can be enhanced by adding light crude oil up to the certain level. Those finding are highlighted in ***Section 9.2.1***. This conclusion represents the new finding of the first objective that addressed in ***Section 1.2*** which aimed to investigate the effect of different levels of light crude oil contamination on the physical and mechanical properties of fine sand.

Higher compressive strength can be attained for oil contaminated sand than for uncontaminated sand, up to a certain amount of contamination, if proper mixing and curing methods were used. Furthermore, cement mortar consisting of fine sand with a light crude oil contamination of 0% to 10%, and a water cement ratio of 0.5, exhibited a higher compressive strength compared to a w/c ratio of 0.4 and 0.6. On the other hand, there was no effect on the strength development of cement mortar containing fine sand with lower levels of oil contamination, but it has a significant effect at higher levels of oil contamination. Those finding are highlighted in ***Section 9.2.2***. This conclusion represents the new finding of the second and third objectives that addressed in ***Section 1.2*** which aimed to investigate the effects of mixing, curing methods, water-to-cement ratio, and curing duration on the compressive strength.

Higher compressive strength of geopolymer mortar can be attained for oil contaminated sand than for uncontaminated sand, up to a certain amount of contamination, when heat curing (HC) and saturated surface dry condition (SSD) were used. Furthermore, higher gain in strength was observed for geopolymer mortar than for OPC mortar. Although the efflorescence was observed for specimens with crude oil content from 0% to 2% by the naked eye as well as in the SEM images; it did not affect the compressive strength, due to low macroporosity in the samples. On the other hand increased from 4% to 10%, the efflorescence products were not visible. Furthermore, the alkalinity of the geopolymer mortar was found decreased with increasing oil contamination levels. Those finding are highlighted in ***Section 9.2.3.*** This conclusion represents the new finding of the fourth objective that addressed in ***Section 1.2*** which aimed to investigate the physical, mechanical and microstructure properties of geopolymer mortar containing oil contaminated sand.

The compressive strength of concrete is affected by light crude oil contamination, and hence, higher compressive strength was observed at low level of crude oil contaminations (up to 2%). However, as the amount of crude oil increase above 4% the compressive strength decreased. Similar results was obtained for the splitting tensile where the optimum value of the splitting tensile was also observed at 1% of crude oil contamination. On the other hand, increasing the crude oil content above 2% caused the fine sand to exceed the equilibrium condition resulting in lower tensile strength. In addition to that the microstructure observation supported these findings. SEM observations revealed an enhanced hydration process and increased C-S-H gel formation for concrete with 1% of crude oil contamination resulting lower total porosity as a consequence higher strength was obtained at these percentages compared to uncontaminated samples. In this objective a prediction equations were developed to estimate the mechanical properties of a mortar and concrete mix containing fine sand contaminated with light crude oil. Those finding are highlighted in ***Section 9.2.4***. This conclusion represents the new finding of the fifth objectives that addressed in ***Section 1.2*** which aimed to investigate the effect of light crude oil contamination on the physical, mechanical and microstructure properties of concrete.

9.3 Proposals for future research

The following aspects need to be further studied in more detail in order to determine the end use application of cement mortar and concrete containing oil contaminated fine sand, and to pave the way for the development of structural components for civil engineering applications:

- The decrease in the mechanical properties of cement mortar and concrete containing oil contaminated fine sand could be enhanced by adding fibres into the mix. The appropriate forms of the fibres and the optimal dosage, which will result in properties equal or higher than for uncontaminated samples, need to be determined. Moreover, the maximum level of light crude oil contamination that will not severely impact on the bond between the cement and the fibres needs to be determined.

- The initial results of the effect of the light crude oil on the mechanical properties of geopolymer mortar showed a high potential to combine some of the major waste products, namely oil contaminated sand and fly ash, and to use them in building and construction. Therefore, further investigation on the effect of different percentages of oil contaminated sand on the mechanical and durability behaviour of the geopolymer concrete is recommended.

- The effect of crude oil on reinforced concrete is a new area of research that could be conducted to investigate the effect of crude oil on steel bars through the resistance of corrosion. Understanding the bond between reinforcement and concrete, and the behaviour of reinforced concrete structures containing oil contaminated sand, warrants further exploration with regards to their potential beneficial use in civil engineering and construction applications.

- Geopolymer contains much higher soluble alkali metal concentrations than conventional cement, and efflorescence could be a significant issue when the products are exposed to humid air or come in contact with water. In this research it has been observed that an increase in oil can reduce the efflorescence in concrete, which is an interesting area of investigation for future research as this issue is becoming of increasing concern to concrete researchers.

References

Abalaka, A & Okoli, O 2012, 'Effects of curing conditions on high strength concrete', *Journal of Civil Engineering and Construction Technology*, vol. 3, no. 10, pp. 273-9.

Abalaka, A & Okoli, O 2013, 'Influence of curing regime on strength development of grade C60 concrete', *International Journal of Modern Engineering Research (IJMER) Vol*, vol. 3, pp. 709-14.

Aghalino, S & Eyinla, B 2009, 'Oil exploitation and marine pollution: Evidence from the Niger Delta, Nigeria', *Journal of Human Ecology*, vol. 28, no. 3, pp. 177-82.

Aguwa J.I. 2006, 'Effect of critical variable-time on concrete production', *journal of science, Technology and mathematics education,* vol. 8, no. 2, pp. 23-39.

Ahad, RA & Ramzi, B 2000, 'Compressive And Tensile Strength Of Concrete Loaded And Soaked In Crude Oil'.

Aikman, M, Kantzas, A & Mirotchnik, K 2002, 'Experimental Work on the Behaviour of Synthetic Soils Contaminated with Light Hydrocarbon, and Subsequent Remediation Thereof', *Journal of Canadian Petroleum Technology*, vol. 41, no. 9.

Ajagbe, W, Ganiyu, A, Owoyele, M & Labiran, J 2013, 'Modeling the Effect of Crude Oil Impacted Sand on the Properties of Concrete Using Artificial Neural Networks', *ISRN Civil Engineering*, vol. 2013.

Ajagbe, WO, Omokehinde, OS, Alade, GA & Agbede, OA 2012, 'Effect of crude oil impacted sand on compressive strength of concrete', *Construction and Building Materials*, vol. 26, no. 1, pp. 9-12.

Al-Harthi, A, Al-Amri, R & Shehata, W 1999, 'The porosity and engineering properties of vesicular basalt in Saudi Arabia', *Engineering Geology*, vol. 54, no. 3, pp. 313-20.

Al-Harthy, A, Taha, R, Abu-Ashour, J, Al-Jabri, K & Al-Oraimi, S 2005, 'Effect of water quality on the strength of flowable fill mixtures', *Cement and Concrete Composites*, vol. 27, no. 1, pp. 33-9.

Al-Mutairi, N.M. 1995, 'Kuwait oil-based pollution: effect on building material'. *Journal of materials in civil engineering,* 7**,** 154-160

Al-Sanad, H, Eid, W & Ismael, N 1995, 'Geotechnical Properties of Oil-Contaminated Kuwaiti Sand', *Journal of geotechnical engineering*, vol. 121, no. 5, pp. 407-12.

Alamari, AM 1988, 'Influence of curing on the properties of concrete and mortars in hot climates ', PhD thesis thesis, Leeds University, UK.

Alawode, O & Idowu, O 2011, 'Effects of Water-Cement Ratios on the Compressive Strength and Workability of Concrete and Lateritic Concrete Mixes', *The Pacific Journal of Science and Technology*, vol. 12, no. 2, pp. 99-105.

Ali, S, D, LH, JW, JD & Occapinti, J 1999, 'Novel filtration process removes dissolved organics from produced water and meets Federal oil and Grease guidelines', in Produced Water Seminar: *proceedings of theProduced Water Seminar* pp. 21-2.

Alizadeh, R, Ghods, P, Chini, M, Hoseini, M, Ghalibafian, M & Shekarchi, M 2008, 'Effect of curing conditions on the service life design of RC structures in the Persian gulf region', *Journal of materials in civil engineering*, vol. 20, no. 1, pp. 2-8.

Allahverdi, A & Kani, EN 2009, 'Construction wastes as raw materials for geopolymer binders', *Int J Civil Eng*, vol. 7, no. 3, pp. 154-60.

Almabrok, M, McLaughlan, R & Vessalas, K 2013, 'Characterisation of cement mortar containing oil-contaminated aggregates', in Australasian Conference On The Mechanics Of Structures And Materials: *proceedings of theAustralasian Conference On The Mechanics Of Structures And Materials* CRC press/Balkema.

Almabrok, M, McLaughlan, R & Vessalas, K 2015a, 'Effect of Curing and Mixing Methods on the Compressive Strength of Mortar Containing Oil', *Journal of Civil Engineering, Science and Technology*, vol. 6, no. 1, pp. 6-11.

Almabrok, MH, McLaughlan, R & Vessalas, K 2011, 'Investigation of oil solidification using direct immobilization method', in Environmental Research Event 2011: *proceedings of the Environmental Research Event 2011* North Stradbroke Island, QLD.

Almabrok, MH, McLaughlan, RG & Vessalas, K 2015b, 'Evaluating the effect of mixing method on the performance of mortar containing oil', *International Journal of Engineering Science Invention*, vol. 4, no. 3, pp. pp.58-64.

Andreev, EG 1995, *Brittle failure of rock materials*, CRC Press.

Arthur, JD, Bruce, PE, Langhus, G & Patel, CPGC 2005, 'Technical summary of oil & gas produced water treatment technologies', *All Consulting, LLC, Tulsa, OK*.

Aryee, A 2013, 'Risks of Offshore Oil Drilling: Causes and Consequences of British Petroleum Oil Rig Explosion ', *Aquatic Science and Technology*, vol. 1, no. 1, p. 17.

AS-1012.2 2014, *Methods of testing concrete - Preparing concrete mixes in the laboratory* Standard Australia, Australia.

AS-1012.9 2014, *Compressive strength tests concrete, mortar and grout specimens* Standard Australia, Australia.

AS-1012.10 2000, *Determination of indirect tensile strength of concrete cylinders*, Australia.

AS-1141.5 2000, *Methods for sampling and testing aggregates - Particle density and water absorption of fine aggregate*.

AS 1141.11.1 2009, *Methods for sampling and testing aggregates - Particle size distribution - Sieving method*.

AS 1289.2.1.1 1992, *Methods of testing soils for engineering purposes - Soil moisture content tests - Determination of the moisture content of a soil - Oven drying method (standard method).*

AS 1289.6.2.2 1998, *Methods of testing soils for engineering purposes - Soil strength and consolidation tests - Determination of shear strength of a soil - Direct shear test using a shear box*.

AS 1289.6.7.3 1999, *Methods of testing soils for engineering purposes - Soil strength and consolidation tests - Determination of permeability of a soil - Constant head method using a flexible wall permeameter*.

AS 1726 1993, *Geotechnical site investigations*.

AS 2350.12 2006, *Preparation of a standard mortar and moulding of specimens*, Method 12: , Australian Standrad, Australia.

ASTM-C192/C192M-14 2007, *Standrad practice for Making and curing concrete test specimens in the laboratory*, American Society for Testing and Materials, USA.

ASTM-C305-14 2013, *Standrad practice for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency*, American Society for Testing and Materials USA.

ASTM-C1679 2014, *Measuring hydration kinetics of hydraulic cementitious mixtures using isothermal calorimetry*, ASTM, Washington DC, USA.

Atlas, R. 1975, 'Effects of temperature and crude oil composition on petroleum biodegradation', *Applied microbiology,* 30**,** 396-403.

Attom, M, Hawileh, R & Naser, M 2013, 'Investigation on concrete compressive strength mixed with sand contaminated by crude oil products', *Construction and Building Materials*, vol. 47, no. 0, pp. 99-103.

Auskern, A & Horn, W 1973, 'Capillary porosity in hardened cement paste', *Journal of Testing and Evaluation*, vol. 1, no. 1, pp. 74-9.

Ayininuola, GM 2009, 'Influence of diesel oil and bitumen on compressive strength of concrete', *Journal of Civil Engineering*, vol. 37, no. 1, pp. 65-71.

Balseiro, A, Espi, A, Marquez, I, Perez, V, Ferreras, M, Marín, JG & Prieto, JM 2005, 'Pathological features in marine birds affected by the Prestige's oil spill in the north of Spain', *Journal of Wildlife Diseases*, vol. 41, no. 2, pp. 371-8.

Bansal, K & Caudle, D 1999, 'Interferences with Processing Production Water for Disposal', in 9th Produced Water Seminar, Houston, TX: *proceedings of the9th Produced Water Seminar, Houston, TX*.

Barbour, S & Yang, N 1993, 'A review of the influence of clay-brine interactions on the geotechnical properties of Ca-montmorillonitic clayey soils from western Canada', *Canadian Geotechnical Journal*, vol. 30, no. 6, pp. 920-34.

Baveye, P, Rogasik, H, Wendroth, O, Onasch, I & Crawford, JW 2002, 'Effect of sampling volume on the measurement of soil physical properties: simulation with X-ray tomography data', *Measurement Science and Technology*, vol. 13, no. 5, p. 775.

Bechhold, H, Dede, L & Reiner, L 1921, 'Dreiphasige emulsionen', *Colloid & Polymer Science*, vol. 28, no. 1, pp. 6-19.

Ben-Mahmoud, K 1995, *Libyan Soil-constitution, classification, properties and cultivation prospects*, Tripoli.

Bentz, DP 1997, 'Three-Dimensional Computer Simulation of Portland Cement Hydration and Microstructure Development', *Journal of the American Ceramic Society*, vol. 80, no. 1, pp. 3-21.

Bentz, DP & Aitcin, P 2008, 'The hidden meaning of water-to-cement ratio', *Concrete international*, vol. 30, no. 5, pp. 51-4.

Betoniyhdistys, S & Risto, M 2004, 'Betonitekniikan oppikirja 2004, by 201', *Helsinki, Suomen Betoniyhdistys ry*.

Bishr, HA, Baghabra AI-Amoudi, OS, Basunbul, IA & Al-Sulaimani, GJ 1995, 'Assessment of concrete compressive strength using the Lok test', *Construction and Building Materials*, vol. 9, no. 4, pp. 227-37.

Black, JR 2012, *Mix Design Process for Alkaline-Activated Class F Fly Ash Geopolymer Concrete*, University of New South Wales at the Australian Defence Force Academy, NSW, Australia,<.

Borger, J, Carrasquillo, RL & Fowler, DW 1994, 'Use of recycled wash water and returned plastic concrete in the production of fresh concrete', *Advanced Cement Based Materials*, vol. 1, no. 6, pp. 267-74.

Borges, JAR, Pires, LF & Belmont Pereira, A 2012, 'Computed tomography to estimate the representative elementary area for soil porosity measurements', *The Scientific World Journal*, vol. 2012.

Bushlaibi, AH & Alshamsi, AM 2002, 'Efficiency of curing on partially exposed high-strength concrete in hot climate', *Cement and Concrete Research*, vol. 32, no. 6, pp. 949-53.

Bustamante, MR, Renaker Jr, JJ & Magley, DA 1991, *Pollution control*, Google Patents.

Burns, ER, Dragila, MI, Selker, JS, Guenther, RB, Parlange, JY & Weisbrod, N 2007, 'Correction of the Buckingham–Darcy Law for flow of high strength salts in variably saturated porous media' *Advances in water resources,* 30**,** 469-482.

Campbell, D, Cox, D, Crum, J, Foster, K, Christie, P & Brewster, D 1993, 'Initial effects of the grounding of the tanker Braer on health in Shetland. The Shetland Health Study Group', *BMJ*, vol. 307, no. 6914, pp. 1251-5.

Charman, J & West, G 2011, 'Particle size distribution of dune sand from Libya', *Quarterly Journal of Engineering Geology and Hydrogeology*, vol. 44, no. 2, pp. 277-80.

Chandra, S & Flodin, P 1987, 'Interactions of polymers and organic admixtures on Portland cement hydration', *Cement and Concrete Research*, vol. 17, no. 6, pp. 875-90.

Chang, J, Yeih, W, Chung, T & Huang, R 2016, 'Properties of pervious concrete made with electric arc furnace slag and alkali-activated slag cement', *Construction and Building Materials*, vol. 109, pp. 34-40.

Chen, X & Wu, S 2013, 'Influence of water-to-cement ratio and curing period on pore structure of cement mortar', *Construction and Building Materials*, vol. 38, pp. 804-12.

Chiau, W-Y 2005, 'Changes in the marine pollution management system in response to the Amorgos oil spill in Taiwan', *Marine pollution bulletin*, vol. 51, no. 8, pp. 1041-7.

Chithiraputhiran, SR 2012, 'Kinetics of Alkaline Activation of Slag and Fly ash-Slag Systems', Arizona State University.

Cioffi, R, Maffucci, L, Santoro, L & Glasser, F 2001, 'Stabilization of chloro-organics using organophilic bentonite in a cement-blast furnace slag matrix', *Waste Management*, vol. 21, no. 7, pp. 651-60.

Coduto, DP 2001, *Foundation design*, Prentice Hall.

Cokca, E, Erol, O & Armangil, F 2004, 'Effects of compaction moisture content on the shear strength of an unsaturated clay', *Geotechnical & Geological Engineering*, vol. 22, no. 2, pp. 285-97.

Cook, E, Puri, V & Shin, E 1992, 'Geotechnical characteristics of crude oil-contaminated sands', in The Second International Offshore and Polar Engineering Conference: *proceedings of theThe Second International Offshore and Polar Engineering Conference* International Society of Offshore and Polar Engineers.

Collins, AG 1971, 'Oil and Gas Wells: Potential Polluters of the Environment?', *Journal (Water Pollution Control Federation)*, pp. 2383-93.

Corapcioglu, MY 1996, *Advances in porous media*, vol. 3, Elsevier.

Cullinane, M, Bricka, R & Francingues, N 1987, 'An assessment of materials that interfere with stabilization/solidification processes', in Proceedings of the 13th Annual Research Symposium: *proceedings of the Proceedings of the 13th Annual Research Symposium* pp. 64-71.

Das, BM 2008, *Advanced soil mechanics*, Psychology Press.

Davidovits, J 1991, 'Geopolymers', *Journal of Thermal Analysis and calorimetry*, vol. 37, no. 8, pp. 1633-56.

Delin, G, Essaid, H, Cozzarelli, I, Lahvis, M & Bekins, B 1998, 'Ground water contamination by crude oil near Bemidji', *Minnesota*, 2327-6932, US Geological Survey.

Delin, GN, Essaid, H & Cozzarelli, I 2012, 'Ground Water Contamination by Crude Oil'.

Diab, H 2011, 'Effect of mineral oil on reinforced concrete structures part I. deterioration of compressive strength', *Journal of Engineering Sciences*, vol. 39, no. 6, pp. pp.1321-33.

Duxson, P, Provis, JL, Lukey, GC, Mallicoat, SW, Kriven, WM & Van Deventer, JS 2005, 'Understanding the relationship between geopolymer composition, microstructure and mechanical properties', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 269, no. 1, pp. 47-58.

Eagle, MC, Richardson, WS, Hay, SS & Cox, C 1993, 'Soil washing for volume reduction of radioactively contaminated soils', *Remediation Journal*, vol. 3, no. 3, pp. 327-44.

Edmeades, RM & Hewlett, PC 1998, 'Cement admixtures', *Leas's chemistry of cement and concrete, 4th ed. Edited by PC Hewlett. Butterworth-Heinemann, UK*, pp. 841-905.

Eijk, RJ 2001, *Hydration of cement mixtures containing contaminants: design and application of the solidified product*, University of Twente.

Ejeh, S & Uche, O 2009, 'Effect of crude oil spill on compressive strength of concrete materials', *Journal of Applied Sciences Research*, vol. 5, no. 10, pp. 1756-61.

El-Barasi, YM & Barrani, M 2012, 'Factors affecting natural vegetation on EL-Harouge mountain, Central part of Libyan desert (Sahara)'.

El-Nemr, KF 2011, 'Effect of different curing systems on the mechanical and physico-chemical properties of acrylonitrile butadiene rubber vulcanizates', *Materials & Design*, vol. 32, no. 6, pp. 3361-9.

Energy, O 2010, 'International Energy Outlook', *Natural Gas: Issues*.

Engelsen, CJ, Mehus, J, Pade, C & Sæther, DH 2005, 'Carbon dioxide uptake in demolished and crushed concrete', *Project report*, pp. 395-2005.

Eni-Oil 2009, *Sustainability Report eni company 2009 in Libya*, http://www.eni.com/attachments/sostenibilita/sustainability-report-09-eng.pdf>.

Erdoğan, T 2003, 'Concrete', *Metu Pres, Ankara, Turkey*.

Fakhru'l-Razi, A, Pendashteh, A, Abdullah, LC, Biak, DRA, Madaeni, SS & Abidin, ZZ 2009, 'Review of technologies for oil and gas produced water treatment', *Journal of Hazardous Materials*, vol. 170, no. 2–3, pp. 530-51.

Felekoğlu, B, Türkel, S & Baradan, B 2007, 'Effect of water/cement ratio on the fresh and hardened properties of self-compacting concrete', *Building and Environment*, vol. 42, no. 4, pp. 1795-802.

Fine, P, Graber, E & Yaron, B 1997, 'Soil interactions with petroleum hydrocarbons: abiotic processes', *Soil Technology*, vol. 10, no. 2, pp. 133-53.

Fingas, MF 2013, 'Modeling oil and petroleum evaporation', *Journal of Petroleum Science Research*.

Foster, SS 1998, 'Groundwater recharge and pollution vulnerability of British aquifers: a critical overview', *Geological Society, London, Special Publications*, vol. 130, no. 1, pp. 7-22.

Fu, TC, Yeih, W, Chang, JJ & Huang, R 2014, 'The Influence of Aggregate Size and Binder Material on the Properties of Pervious Concrete', *Advances in Materials Science and Engineering*, vol. 2014.

Gilbert, TT, Nirmalakhandan, N & Jorge, LG-T 2002, 'Performance evaluation of an activated sludge system for removing petroleum hydrocarbons from oilfield produced water', *Advances in Environmental Research*, vol. 6, no. 4, pp. 455-70.

Givi, AN, Rashid, SA, Aziz, FNA & Salleh, MAM 2010, 'Assessment of the effects of rice husk ash particle size on strength, water permeability and workability of binary blended concrete', *Construction and Building Materials*, vol. 24, no. 11, pp. 2145-50.

Gonnerman, H & Shuman, E 1928, 'Flexure and tension tests of plain concrete', *Major series*, vol. 171, no. 209, p. 149.

Gowripalan, N, Cabrera, JG, A.R, Ca & Wainwright, PJ 1992, 'Effect of Curing on Durability,Durable Concrete', *ACI Compilation 24. American Concrete Institute, Farmington Hills, Michigan, USA*,, pp. 47-54.

Grande, T & Barbosa, D 2003, 'Soil Decontamination by Supercritical Extraction', *Environmental, Agriculture and Food Chemistry Journal*, vol. 2, pp. 331-6.

Güneyisi, E, Özturan, T & Gesoğlu, M 2005, 'A study on reinforcement corrosion and related properties of plain and blended cement concretes under different curing conditions', *Cement and Concrete Composites*, vol. 27, no. 4, pp. 449-61.

Guo, X, Shi, H & Dick, WA 2010, 'Compressive strength and microstructural characteristics of class C fly ash geopolymer', *Cement and Concrete Composites*, vol. 32, no. 2, pp. 142-7.

Halliburton 2010a, *Halliburton, Water management [online]. Available from*, viewed 19/09, < http://www.halliburton.com/ps/default.aspx?navid=1787&pageid=4051 >.

Halliburton 2010b, *Water management [online]. Available from:*, viewed 17/09, < http://www.halliburton.com/ps/default.aspx?navid=1787&pageid=4051 >.

Hamad, BS & Rteil, AA 2003, 'Effect of used engine oil on structural behavior of reinforced concrete elements', *Construction and Building Materials*, vol. 17, no. 3, pp. 203-11.

Hamad, BS, Rteil, AA & El-Fadel, M 2003, 'Effect of used engine oil on properties of fresh and hardened concrete', *Construction and Building Materials*, vol. 17, no. 5, pp. 311-8.

Han, F, Liu, R, Wang, D & Yan, P 2014, 'Characteristics of the hydration heat evolution of composite binder at different hydrating temperature', *Thermochimica Acta*, vol. 586, pp. 52-7.

Hardjito, D & Rangan, BV 2005, 'Development and properties of low-calcium fly ash-based geopolymer concrete', *Perth, Australia: Curtin University of Technology*.

Hardjito, D, Wallah, SE, Sumajouw, DM & Rangan, BV 2004, 'On the development of fly ash-based geopolymer concrete', *ACI Materials Journal*, vol. 101, no. 6.

Hardjito, D, Sumajouw, DM, Wallah, S & Rangan, B 2005, 'Fly ash-based geopolymer concrete', *Australian Journal of Structural Engineering*, vol. 6, no. 1, p. 77.

Hardjito, D, Wallah, S, Sumajouw, D & Rangan, B 2005, 'Introducing fly ash-based geopolymer concrete: manufacture and engineering properties', in 30th Conference on our World in Concrete and Structures: *proceedings of the30th Conference on our World in Concrete and Structures* pp. 23-4.

Harris, A, Manning, M, Tearle, W & Tweed, C 2002, 'Testing of models of the dissolution of cements—leaching of synthetic CSH gels', *Cement and Concrete Research*, vol. 32, no. 5, pp. 731-46.

Hassan, HF, Taha, R, Al Rawas, A, Al Shandoudi, B, Al Gheithi, K & Al Barami, AM 2005, 'Potential uses of petroleum-contaminated soil in highway construction', *Construction and Building Materials*, vol. 19, no. 8, pp. 646-52.

Hassan, HS 2013, *Libyan Oil and Hydrocarbon Potential*, SEPM STRATA, <http://sepmstrata.org/Libya>.

Hassas S. Hassan 2009, *Tripolitanian Basin Stratigraphy and Hydrocarbon Potential*, viewed 10/09, < http://sepmstrata.org/Libya>.

Hayri, U & Baradan, B 2011, 'The effect of curing temperature and relative humidity on the strength development of Portland cement mortar', *Scientific Research and Essays*, vol. 6, no. 12, pp. 2504-11.

Manual of soil laboratory testing. Volume 1: Soil Classification and Compaction Tests. (2006) 1 Caithness: Whittles publishing.

Head, KH & Epps, R 2010, *Manual of soil laboratory testing*, vol. 2, Pentech Press London.

Hebatpuria, VM, Arafat, HA, Rho, HS, Bishop, PL, Pinto, NG & Buchanan, RC 1999, 'Immobilization of phenol in cement-based solidified/stabilized hazardous wastes using regenerated activated carbon: leaching studies', *Journal of Hazardous Materials*, vol. 70, no. 3, pp. 117-38.

Henrichsen, A & Laugesen, P 1994, 'Monitoring of concrete quality in high performance civil engineering constructions', in MRS Proceedings: *proceedings of theMRS Proceedings* Cambridge Univ Press, p. 49.

Heron, L, P, D & B, T 2007, 'Prospects in Libya's mature and frotier basins', *First break*, vol. 25, pp. 73-9.

Hudyma, N, Avar, BB & Karakouzian, M 2004, 'Compressive strength and failure modes of lithophysae-rich Topopah Spring Tuff specimens and analog models containing cavities', *Engineering Geology*, vol. 73, no. 1, pp. 179-90.

Ishida, T & Maekawa, K 2000, 'Modeling of pH profile in pore water based on mass transport and chemical equilibrium theory', in Proceedings-japan society of civil engineers: *proceedings of theProceedings-japan society of civil engineers* Dotoku Gakkai, pp. 203-16.

Izdebska-Mucha, D, Trzcińsk, J, Żbik, M & Frost, RL 2011, 'Influence of hydrocarbon contamination on clay soil microstructure', *Clay Minerals*, vol. 46, no. 1, pp. 47-58.

Jackson, N & Dhir, RK 1989, *Structural Engineering Materials*, CRC Press.

Jain, S & Srivastava, S 1969, 'Mechanism of Emulsification with Special Reference to Solid Stabilized Emulsions', *Bulletin of the Chemical Society of Japan*, vol. 42, no. 5, pp. 1171-8.

James, O, Ndoke, P & Kolo, S 2012, 'Effect Of Different Curing Methods On The Compressive Strength Of Concrete', *Pan*, vol. 13, no. 75µm, p. 10.03.

Jasim, AT & Jawad, FA 2010, 'Effect of oil on strength of normal and high performance concrete', *Al-Qadisiya Journal For Engineering Sciences*, vol. 3, no. 1, p. 8.

Jézéquel, P-H & Collin, V 2007, 'Mixing of concrete or mortars: dispersive aspects', *Cement and Concrete Research*, vol. 37, no. 9, pp. 1321-33.

Jia, Y, Wu, Q, Shang, H, Yang, ZN & Shan, H 2011, 'The influence of oil contamination on the geotechnical properties of coastal sediments in the Yellow River Delta, China', *Bulletin of Engineering Geology and the Environment*, vol. 70, no. 3, pp. 517-25.

Jiménez, AF & Palomo, A 2005, 'Composition and microstructure of alkali activated fly ash binder: effect of the activator', *Cement and Concrete Research*, vol. 35, no. 10, pp. 1984-92.

K. Vijai, R. Kumutha & B. G. Vishnuram 2010, 'Influence of Curing Types on Strength of Geopolymer Concrete', *NBM Construction information*, p. 5.

Kadafa, AA 2012, 'Oil exploration and spillage in the Niger Delta of Nigeria', *Civil and Environmental Research*, vol. 2, no. 3, pp. 38-51.

Kaliyan, N & Vance Morey, R 2009, 'Factors affecting strength and durability of densified biomass products', *Biomass and Bioenergy*, vol. 33, no. 3, pp. 337-59.

Kambic, M & Hammaker, J 2012, 'Geopolymer concrete: the future of green building materials'.

Kay, B 1990, 'Rates of change of soil structure under different cropping systems', in *Advances in Soil Science 12*, Springer, pp. 1-52.

Kay, B 1998, 'Soil structure and organic carbon: a review', *Soil processes and the carbon cycle*, pp. 169-97.

Khale, D & Chaudhary, R 2007, 'Mechanism of geopolymerization and factors influencing its development: a review', *Journal of materials science*, vol. 42, no. 3, pp. 729-46.

Kharita, M, Yousef, S & AlNassar, M 2010, 'The effect of the initial water to cement ratio on shielding properties of ordinary concrete', *Progress in Nuclear Energy*, vol. 52, no. 5, pp. 491-3.

Khatib, Z & Verbeek, P 2003, 'Water to value-produced water management for sustainable field development of mature and green fields', *Journal of Petroleum Technology*, vol. 55, no. 01, pp. 26-8.

Khayat, K 1999, 'Workability, testing, and performance of self-consolidating concrete', *ACI Materials Journal*, vol. 96, no. 3.

Khosravi, E, Ghasemzadeh, H, Sabour, MR & Yazdani, H 2013, 'Geotechnical Properties of Gas Oil-Contaminated Kaolinite', *Engineering Geology*, vol. 166, pp. 11-6.

Kim, J-K, Moon, Y-H & Eo, S-H 1998, 'Compressive strength development of concrete with different curing time and temperature', *Cement and Concrete Research*, vol. 28, no. 12, pp. 1761-73.

Kim, Y-Y, Lee, K-M, Bang, J-W & Kwon, S-J 2014, 'Effect of W/C ratio on durability and porosity in cement mortar with constant cement amount', *Advances in Materials Science and Engineering*, vol. 2014.

Klein, A & Sarsby, RW 2000, 'Problems in defining the geotechnical behaviour of wastewater sludges', *ASTM SPEC TECH PUBL*, no. 1374, pp. 74-87.

Kocaman, B, Yanik, R, Kose, C & Ozturk, A 2011, 'Effect of Different Cure Conditions on Compressive Strength of Concrete Having Different Properties', *Journal of Animal and Veterinary Advances*, vol. 10, no. 14, pp. 1756-9.

Kolyvas, C 2007 'Curing of concrete', MSc thesis, Delft University of Technology.

Kosmatka, S, Kerkhoff B, Panarese, W, MacLeod, Na & McGrath RJ 2002, 'Design and control of concrete mixtures Cement Association of Canada', *Ottawa, Ontario, Canada*.

Kosmatka, SH, Panarese, WC, Allen, GE & Cumming, S 2002, *Design and control of concrete mixtures*, vol. 5420, Portland Cement Association Skokie, IL.

Kostecki, P, T., Bonazountas, M., Calabrese, E., J. 1997, 'Contaminated Soils', in Amherst, MA.: *proceedings of theAmherst, MA.* Amherst Scientific Publishers, pp. pp.289-90.

Kourounis, S, Tsivilis, S, Tsakiridis, PE, Papadimitriou, GD & Tsibouki, Z 2007, 'Properties and hydration of blended cements with steelmaking slag', *Cement and Concrete Research*, vol. 37, no. 6, pp. 815-22.

Kovler, K 2012, 'Effect of superabsorbent polymers on the mechanical properties of concrete', in *Application of Super Absorbent Polymers (SAP) in Concrete Construction*, Springer, pp. 99-114.

Kumar, S, Kumar, R & Mehrotra, S 2010, 'Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymer', *Journal of materials science*, vol. 45, no. 3, pp. 607-15.

Kwon, S-J & Na, U-J 2011, 'Prediction of durability for RC columns with crack and joint under carbonation based on probabilistic approach', *International Journal of Concrete Structures and Materials*, vol. 5, no. 1, pp. 11-8.

Le Heron, DP & Thusu, B 2007, 'Prospects in Libya's mature and frontier basins', *First Break*, vol. 25, no. 2, pp. 73-9.

Lea, FM 1970, 'The chemistry of cement and concrete'.

Lenhard, R & Parker, J 1988, 'Experimental validation of the theory of extending two-phase saturation-pressure relations to three-fluid phase systems for monotonic drainage paths', *Water Resources Research*, vol. 24, no. 3, pp. 373-80.

Lloyd, N & Rangan, V 2009, 'Geopolymer Concrete—Sustainable Cementless Concrete', in Proceedings of the 10th ACI International Conference on Recent Advances in Concrete Technology and Sustainability Issues: *proceedings of theProceedings of the 10th ACI International Conference on Recent Advances in Concrete Technology and Sustainability Issues* pp. 33-54.

Lloyd, N & Rangan, BV 2010, 'Geopolymer concrete: a review of development and opportunities', in Proceedings, 35th conference on our world in concrete and structures, Singapore Concrete Institute, Singapore: *proceedings of theProceedings, 35th conference on our world in concrete and structures, Singapore Concrete Institute, Singapore* pp. 25-7.

Lloyd, N & Rangan, BV 2010, 'Geopolymer Concrete: A Review of Development and Opportunities', in 35th Conference on Our World in Concrete & Structures: *proceedings of the35th Conference on Our World in Concrete & Structures*.

Lokuge, W, Karunasena, W & Heemskerk, C 2013, 'Effect of strain rate on geopolymer concrete', *Proceedings of Concrete 2013*.

Ltd, C 2009 *C. Putoline HPX Fork & Suspension Oil* http://www.championmotouk.com/product-info-t.php?Putoline-HPX-Fork-Suspension-Oil-pid10650.html.

Luciani, G 1994, 'The oil rent, the fiscal crisis of the state and democratization', *Democracy without democrats*, pp. 130-55.

Luping, T 1986, 'A study of the quantitative relationship between strength and pore-size distribution of porous materials', *Cement and Concrete Research*, vol. 16, no. 1, pp. 87-96.

Lyons, RA, Temple, J, Evans, D, Fone, DL & Palmer, SR 1999, 'Acute health effects of the Sea Empress oil spill', *Journal of Epidemiology and Community Health*, vol. 53, no. 5, pp. 306-10.

Madderom, FW & President, V 1980, 'Excess water can be a costly ingredient in concrete', *Concrete Construction*.

Mamlouk, MS & Zaniewski, JP 2011, *Materials for civil and construction engineers*, Pearson Higher Ed.

Manoli, E & Samara, C 1999, 'Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis', *TrAC Trends in Analytical Chemistry*, vol. 18, no. 6, pp. 417-28.

Martínez-Palou, R, Mosqueira, MdL, Zapata-Rendón, B, Mar-Juárez, E, Bernal-Huicochea, C, de la Cruz Clavel-López, J & Aburto, J 2011, 'Transportation of heavy and extra-heavy crude oil by pipeline: A review', *Journal of Petroleum Science and Engineering*, vol. 75, no. 3–4, pp. 274-82.

Mashalah, K, Amir, H & Majid, T 2006, 'The effects of crude oil contamination on geotechnical properties of Bushehr coastal soils in Iran', *The Geological Society of London. IAEG2006 Paper number*, vol. 214.

Mashalah, K, Amir, HC & Majid, T 2007, 'Effects of crude oil contamination on geotechnical properties of clayey and sandy soils', *Engineering Geology*, vol. 89, no. 3–4, pp. 220-9.

Masters, GM & Ela, W 2008, *Introduction to environmental engineering and science*, vol. 3, Prentice Hall Englewood Cliffs, NJ.

Mees, EE 2008, 'Ras Lanuf Extinguished After Seven Days', *Middle east economic survey*, vol. 51, no. 35, p. 34.

Meegoda, NJ & Ratnaweera, P 1994, 'Compressibility of contaminated fine-grained soils'.

Mehta, KP & Monteiro, PJM 1993, *Concrete structure, properties, and materials.*, Prentice Hall, New Jersey.

Mehta, PK 1986, 'Concrete. Structure, properties and materials'.

Memon, FA, Nuruddin, MF, Demie, S & Shafiq, N 2011, 'Effect of curing conditions on strength of fly ash-based self-compacting geopolymer concrete', *World Acad Sci Eng Technol*, vol. 80, pp. 860-3.

Menon, V & Wasan, D 1988, 'A review of the factors affecting the stability of solids-stabilized emulsions', *Separation science and technology*, vol. 23, no. 12-13, pp. 2131-42.

Meo, SA, Al-Drees, AM, Meo, IMU, Al-Saadi, MM & Azeem, MA 2008, 'Lung function in subjects exposed to crude oil spill into sea water', *Marine pollution bulletin*, vol. 56, no. 1, pp. 88-94.

Merrigan, M 1986, 'Efflorescence: cause and control', *MASONRY SOC. J. Masonry Soc. J.*, vol. 5, no. 1.

Miller Jr, RG 1997, *Beyond ANOVA: basics of applied statistics*, CRC Press.

Mindess, S, Young, JF & Darwin, D 2003, *Concrete*.

Mirza, C 1996, 'Discussion: Geotechnical Properties of Oil-Contaminated Kuwaiti Sand', *Journal of geotechnical engineering*, vol. 122, no. 9, pp. 786-8.

Munoz, J, Tejedor, I, Anderson, M & Cramer, S 2005, 'Effects of coarse aggregate clay-coatings on concrete performance', *Innovative Pavement Research Foundation Research Report*.

Nagaraj, T & Banu, Z 1996, 'Generalization of Abrams' law', *Cement and Concrete Research*, vol. 26, no. 6, pp. 933-42.

Najafi Kani, E, Allahverdi, A & Provis, JL 2012, 'Efflorescence control in geopolymer binders based on natural pozzolan', *Cement and Concrete Composites*, vol. 34, no. 1, pp. 25-33.

Nasvi, M, Ranjith, P, Sanjayan, J & Bui, H 2014, 'Effect of temperature on permeability of geopolymer: A primary well sealant for carbon capture and storage wells', *Fuel*, vol. 117, pp. 354-63.

Nataraja, M 2002, 'Concrete Mix Design'.

National Oil Corporation 2011 *PFC Energy and NOC*, viewed 12/09, < http://en.noclibya.com.ly/>.

Natural Resources and Environment Policy Division 2009, *Oil spill on the Moreton Bay Ramsar site*, Department of Environment and Resource Management Queenslan.

Nematzadeh, M & Naghipour, M 2012, 'Compressing fresh concrete technique and the effect of excess water content on physical–mechanical properties of compressed concrete', *Materials & Design*, vol. 37, pp. 256-67.

Neuwald, AD 2010, *Water-to-Cement Ratio and Aggregate Moisture Corrections*, National Precast Concrete Association, City Center Drive, Suite 200, Carmel, IN 46032, USA,,<.

Neville, A 1995, *Properties of concrete (4th and final ed.) Longman Group Limited*, London.

Neville, A 1996, *Properties of concrete (4th and final ed.) Addison Wesley Logman*, England.

Neville A.M. (ed.) 2000, *Properties of Concrete*, 4th Edition, Pitman Publishing Ltd, , 39 Parker Street, London.

Neville, AM 1995, *Properties of concrete*.

Neville, MA 1981, 'Properties of concrete', *Pitman, London*, p. 18.

NTSB 2010, *Hazardous Liquid Pipeline Rupture and Release*, Washington, D.C. 20594.

Nudelman, N, Ríos, S & Katusich, O 2002, 'Organic co-solvent effect on the estimation of the equilibrium aqueous concentrations of oil residuals in Patagonian soil', *Environ Technol*, vol. 23, no. 9, pp. 961-70.

Nuruddin, F, Shafiq, N & Beddu, S 2010, 'Effects of Used Engine Oil on MIRHA Concrete'.

Nwofor, T 2012, 'Durability of block work: the effect of varying water/cement ratio of mortar joint', *Advances in Applied Science Research*, vol. 3, no. 3.

Obeta, I & Eze-Uzomaka, O 2013, 'Geotechnical properties of waste engine oil contaminated laterites‖', *Nigerian Journal of Technology*, vol. 32, no. 2, pp. 203-10.

Odler, I 1998, 'Hydration, setting and hardening of Portland cement', *Lea's chemistry of cement and concrete*, vol. 4, pp. 241-97.

Olivia, M & Nikraz, H 2012, 'Properties of fly ash geopolymer concrete designed by Taguchi method', *Materials & Design*, vol. 36, pp. 191-8.

Oluokun, FA 1994, 'Fly ash concrete mix design and the water-cement ratio law', *ACI Materials Journal*, vol. 91, no. 4.

Onwurah, I, Ogugua, V, Onyike, N, Ochonogor, A & Otitoju, O 2007, 'Crude oil spills in the environment, effects and some innovative clean-up biotechnologies'.

Osuji, L & Ezebuiro, P 2006, 'Hydrocarbon contamination of a typical mangrove floor in Niger Delta, Nigeria', *International Journal of Environmental Science and Technology*, vol. 3, no. 3, pp. 313-20.

Osuji, S & Nwankwo, E 2015a, 'Effect of crude oil contamination on the compressive strength of concrete', *Nigerian Journal of Technology*, vol. 34, no. 2, pp. 259-65.

Osuji, S & Nwankwo, E 2015b, 'Effect of crude oil contamination on the compressive strength of concrete', *Nigerian Journal of Technology (NIJOTECH)*, vol. 34, no. 2, pp. 259-65.

Pade, C & Guimaraes, M 2007, 'The CO 2 uptake of concrete in a 100 year perspective', *Cement and Concrete Research*, vol. 37, no. 9, pp. 1348-56.

Palomo, A, Alonso, S, Fernandez-Jiménez, A, Sobrados, I & Sanz, J 2004, 'Alkaline activation of fly ashes: NMR study of the reaction products', *Journal of the American Ceramic Society*, vol. 87, no. 6, pp. 1141-5.

Pan, S-Y, Chang, E & Chiang, P-C 2012, 'CO 2 capture by accelerated carbonation of alkaline wastes: a review on its principles and applications', *Aerosol and Air Quality Research*, vol. 12, no. 5, pp. 770-91.

Pandey, S & Sharma, R 2000, 'The influence of mineral additives on the strength and porosity of OPC mortar', *Cement and Concrete Research*, vol. 30, no. 1, pp. 19-23.

Pane, I & Hansen, W 2005, 'Investigation of blended cement hydration by isothermal calorimetry and thermal analysis', *Cement and Concrete Research*, vol. 35, no. 6, pp. 1155-64.

Pantazopoulou, S & Mills, R 1995, 'Microstructural aspects of the mechanical response of plain concrete', *ACI Materials Journal*, no. 92, pp. 605-16.

Paria, S & Yuet, PK 2006, 'Solidification-stabilization of organic and inorganic contaminants using portland cement: a literature review', *Environmental Reviews*, vol. 14, no. 4, pp. 217-55.

Parrott, L 1991, 'Factors influencing relative humidity in concrete', *Magazine of concrete Research*, vol. 43, no. 154, pp. 45-52.

Patil, AA, Chore, H & Dode, P 2014, 'Effect of curing condition on strength of geopolymer concrete', *Advances in Concrete Construction*, vol. 2, no. 1, pp. 29-37.

Phair, J & Van Deventer, J 2001, 'Effect of silicate activator pH on the leaching and material characteristics of waste-based inorganic polymers', *Minerals Engineering*, vol. 14, no. 3, pp. 289-304.

Phair, J, Van Deventer, J & Smith, J 2000, 'Mechanism of polysialation in the incorporation of zirconia into fly ash-based geopolymers', *Industrial & engineering chemistry research*, vol. 39, no. 8, pp. 2925-34.

Popovics, S 1990, 'Analysis of concrete strength versus water-cement ratio relationship', *ACI Materials Journal*, vol. 87, no. 5.

Potgieter, JH & Kaspar, H 1999, 'Hydration of Cement', *South African Journal of Chemistry*, vol. 52, no. 4.

Powers, T & Brownyard, T 1947, 'Studies of the physical properties of hardened Portland cement paste', in ACI Journal Proceedings: *proceedings of theACI Journal Proceedings*.

Price, R, Boyd, P, Noel, J & Martin, R 1994, *Relation between static and dynamic rock properties in welded and nonwelded tuff*, Sandia National Labs., Albuquerque, NM (United States). Funding organisation: USDOE, Washington, DC (United States).

Price, WH 1951, 'Factors influencing concrete strength', in ACI Journal Proceedings: *proceedings of theACI Journal Proceedings* ACI.

Puri, VK 2000, 'Geotechnical aspects of oil-contaminated sands', *Soil and Sediment Contamination*, vol. 9, no. 4, pp. 359-74.

Qiao, B, Chu, J-c, Zhao, P, Yu, Y & Li, Y 2002, 'Marine oil spill contingency planning', *J Environ Sci (China)*, vol. 14, no. 1, pp. 102-7.

Rahman, Z, Umar, H & Ahmed, N 2010, 'Geotechnical characteristics of oil contaminated granitic and metasedimentary soils', *Asian Journal, Applied Science*, vol. 3, pp. 273-49.

Rahman, Hamzah, U, Taha, MR, Ithnain, NS & Ahmad, N 2010b, 'Influence of oil contamination on geotechnical properties of basaltic residual soil', *American Journal of Applied Sciences*, vol. 7, no. 7, p. 954.

Rakhimova, N & Rakhimov, R 2015, 'Characterisation of ground hydrated Portland cement-based mortar as an additive to alkali-activated slag cement', *Cement and Concrete Composites*, vol. 57, pp. 55-63.

Rangan, BV 2008, 'Fly ash-based geopolymer concrete', *Your Building Administrator*, vol. 2.

Rangan, BV, Hardjito, D, Wallah, SE & Sumajouw, DM 2005, 'Studies on fly ash-based geopolymer concrete', in Proceedings of 4th World Congress on Geopolymer, Saint Quentin, France: *proceedings of theProceedings of 4th World Congress on Geopolymer, Saint Quentin, France* pp. 133-7.

Rao, GA 2001, 'Role of water–binder ratio on the strength development in mortars incorporated with silica fume', *Cement and Concrete Research*, vol. 31, no. 3, pp. 443-7.

Rao, KM, Rao, VT & and Babu, GR 2008, 'Interaction of clay soil with textile dye waste', *Electronic Journal of Geotechnical Engineering*.

Ravina, D & Soroka, I 1994, 'Slump loss and compressive strength of concrete made with WRR and HRWR admixtures and subjected to prolonged mixing', *Cement and Concrete Research*, vol. 24, no. 8, pp. 1455-62.

Ray, JP & Engelhardt, FR 1993, *Produced Water: Technological/Environmental Issues and Solutions*, 1st edn, Springer-Verlag; Reprint edizione

Rehman, H, Abduljauwad, SN & Akram, T 2007, 'Geotechnical behavior of oil-contaminated fine-grained soils', *Electronic Journal of Geotechnical Engineering*, vol. 12, pp. 1-12.

Riser, R 1998, *Remediation of petroleum contaminated soils: biological, physical & chemical processes*, United States: Lewis Publisher, Boca Raton, Florida.

Robert, M & Benmokrane, B 2010, 'Effect of aging on bond of GFRP bars embedded in concrete', *Cement and Concrete Composites*, vol. 32, no. 6, pp. 461-7.

Roy, DM & Gouda, GR 1973, 'Porosity-Strength Relation in Cementitious Materials with Very High Strengths', *Journal of the American Ceramic Society*, vol. 56, no. 10, pp. 549-50.

Rößler, M & Odler, I 1985, 'Investigations on the relationship between porosity, structure and strength of hydrated portland cement pastes I. Effect of porosity', *Cement and Concrete Research*, vol. 15, no. 2, pp. 320-30.

Rudawska, A 2012, *Adhesive properties*, INTECH Open Access Publisher.

Safiuddin, M, Raman, S & Zain, M 2007, 'Effect of different curing methods on the properties of microsilica concrete', *Australian journal of basic and applied sciences*, vol. 1, no. 2, pp. 87-95.

Satpute, BM, Wakchaure, RM & Patankar, VS 2012, 'Effect of Duration and Temperature of Curing on Compressive Strength of Geopolymer Concrete', *International Journal of Engineering and Innovative Technology (IJEIT)*, vol. 1, no. 5.

Saul, A 1951, 'Principles underlying the steam curing of concrete at atmospheric pressure', *Magazine of concrete Research*, vol. 2, no. 6, pp. 127-40.

Schulze, J 1999, 'Influence of water-cement ratio and cement content on the properties of polymer-modified mortars', *Cement and Concrete Research*, vol. 29, no. 6, pp. 909-15.

Scurtu Ciprian Teodor 2009, 'Treatment of produced water:targeting dissolved compounds to meet a zero harmful discharge in oil and gas production', Norwegian University of Science and Technology.

Seed, HB, Mitchell, J & Chan, C 1961, 'The strength of compacted cohesive soils, in Shear strength of cohesive soils', *ASCE*, pp. 877-964.

Sersale, R, Cioffi, R, Frigione, G & Zenone, F 1991, 'Relationship between gypsum content, porosity and strength in cement', *Cement and Concrete Research*, vol. 21, no. 1, pp. 120-6.

Shakesby, R, Wallbrink, P, Doerr, S, English, P, Chafer, C, Humphreys, G, Blake, W & Tomkins, K 2007, 'Distinctiveness of wildfire effects on soil erosion in south-east Australian eucalypt forests assessed in a global context', *Forest Ecology and Management*, vol. 238, no. 1, pp. 347-64.

Shamsai, A, Peroti, S, Rahmani, K & Rahemi, L 2012, 'Effect of water-cement ratio on abrasive strength, porosity and permeability of nano-silica concrete', *World Applied Sciences Journal*, vol. 17, no. 8, pp. 929-33.

Shao, Y & Morshed, AZ 2015, 'Early carbonation for hollow-core concrete slab curing and carbon dioxide recycling', *Materials and structures*, vol. 48, no. 1-2, pp. 307-19.

Sharma, HD & Reddy, KR 2004, *Geoenvironmental engineering: site remediation, waste containment, and emerging waste management technologies*, John Wiley & Sons, Inc.

Shetty, C, Nikolov, A, Wasan, D & Bhattacharyya, B 1992, 'Demulsification of water in oil emulsions using water soluble demulsifiers', *Journal of dispersion science and technology*, vol. 13, no. 2, pp. 121-33.

Shin, E & Das, B 2000, 'Some physical properties of unsaturated oil-contaminated sand', *Geotechnical special publication*, pp. 142-52.

Silva, Aa & Fiuza, A 2005, 'Stabilization Uuse of solvent extraction to remediate soils contaminated with hydrocarbons', *the journal of hazardous materials*, pp. 224-9.

Simeonov, P & Ahmad, S 1995, 'Effect of transition zone on the elastic behavior of cement-based composites', *Cement and Concrete Research*, vol. 25, no. 1, pp. 165-76.

SImetric. 2011, *specific gravity of liquids.*, http://www.simetric.co.uk/si_liquids.htm.

Singh, S, Srivastava, R & John, S 2008, 'Settlement characteristics of clayey soils contaminated with petroleum hydrocarbons', *Soil & Sediment Contamination*, vol. 17, no. 3, pp. 290-300.

Škvára, F, Kopecký, L, Myšková, L, Šmilauer, V, Alberovska, L & Vinšová, L 2009, 'Aluminosilicate polymers–influence of elevated temperatures, efflorescence', *Ceramics–Silikáty*, vol. 53, no. 4, pp. 276-82.

Smith, I 2013, *Smith's elements of soil mechanics*, Wiley. com.

Sora, IN, Pelosato, R, Zampori, L, Botta, D, Dotelli, G & Vitelli, M 2005, 'Matrix optimisation for hazardous organic waste sorption', *Applied Clay Science*, vol. 28, no. 1, pp. 43-54.

Soroka, I 1980, 'Portland Cement Paste and ConcreteChemical Publishing Co', *New York*.

Spears, RE 1983, 'The 80 percent solution to inadequate curing problems', *Concrete international*, vol. 5, no. 4, pp. 15-8.

Speight, JG 2014, *The chemistry and technology of petroleum*, CRC press.

Spence, RD & Shi, C 2004, *Stabilization and solidification of hazardous, radioactive, and mixed wastes*, CRC press.

Stark, J 2011, 'Recent advances in the field of cement hydration and microstructure analysis', *Cement and Concrete Research*, vol. 41, no. 7, pp. 666-78.

Stegemann, J & Cote, P 1996, 'A proposed protocol for evaluation of solidified wastes', *Science of the Total Environment*, vol. 178, no. 1, pp. 103-10.

Strassner, J 1968, 'Effect of pH on interfacial films and stability of crude oil-water emulsions', *Journal of Petroleum Technology*, vol. 20, no. 03, pp. 303-12.

Sumajouw, M & Rangan, BV 2006, *Low-calcium fly ash-based geopolymer concrete: reinforced beams and columns*, Research Report GC 3, Faculty of Engineering, Curtin University of Technology, Perth, Australia.

Tasdemir, C 2003, 'Combined effects of mineral admixtures and curing conditions on the sorptivity coefficient of concrete', *Cement and Concrete Research*, vol. 33, no. 10, pp. 1637-42.

Taylor, GD 2013, *Materials in construction: An introduction*, Routledge.

Taylor, HF 1997, *Cement chemistry*, Thomas Telford.

Taylor, SE 1992, 'Resolving crude oil emulsions[demulsifiers]', *Chemistry and Industry*, pp. 770-3.

Temuujin, J, Van Riessen, A & Williams, R 2009, 'Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes', *Journal of Hazardous Materials*, vol. 167, no. 1, pp. 82-8.

Temuujin, J, Williams, R & Van Riessen, A 2009, 'Effect of mechanical activation of fly ash on the properties of geopolymer cured at ambient temperature', *Journal of Materials Processing Technology*, vol. 209, no. 12, pp. 5276-80.

Tuncan, A & Pamukcu, S 1992, 'Predicted mechanism of crude oil and marine clay interactions', *Proceedings of the Environmental Geotechnology, May*, pp. 25-7.

U.S Energy Information Adminstration. 2011, *Independent Statistics & Analysis*
U.S. Energy Information Administration viewed 10/10, <http://www.eia.doe.gov>.

Uddin, M, Jameel, M, Sobuz, HR, Hasan, NM, Islam, M & Amanat, KM 2012, 'The Effect of Curing Time on Compressive Strength of Composite Cement Concrete', in Applied Mechanics and Materials: *proceedings of theApplied Mechanics and Materials* Trans Tech Publ, pp. 4105-9.

Uddin, MA, Jameel, M, Sobuz, HR, Islam, MS & Hasan, NMS 2013, 'Experimental study on strength gaining characteristics of concrete using Portland Composite Cement', *KSCE Journal of Civil Engineering*, vol. 17, no. 4, pp. 789-96.

Ukpong, EC & Umoh, IC 2015, 'Effect of crude oil spillage on geotechnical properties of lateritic soil in okoroete, eastern obololo', *International Journal of Engineering and Applied Sciences*, vol. 7, pp. 12-24.

USEPA 1997, *Pollution Prevention and Toxics*, Washington, DC,,<.

Valcke, SL, Polder, RB & Beijersbergen van Henegouwen, J 2012, 'Understanding transport properties of geopolymer mortar using polarization and fluorescence microscopy', in Second International Conference on Microstructural-related Durability of Cementitious Composites, RILEM Proceedings pro083, 11-13 April, 2012, Amsterdam, The Netherlands; Authors version: *proceedings of theSecond International Conference on Microstructural-related Durability of Cementitious Composites, RILEM Proceedings pro083, 11-13 April, 2012, Amsterdam, The Netherlands; Authors version* RILEM Publications SARL.

Vanden, A & Protz, R 1999, 'The representative elementary area (REA) in studies of quantitative soil micromorphology', *Geoderma*, vol. 89, no. 3, pp. 333-46.

Venosa, AD & Zhu, X 2003, 'Biodegradation of crude oil contaminating marine shorelines and freshwater wetlands', *Spill Science & Technology Bulletin*, vol. 8, no. 2, pp. 163-78.

Vijai, K, Kumutha, R & Vishnuram, B 2013, 'Experimental investigations on mechanical properties of geopolymer concrete composites'.

Vipulanandan, C & Krishnan, S 1993, 'Leachability and biodegradation of high concentrations of phenol and o-chlorophenol', *Hazardous waste and hazardous materials*, vol. 10, no. 1, pp. 27-47.

Vu, XH, Malecot, Y, Daudeville, L & Buzaud, E 2009, 'Effect of the water/cement ratio on concrete behavior under extreme loading', *International Journal for Numerical and Analytical Methods in Geomechanics*, vol. 33, no. 17, pp. 1867-88.

Wadsö, L 2003, 'An experimental comparison between isothermal calorimetry, semi-adiabatic calorimetry and solution calorimetry for the study of cement hydration', *Nordtest report TR*, vol. 522.

Wassermann, R, Katz, A & Bentur, A 2009, 'Minimum cement content requirements: a must or a myth?', *Materials and structures*, vol. 42, no. 7, pp. 973-82.

Waziri, B, Mohammed, A & Bukar, A 2011, 'Effect of water-cement ratio on the strength properties of Quarry-Sand Concrete (QSC)', *Continental Journal of Engineering Sciences*, vol. 6, no. 2, pp. 16-21.

Winter, N 2009, 'Understanding cement', *WHD Microanalysis Consultants Ltd, United Kingdom*.

Winter, NB 2012, *Understanding cement: an introduction to cement production, cement hydration and deleterious processes in concrete*, Microanalysis Consultants.

Yang, Z, Ha, N, Jang, M & Hwang, KH 2009, 'Geopolymer concrete fabricated by waste concrete sludge with silica fume', in Materials Science Forum: *proceedings of theMaterials Science Forum* Trans Tech Publ, pp. 791-4.

Yazan, K 2005, 'Effects of retempering with superplasticizer on properties of prolonged mixed mineral admixture containing concrete at hot weather conditions', Middle east Technical University.

Yip, CK, Lukey, G & Van Deventer, J 2005, 'The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation', *Cement and Concrete Research*, vol. 35, no. 9, pp. 1688-97.

Yost, JR, Radlińska, A, Ernst, S & Salera, M 2013, 'Structural behavior of alkali activated fly ash concrete. Part 1: mixture design, material properties and sample fabrication', *Materials and structures*, pp. 1-13.

Yuan, CZ & Gud, W 1998, 'Effect of bond between aggregate and cement paste on the mechanical behaviour of concrete', in MRS Symp Proc: *proceedings of theMRS Symp Proc* pp. 41-7.

Yudenfreund, M, Hanna, KM, Skalny, J, Older, I & Brunauer, S 1972, 'Hardened Portland cement pastes of low porosity V. Compressive strength', *Cement and Concrete Research*, vol. 2, no. 6, pp. 731-43.

Zhang, Z, Yao, X & Zhu, H 2010, 'Potential application of geopolymers as protection coatings for marine concrete: II. Microstructure and anticorrosion mechanism', *Applied Clay Science*, vol. 49, no. 1, pp. 7-12.

Zhang, Z, Yao, X & Wang, H 2012, 'Potential application of geopolymers as protection coatings for marine concrete III. Field experiment', *Applied Clay Science*, vol. 67, pp. 57-60.

Zhang, Z, Wang, H, Provis, JL & Reid, A 2013, 'Efflorescence: a critical challenge for geopolymer applications?', in Concrete Institute of Australia's Biennial National Conference 2013: *proceedings of theConcrete Institute of Australia's Biennial National Conference 2013* Concrete Institute of Australia, pp. 1-10.

Zhang, Z, Provis, JL, Reid, A & Wang, H 2014, 'Fly ash-based geopolymers: The relationship between composition, pore structure and efflorescence', *Cement and Concrete Research*, vol. 64, pp. 30-41.

Zhao, D 1996, *Experimental study of stress-strain and shear strength behavior of contaminated cohesive soils*.

Zhuang, XY, Chen, L, Komarneni, S, Zhou, CH, Tong, DS, Yang, HM, Yu, WH & Wang, H 2016, 'Fly ash-based geopolymer: clean production, properties and applications', *Journal of Cleaner Production*, vol. 125, pp. 253-67.

Živica, V 2009, 'Effects of the very low water/cement ratio', *Construction and Building Materials*, vol. 23, no. 12, pp. 3579-82.