EFFECT OF CRUDE OIL CONTAMINATED SAND ON THE ENGINEERING PROPERTIES OF CONCRETE

BY

WASIU OLABAMIJI AJAGBE
B.Sc, M.Sc (Ibadan)

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University of Ibadan
Ibadan

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ABSTRACT

A considerable fraction of sand in Niger Delta Area of Nigeria is contaminated with crude oil. The contaminated sand is largely utilised by local contractors for the production of concrete. However, there is need to establish its suitability in concreting. Previous works have centered on hardened uncontaminated concrete in crude oil environment but not on concrete made with Crude Oil Contaminated Sand (COCS). This research was designed to evaluate the effect of COCS on some engineering properties of fresh and hardened COCS concrete.

Levels of crude oil contamination were determined using gravimetry method of Total Petroleum Hydrocarbon (TPH) test on nine sand samples randomly collected from some oil spill sites in Rivers State. Based on the test results, seven types of artificially contaminated sand were prepared with crude oil levels of 0.0, 2.5, 5.0, 10.0, 15.0, 20.0 and 25.0%. Workability (slump, compacting factor and flow), compressive strength, linear shrinkage, water absorption, and fire resistance were determined using concrete cubes, flexural strength using concrete beams, and surface resistivity using concrete cylinders in accordance with standard methods. Data obtained were analysed using ANOVA at $p = 0.05$. Eight models were developed using historic response surface methodology to predict the engineering properties of COCS concrete at water-cement ratio (w/c) of 0.5. Also, COCS concrete design mixes with contamination level and w/c ratio suitable for reinforced concrete were formulated.

The TPH varied from 8.6 ± 0.2 to 14.1 ± 1.3%. The workability of concrete was improved by the presence of COCS. Slump, compacting factor and flow of the fresh concrete increased with increase in contamination from 30.0 to 200.0 mm, 0.5 to 0.9 and 15.0 to 85.0%, respectively. Compressive strength, flexural strength, linear shrinkage and water absorption of the hardened concrete reduced with levels of contamination from 31.5 ± 2.3 to 3.5 ± 0.0 N/mm^2, 5.9 ± 0.8 to 0.1 ± 0.0 N/mm^2, 0.1 ± 0.0 to 0.0 cm and 0.2 to 0.0 kg respectively. At a temperature of 200.0˚C, the percentage strength reduction increased from 18.4 to 94.8% for 2.5 to 25.0% contamination. Surface resistivity ranged from 25.1 ± 0.2 to 32.3 ± 0.2 kΩ-cm. The compressive and flexural strengths of COCS concrete were reduced by more than 50.0% at crude oil contamination level greater than 10.0%. The water absorption and surface resistivity values indicated that COCS concrete exhibited greater resistance to water and chloride penetration respectively, it shrank less when compared with the uncontaminated concrete, but exhibited poor fire resistance. Coefficient of determination, R^2, of the models developed ranged from 0.823 to 0.999. Concrete design mix ratio of 1part of cement to1.6 part of COCS (10.0% crude oil) to 2.4 part of coarse aggregate was found to be appropriate at 0.45 w/c. This mix gave minimum compressive strength of 21.0 N/mm^2 which is acceptable for reinforced concrete structures.

Concretes produced with sand contaminated with less than ten percent crude oil were found suitable for use in low strength structures. Mix re-design using lower w/c improved the strength of the concrete.

Keywords: Crude oil-contaminated sand, Concrete properties, Compressive strength.

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DEDICATION

This thesis is dedicated to my late father, and brothers and sisters on the path of ALLAH.

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CERTIFICATION

I certify that this work was carried out by W. O. Ajagbe in the Department of Civil Engineering, Faculty of Technology, University of Ibadan.

Supervisor
Prof. O. A. Agbede
B. Sc., M. Sc. (Ife), Ph.D. (London), MNSE
MNSE, MNMGS, MNAH, MIWEM, MAGID
Professor of Civil Engineering
Department of Civil Engineering,
University of Ibadan, Nigeria

Supervisor
Dr. B.I.O Dahunsi
B. Sc. (Ife), M. Sc., Ph.D. (Ibadan)
MNSE, AMASCE, M.INEnv, Reg. Engr. (COREN)
Senior Lecturer, Department of Civil Engineering,
University of Ibadan, Nigeria

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CHAPTER ONE

INTRODUCTION

1.1 Background to the Research

Petroleum is a critically important but nonrenewable natural resource. It is a complex, naturally occurring mixture of organic compounds that is produced by the incomplete decomposition of biomass over a geologically long period of time. Petroleum compounds can occur in a gaseous form that is often called natural gas, as a liquid called crude oil, and as a solid or semisolid asphalt or tar associated with oil sands and shale (Nigerian Environmental Study/Action Team, 1991). Both crude oil and natural gas are predominantly a mixture of hydrocarbons (Wikipedia, 2010). Crude oil is a dark, sticky liquid which can be distilled or refined to make fuels, lubricating oils, asphalts and other valuable products. Because most petroleum is extracted in locations that are remote from places where consumption occurs, it is a commodity that must be transported in a very large quantity. The most important methods of transportation are by oceanic tanker and overland pipeline. These transportation methods can pollute the environment by accidental oil spills and by operational discharge (i.e. the cleaning of storage and ballast tanks).

One of the problems that characterize oil producing communities in Nigeria is that of oil spillage. It is a major environmental concern in the Niger Delta where over 80% of the country's crude oil is produced. Other areas are not left out as oil spills occur as a result of pipeline vandalism and inadequate care on oil production operations. Thousands of barrels of oil have been let loose into the environment through oil pipelines and tanks in the country. Between 1976 and 1996, Nigeria recorded a total of 4,835 oil spill incidents, which resulted in a loss of 1,896,960 barrels of oil to the environment (Nwilo and Badejo, 2004). Oil spill has led to very serious pollution of lands and water in such areas. Some major spills in the coastal zone are the Gulf Oil Company of Nigeria's (GOCON) Escravos spill in 1978 of about 300,000 barrels, Shell Petroleum Development Company of Nigeria's (SPDC- a subsidiary of the Royal Dutch Shell) Forcados terminal tank failure in 1978 of about 580,000 barrels and Texaco Funiwa-5 blow out in 1980 of about 400,000 barrels. Other oil spill incidents are those of the Abudu pipeline in 1982 of about 18,818 barrels (Niger Delta Environmental Survey (NDES), 1997). Others are Jesse fire incident which claimed about a thousand lives and the Idoho oil spill of January 1998, of about 40,000 barrels. The most publicized of all oil spills in Nigeria occurred on January 17, 1980 when a total of 37.0 million litres of crude oil got spilled into the environment. The heaviest recorded spills so far occurred in 1979 and 1980 with a net volume of 694,117.13 barrels and 600,511.02 barrels respectively (Nwilo and Badejo, 2004). An estimated 9 to 13 million barrels (1.5 million tons) of oil has spilled in the Niger Delta ecosystem over the past 53 years, representing about 50 times the estimated volume spilled in the Exxon Valdez Oil Spill in Alaska in 1989 (Leschine, *et al*., 1993; Weiner *et al*., 1997).

The harmful effects of oil spill on the environment are many. Oil kills plants and animals in the estuarine zone. Oil settles on beaches and kills organisms that live there; it also settles on ocean floor and kills benthic (bottom-dwelling) organisms such as crabs. Oil poisons algae, disrupts major food chains and decreases the yield of edible crustaceans. It also coats birds, impairing their flight or reducing the insulative mm, property of their feathers, thus making the birds more vulnerable to cold. Oil endangers fish hatcheries in coastal waters and as well contaminates the flesh of commercially valuable fish. In a bid to clean oil spills by the use of oil dispersants, serious toxic effects will be exerted on plankton thereby poisoning marine animals. This can further lead to food poisoning and loss of lives. Another effect of oil slicks is loss of economic resources to the government when spilled oil is not quickly recovered, it will be dispersed abroad by the combine action of tide, wind and current. The oil will therefore spread into thin films, dissolve in water and undergo photochemical oxidation, which will lead to its decomposition. Oil spill has also destroyed farmlands, polluted ground and drinkable water and caused drawbacks in fishing off the coastal waters (Nwilo and Badejo, 2008).

Over the past two decades, the amount of hydrocarbon contamination of soil and environment has continually increased, and presently it constitutes a significant fraction of waste materials in the environment. It has been reported that the presence of contamination (organic or inorganic) greatly influences the quality of soil (an essential component of concrete), as they are either attached physically or chemically to the soil particles or trapped in the voids between the particles.

Concrete is a mixture of water, stone (fine and coarse aggregates) and a binder, nowadays usually Portland cement, which hardens to a stone-like mass (Scott, 1991). The binder which is made up of cement and water are key ingredients. When cement and water are mixed they form a paste that binds the aggregates together. The water needs to be pure in order to prevent side reactions from occurring as this may weaken the concrete or otherwise interfere with the hydration process. The role of water is important because the water to cement ratio is the most critical factor in the production of 'perfect' concrete. Too much water reduces concrete strength, while too little will make the concrete unworkable. Concrete needs to be workable so that it may be consolidated and shaped into different forms. Because concrete must be both strong and workable, a careful balance of the water to cement ratio is required when making concrete.

The filler which constitutes fine aggregate (sand) is made up of particles which can pass through 5 mm BS 410 test sieve and coarse aggregates larger than 5 mm BS 410 test sieve. Aggregates should be clean, hard, and well graded, without natural cleavage planes such as those that occur in slate or shale. The quality of aggregates is very important since they make up about 60 to 75% of the volume of the concrete; it is impossible to make good concrete with poor aggregates. The grading of both fine and coarse aggregates is very significant because having a full range of sizes reduces the amount of cement paste needed. Well-graded aggregates tend to make the mix more workable as well (Neville, 1993).

The relative quantities of the mixture of concrete ingredients control its properties in wet or green state as well as in hardened state. Concrete making is not just a matter of mixing ingredients to produce a plastic mass, but good concrete has to satisfy performance requirements in the plastic or green state and also the hardened state. In the plastic state the concrete should be workable and free from segregation and bleeding. In its hardened state concrete should be strong, durable, and impermeable; and it should have minimum dimensional changes (Gambhir, 2005).

In general, compressive strength is considered to be the most important property and the quality of concrete is often judged by its strength (Gambhir, 2005; Shetty, 2002; Gupta and Gupta, 2004; Mehta and Monteiro, 2006). There are, however, many occasions when other properties are more important. For example, low permeability and low shrinkages are required for water retaining structures. Although, in most cases an improvement in compressive strength results in an improvement of the other properties of concrete, there are exceptions. For example, increasing the cement content of a mix improves compressive strength but results in higher shrinkage which in extreme cases can adversely affect durability and permeability. Since the properties of concrete change with age and environment it is not possible to attribute absolute value to any of them.

The compressive strength of concrete depends on the properties of its ingredients, the proportion of mix, the method of compact, the presence of contaminants and their degree and other controls during placing and curing. One very important factor that affects the compressive strength is contaminant and their degree. The ingredients of concrete are naturally contaminated, and by man's activities but the extent or degree of contamination may differ from the ingredient source. These may be silica, sea water (salts), clay minerals, anaerobic bacteria, chlorides, sulphates (sulfates), crude oil (hydrocarbon) contaminants etc. The presence of contaminant in large degree in aggregates does not only affect the appearance of concrete (in terms of colour and smell) but also the strength developed by the concrete and its durability (British Cement Association, 2001).

Durability is a very important concern in using concrete for a given application. Concrete provides good performance through the service life of the structure when concrete is mixed properly and care is taken in curing it. Good concrete can have a long life span under the right conditions. Water, although important for concrete hydration and hardening, can also play a role in decreasing durability once the structure is built. This is because water can transport harmful chemicals to the interior of the concrete leading to various forms of deterioration.

Considering therefore, the influence of 'clean' soil in preserving concrete properties, and the overall significance of quality and acceptable concrete to the construction industry, it is imperative to conduct a study to examine such factors that threatens the achievement of the desired workability, strength and durability of concrete. The contaminant in focus is crude oil on sand and its effect on the fresh and hardened properties of concrete are examined in this research. Three areas, Bodo, B-Dere and Bomu, in Gokana Local Government of Rivers State of the Niger Delta were used as reference for gathering background data for the research.

1.2. Research Problems

The establishment of Niger Delta Development Commission (NDDC) have been encouraging the construction of concrete structures of various kinds in the area towards the actualization of Niger Delta Region Development Master Plan (NDRDMP). In some areas, it may be difficult to obtain sufficient quantities of uncontaminated fine aggregates but contaminated aggregates are available. Therefore, the occasional use of contaminated aggregates for construction purposes, particularly by the local contractors, has to be considered. The agony of building collapses among all other things has become an endemic plague constantly striking in recent years in this country without it being properly addressed and prevented. Hence, the unconditional use of crude oil contaminated sand in the production of concrete must be subjected to tests and its suitability validated. In addition, reclamation of polluted site is the best form of cleaning the environment, thus a research into the effect of Crude Oil Contaminated Sand (COCS) on the properties of concrete poise to find a use for the contaminated material, and, in return, produce a marketable good that can offset the environmental cleaning cost.

1.3. Research Objectives

The general objective of this research is to investigate the effect of COCS on the engineering properties of concrete. The specific objectives are as follows:

1) To investigate the percentage of Total Petroleum Hydrocarbon (TPH) in the sands of three contaminated sites.

2) To determine the effect of COCS on the workability of fresh concrete.

3) To determine the effect of COCS on the strength and durability of hardened concrete.

4) To develop mathematical model for the fresh and hardened properties of COCS concrete.

5) To design mix proportions for improved compressive strength of COCS concrete.

1.4. Justification of Research

Concrete being the most widely used construction materials, is also the material of choice where strength, permanence, durability, impermeability, fire resistance and abrasion resistance are required (Newman, 2003). The use of this material is inevitable in a crude oil polluted environment such as in the Niger Delta. Therefore, a research into the effect of COCS on the properties of concrete will bring about the following:

a) Reclamation of the contaminated areas.

b) Inculcation of necessary factors of safety into the design of reinforced concrete structures in the polluted areas.

c) Utilization of the COCS concrete in special circumstances, following the knowledge of the effect that COCS has on some properties of concrete.

d) Establishment of the effect of COCS when used as concrete material in concrete structures, unlike the effect of crude oil on concrete structures in a crude oil polluted environment which had been largely considered in previous researches.

1.5 Scope of Research

The study was carried out using dead (stored) crude oil as the hydrocarbon contaminant in sand. Where more than one test is available for a particular concrete property, the most relevant of the tests to this research was considered, in addition to availability of test apparatus. Only the fine aggregate component of concrete was contaminated with crude oil, prior to concrete production.

1.6. Area of Study

While oil was first discovered in commercial quantity in 1956 in Oloibiri town in the present day Bayelsa State, the second discovery of oil in commercial volume was at Bomu in 1958. The Bomu oil field contributed major supply to the first shipment of oil from Nigeria in 1958. Bomu in Ogoni town is administratively located in Gokana Local Government Area (LGA) of Rivers state. There are 96 oil wells connected to the five flow stations in Ogoni, operated by SPDC. Three of the Ogoni flow stations named Bomu, B-

Dere and Bodo West are situated in Gokana LGA and constituted the area of study for this research (Fig. 1.1).

Gokana LGA is among the 23 LGAs in Rivers State of Nigeria. It was created out of Gokana/Tai/Eleme LGA in September 23, 1991. The council head quarter is located in Kpor. The LGA is located within the South-East Senatorial District of the state and has both riverine and upland communities.

The LGA is bounded in the North by Tai LGA, in the East by Khana LGA, in the West by Ogu/Bolo Local Government Area, in the South by Bonny LGA and in the South – East by Andoni LGA. Gokana is about 50km south of Port Harcourt and 30km from the Onne industrial axis. It is blessed with large expanse of mangrove and thick rain forest.

Fig. 1.1. Map Showing Area of Case Study, Rivers State, Nigeria

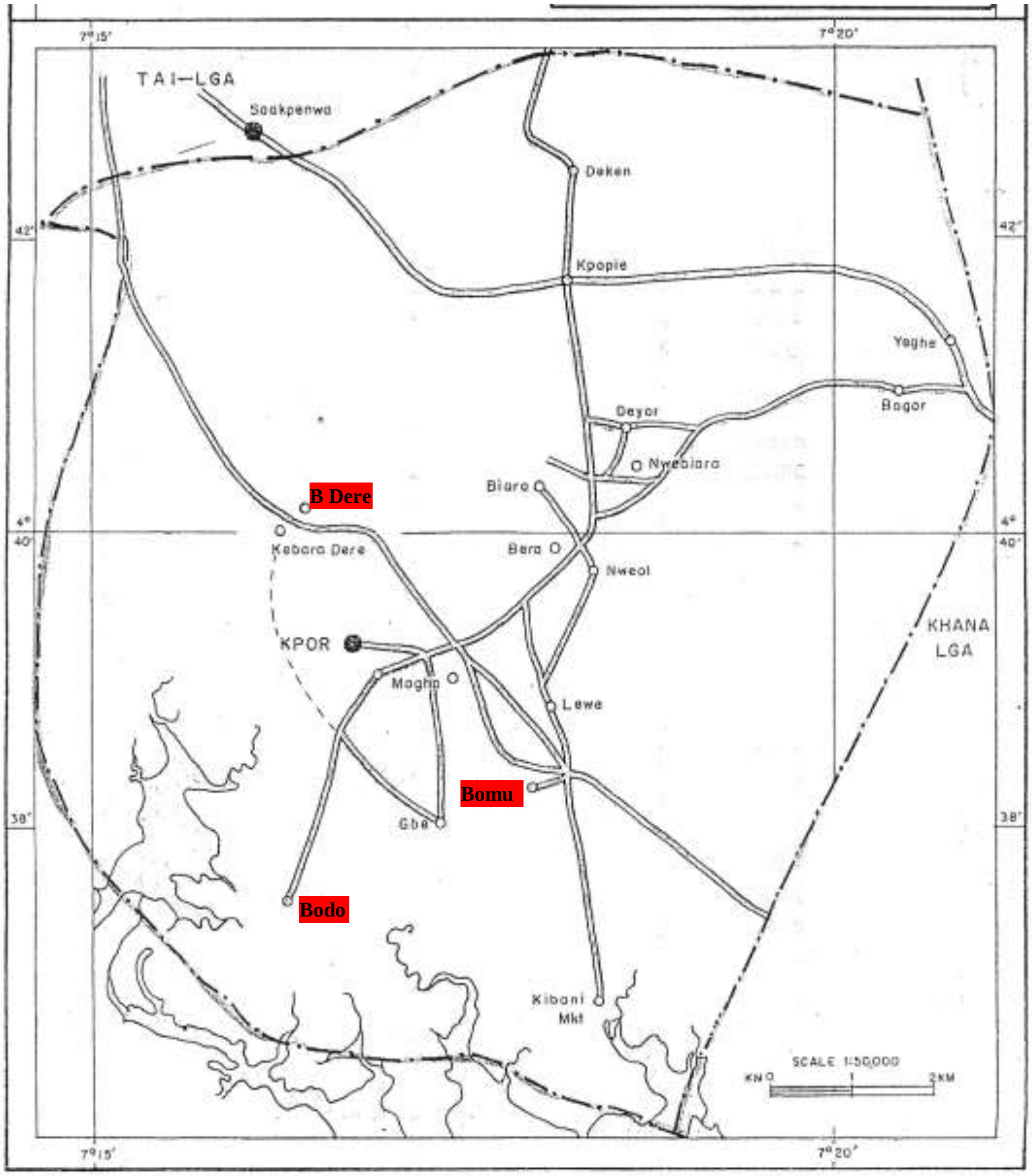


Fig. 1.2. Map Showing Sample Locations in Gokana Local Government Area

CHAPTER TWO

LITERATURE REVIEW

2.1 Concrete

Concrete is a composite material composed of coarse granular material (the aggregate or filler) embedded in a hard matrix of material (the cement or binder) that fills the space between the aggregate particles and glues them together. Concrete can also be considered as a composite material that consists essentially of a binding medium within which are embedded particles or fragments of aggregates (Sun et al., 2007). West (2002) observed that concrete can be defined completely by two parameters, namely its yield value (the stress is required to get concrete to flow) and its plastic viscosity (how ’runny’ it is when it does flow). Concrete can be reliably and repeatably characterised using these two parameters, to a high degree of accuracy, such that that any change to the concrete constituents can be diagnosed with some confidence. Concrete is the most versatile material of construction the world over. It has achieved the distinction of being the “largest man-made material” with the average per capita consumption exceeding 2 kg. Concrete is the material of choice for a variety of applications such as housing, bridges, highway pavements, industrial structures, water-carrying and retaining structures, etc. The credit for this achievement goes to well-known advantages of concrete such as easy availability of ingredients, adequate engineering properties for a variety of structural applications, adaptability, versatility, relative low cost, etc. Moreover, concrete has an excellent ecological profile compared with other materials of construction (Kulkarni, 2009). Shetty (2002), opined that cement concrete is one of the seemingly simple but actually complex materials. Many of its complex behaviours are yet to be identified to employ this material advantageously and economically. The behaviour of concrete with respect to long-term drying shrinkage, creep, fatigue, morphology of gel structure, bond, fracture mechanism, and polymer modified concrete, and fibrous concrete are some of the areas of active research in order to have a deeper understanding of the complex behaviour of this material.

Concrete is a site-made material unlike other materials of construction and as such can vary to a very great extent in its quality, properties and performance owing to the use of natural materials except cement. From materials of varying properties, to make concrete of stipulated qualities, an intimate knowledge of the interaction of various ingredients that go into the making of concrete is required, both in the plastic condition and in the hardened condition (Shetty, 2002). In addition, Neville and Brooks (1990) observed that concrete has to be satisfactory in its hardened state and also in its fresh state. Generally, the requirements in the fresh state are that the consistency of the mix is such that the concrete can be compacted and that the mix is cohesive enough to be transported and placed without segregation by the means available. As far as the hardened state is concerned, the usual requirement is a satisfactory comprehensive strength.

2.2. Concrete Materials/Composition

Concrete composition refers to the various constituents or ingredients that are needed in varying proportions for the production of concrete. These are cement, fine aggregate, coarse aggregate and water. Concrete is made up of two major components which are cement paste and inert materials. The cement paste consists of Portland cement, water and some air either in the form of naturally entrapped air voids or minute, intentionally entrained air bubbles.

The inert materials are usually composed of fine aggregates, which is material such as sand, and coarse aggregate which is a material such as gravel, crushed stone or slag (Microsoft Encarta, 2009). It is obtained by mixing cementitious materials, water and aggregate (and sometimes admixtures) in required proportions. The mixture, when placed in forms and allowed to cure, hardens into rock-like mass known as concrete.

Concrete is made from cement, aggregate and water with the occasional addition of an admixture (Cement and Concrete Association, 1979). In practice, the choice of materials for any particular job is subject to constraints imposed by design requirements for strength, durability and when necessary, appearance of the concrete. There is some variety in the properties of cement, thus concrete is always a heterogeneous material with variable properties.

2.3. Properties of Concrete

The properties of concrete refer to its characteristics or basic qualities. The special property desired of concrete is a function of the particular purpose for which the concrete is intended. For concrete to be suitable for a particular purpose it is necessary to select the constituent materials and to combine them in such a manner as to develop the special properties required as economically as possible. The properties of concrete can also be addressed in terms of its state/condition i.e. in its fresh or hardened state. Visually, thought of as two major components: paste and essentially inert materials. The paste consists of Portland cement, water, and some air, either in the form of naturally entrapped air voids or minute initially entrained air bubbles. The inert materials are usually composed of sand and gravel, crushed stone and slag.

2.3.1. Fresh concrete

According to Shetty (2002), fresh concrete or plastic concrete is a freshly mixed material which can be moulded into any shape. Concrete is termed 'fresh' when the constituents are first mixed together and is in the 'plastic' state. The relative quantities of cement, aggregates and water mixed together, control the properties of concrete in the wet state as well as in the hardened state. Fresh concrete is a transient material with continuously changing properties. It is however, essential that these are such that the concrete can be handled, transported, placed, compacted and finished to form a homogenous, usually void-free, solid mass that realizes the full potential hardened properties (Domone, 2003). Among these qualities, two properties cover all that is required of the freshly mixed concrete; they are (a) workability and (b) Stability. Both are essentially 'practical' properties and are therefore intuitive to everyone dealing with concrete production. However, each is highly complex and not easily, precisely defined.

2.3.1.1. Workability and its measurement

Domone (2003) observed that a satisfactory definition of workability is by no means straight forward. Workability, according to Indian Standard, IS: 6461 Pt VII (1973), is that property of freshly mixed concrete or mortar which determines the ease and homogeneity with which it can be mixed, placed, compacted and finished while Road Research Laboratory, U.K. based on extensive study of the field of compaction and workability, defined workability as "the property of concrete which determines the amount of useful internal work necessary to produce full compaction.” Another definition which envelopes a wider meaning is that, it is the “ease with which concrete can be compacted hundred percent having regard to mode of compaction and place of deposition” (Shetty, 2002). ASTM (1993) considered workability as the amount of work needed to produce full compaction; thereby relating it to the placing rather than the handling process. A more recent ACI definition has encompassed other operations; it is ‘that property of freshly mixed concrete or mortar which determines the ease and homogeneity with which it can be mixed, placed, consolidated and finished’ (ACI, 1990). This makes no attempt to define how the workability can be measured or specified. A similar criticism applies to the ASTM definition of ‘that property determining the effort required to manipulate a freshly mixed quantity of concrete with minimum loss of homogeneity’ (ASTM, 1993).

Workability depends on water content, aggregate (shape and size distribution), cementitious content and age (level of hydration), and can be modified by adding chemical admixtures. Raising the water content or adding chemical admixtures will increase concrete workability. Excessive water will lead to increase bleeding (surface water) and/or segregation of aggregates (when the cement and aggregates start to separate), with the resulting concrete having reduced quality. The use of an aggregate with an undesirable gradation can result in a very harsh mix design with a very low slump, which cannot be readily made more workable by addition of reasonable amounts of water.

Numerous tests have been devised for this purpose. Domone (2003) identified four tests that have a current British Standard: slump, compacting factor, Vebe and flow table (or more simply, flow). Shetty (2002) included Kelly Ball test as being among the commonly employed methods of measuring workability.

2.4. Concrete in Its Hardened State

After water is added, the outer layers dissolve and, as the cement cures, it becomes solid again. A chemical reaction has occurred. If there are no moistures, there will be no chemical reaction. When Portland cement is mixed with water, the compounds of the cement react to form a cementing substance. As the hydration reactions proceed, not only do the reaction product take up what was originally ‘free’ water, but in the gel and other reaction product begin to occupy more space, and the mobility of the space is decreased.

Finally, increasing number of particles of gel and product make sufficiently close contact and develop bonds of increasing strength, and if the mass is left undisturbed, it begins to develop rigidity. In normally and correctly mixed cement, each particle of sand and coarse aggregate is completely surrounded and coated by this paste, and all spaces between the particles are filled with it. As the cement set and hardens, it binds the aggregate into a solid mass-the hardened cement paste, and at some point, the mass can sustain more or less arbitrary load without flowing, and the paste is said to have set (Bogue and Lerch, 1984).

2.4.1. Concrete strength

Mehta and Monteiro (2006) opined that strength of concrete is commonly considered its most valuable property especially by designers and quality control engineers, although, in many practical cases, other characteristics, such as durability and permeability, may in fact be more important. Nevertheless, strength usually gives an overall picture of quality of concrete because strength is directly related to the structure of the hydrated cement paste. Moreover, the strength of concrete is almost invariably a vital element of structural design and is specified for compliance purposes.

The strength of concrete in compression and tension (both direct tension and flexural tension) are closely related, but the relationship is not of the type of direct proportionality. The ratio of the two strengths depends on general level of strength of concrete. Some factors affect tensile and compressive strength differently e.g. the tensile is less sensitive to variations in the water/cement (W/C) ratio. Consequently, the ratio of tensile to compressive strength is not constant and decreases with increasing concrete strength. In most cases, it varies from 0.01 to 0.20 for strong and weak concretes respectively, when the tensile strength is determined in flexure (Soroka, 1993). Of the various strengths of concrete the determination of compressive strength is of most important because concrete is primarily meant to withstand compressive stresses. In situations where the shear or tension strength is of importance, the compressive strength is usually used as a measure of these properties (Gupta and Gupta, 2004).

2.4.1.1. Effects of mixing water on concrete strength

The quality of mixing water plays a significant role on the strength of concrete: impurities in water can interfere with the setting of cement, adversely affect the strength of the concrete or cause staining of concrete surface and also can lead to corrosion of the reinforcement in concrete. The mixing water should not contain undesirable organic substances or inorganic constituents in excessive proportion (Lamond and Pielert, 2006). Sea water as a total salinity of about 3.5 percent (78% of the dissolved solids being NaCl and 15% of $MgCl_2$ and $MgSO_4$) and produce a slightly higher early strength but a lower long-term strength: the loss of strength is usually no more than 15 percent and therefore can be tolerated (Wegian, 2010).

2.4.1.2. Effects of water/cement ratio on concrete strength

The strength of concrete at a given age and cured in water at a prescribed temperature depends on two major factors: the water/cement ratio and the degree of compaction. When concrete is fully compacted (i.e. hardened concrete with about 1 percent of air voids), its strength is taken to be inversely proportional to the water/cement ratio. This relation was described by a so-called law established by Duff Abrams in 1919. He found strength to be equal to:

$$fc = \frac{K1}{K_2^{w/c}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.1)$$

Where w/c is the water/cement ratio of the mix and K_1 and K_2 are empirical constants.

Abram’s rule is similar to Rene Feret’s rule formulated in 1896 in that both strength of concrete to the volumes of water and cement is

$$fc = K\left(\frac{C}{C + w + a}\right)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.2)$$

Where fc is the strength of concrete, c absolute volume of cement, *w* is absolute volume of water and *a* is absolute volume of air and k is constant.

The water/cement ratio determines the porosity of the hardened cement paste at any stage of hydration. Thus the water/cement ratio and degree of compaction both affect the volume of voids in concrete, and this is why volume of air is included in Feret’s concrete expression. It also seems that mixes with very low water/cement ratio and an extremely high cement content exhibit retrogression of strength when large aggregate is used. Thus, at later years, in this type of mix, a lower water/cement ratio would not lead to a higher strength. This behaviour is due to stresses induced by shrinkage, whose restraint by aggregate particles causes cracking of the cement paste or loss of the cement aggregate bound (Neville, 1999).

Vandegrift and Schindler (2006) stated that for a given cement and acceptable aggregate, the strength that may be developed by a workable, properly placed mixture of cement, aggregate, and water (under the same mixing, curing and testing conditions) is influenced by the:

(a) ratio of cement to mixing water
(b) ratio of cement to aggregate
(c) grading, surface texture, shape, strength and stiffness of aggregate particles.
(d) maximum size of the aggregate

As pointed out by Nielsen and Hoang (2010), "the strength of concrete results from: (1) the strength of the mortar; (2) the bound between the mortar and the coarse aggregate; and (3) the strength of the coarse aggregate particles, i.e. its ability to resist the applied stress".

2.4.1.3. Influence of properties of coarse aggregate on strength of concrete

The stress at which cracks develop depends largely on the properties of coarse aggregate: smooth gravel leads to cracking at lower stress than rough and angular crushed rock, this is due to the fact that mechanical bond is influenced by the surface properties and, to a certain degree, by the shape of the coarse aggregate (Neville, 1999).

Mamlouk and Zaniewski (2011) observed that the relation between the flexural and the compressive strength depends on the type of coarse aggregate used, because the properties of aggregate, especially its shape and surface texture affect the ultimate strength in compression very much less than the strength in tension or the cracking load in compression. The influence of the type of coarse aggregate on the strength of concrete varies in magnitude and depends on the water/cement ratio of the mix. For water/cement ratio below 0.4, the use of crushed aggregate has resulted in strengths up to 38% higher than when gravel is used. With an increase in the water/cement ratio, the influence of aggregate falls off, presumably because the strength of the hydrated cement paste itself becomes paramount and at a water/cement ratio of 0.65, no difference in the strengths of concrete made with crushed rock and gravels has been observed.

The influence of aggregate on flexural strength seems to depend also on the moisture condition of the concrete and the time of test. The shape and surface texture of coarse aggregate affect also the impact strength of concrete, the influence being qualitatively the same as on the flexural strength (Lamond and Pielert, 2006). It was further observed that the flexural strength of concrete is generally lower than the flexural strength of corresponding mortar. Mortar would thus seem to set the upper limit to the flexural strength of concrete and thus, the presence of the coarse aggregate generally reduces the flexural strength. On the other hand, the compressive strength of concrete is higher than the compressive strength of mortar, which indicates that the mechanical interlocking of the coarse aggregate contributes to the strength of concrete in compression. Hence, at this stage, coarse aggregate acts as crack arresters, so that, under an increasing load, another crack is likely to open.

2.4.1.4. Effects of aggregate/cement ratio on concrete strength

The richness of a concrete mix affects the strength of a concrete. For a constant water/cement ratio, a leaner mix leads to a higher strength. The reasons for this are not clear, in certain cases; some water may be absorbed by the aggregate: a large amount of aggregate absorbs a greater quantity of water, the effective water/cement ratio being thus reduced. In other cases, a high aggregate content could lead to a lower shrinkage and lower bleeding, and therefore to less damage to the bond between the aggregate and the cement paste; likewise, the thermal changes caused by the heat of hydration of cement would be smaller (Neville, 1999). The most likely explanation lies in the fact that the total water content per cubic metre of concrete is lower in a leaner mix than in a rich one. As a result, in a leaner mix, the voids form a smaller fraction of the total volume of concrete and it is these voids that have an adverse effect on strength.

Studies on the influence of aggregate content on the strength of concrete with a given quality of cement paste indicate that, when the volume of aggregate (as a percentage of the total volume) is increased from zero to 20, there is a gradual decrease in compressive strength, but between 40 to 80 percent there is an increase. The influence of the volume of aggregate on tensile strength is broadly similar (Neville, 1999).

2.4.1.5. Concrete strength in tension

The actual strength of hydrated cement paste or other similar brittle materials such as stone is very much lower than the theoretical strength estimated on the basis of molecular cohesion, and calculated from the surface energy of a solid assumed to be perfectly homogeneous and flawless. Hydrated cement paste is known to contain numerous discontinuities–pores, micro cracks and voids – but the exact mechanism through which they affect the strength is not known. The voids themselves need not act as flaws but the flaws can be cracks in individual crystals associated with the void or caused by shrinkage or poor bond (Neville, 1999).

2.4.1.7. Influence of early temperature on concrete strength

The curing temperate speeds up the chemical reaction of hydration and this affects beneficially the early strength of concrete without any ill effect on the latter strength. Although a high temperature during placing and setting increases the early strength of concrete, it adversely affects the strength after 7 days. The reason is that at high temperature, a rapid initial hydration appears to form products of a poorer physical structure, probably more porous, so that a proportion of pores will always remain unfilled. This conforms to gel/space ratio rule that a lower strength will result than a less porous though slowly hydrating cement paste. This explanation of the adverse effect of a high early temperature on later strength is that the rapid initial rate of hydration at high temperature retard the subsequent hydration and produces a non-uniform distribution of the product of hydration within the cement paste. The reason for this is that, at high initial rate of hydration, there is insufficient time available for the diffusion of the products of hydration away from the cement particles for a uniform precipitation in the interstitial space.

As a result, a high concentration of the products of hydration is built up in the vicinity of the hydrating particles, and this retards the subsequent hydration and adversely affect the long-term strength because the gel/space ratio in the interstices is lower than would be otherwise the case for an equal degree of hydration: the local weaker area lower the strength of the hydrated cement paste as a whole.

2.4.1.8. Flexural strength test of concrete

A prismatic beam of concrete is supported on a steel roller bearing near each end is loaded through similar steel bearings placed at the third points on the top surface (2-point loading). Test details are described in BS EN 12390-5. The reference also described a method whereby the load is applied through a single roller at centre span (centre-point loading).

For two-point loading a constant bending moment is produced in the zone between the upper roller bearings. This induces a symmetrical triangular stress distribution along vertical sections (assuming elasticity) from compression above the neutral axis at mid height to tension below the neutral axis. The flexural strength (the maximum tensile stress at the bottom surface) is FL/bd^2 where F is the total load, L is the distance between the lower supporting rollers and b and d are the breadth and depth of the beam. The Standard gives details of the testing rig and requires that the compression testing machine used to apply load shall conform to BS EN 12390-4.

For centre-point loading the flexural strength is $3FL/2bd^2$ which has been found to give results 13 per cent higher than two-point loading (Newman, 2003).

2.4.2. Durability of concrete

For a long time, concrete was considered to be very durable material requiring little or no maintenance (Bogue and Lerch, 1984). The assumption is largely true, except when it is subjected to highly aggressive environments. Concrete structures are built in highly polluted and contaminated urban and industrial areas, aggressive marine environments, harmful sub-soil water in coastal area and many other hostile conditions where other materials of construction are found to be non-durable. Since the use of concrete in recent years have spread to highly harsh and hostile conditions, the earlier impression that concrete is a very durable material is being threatened, particularly on account of premature failures of number of structures in the recent past.

In the past, only strength of concrete was considered in the concrete mix design procedure assuming strength of concrete is an all pervading factor for all other desirable properties of concrete including durability. For the first time, this pious opinion was proved wrong in late 1930s when Troxell (1988), found that series of failures of concrete pavement have taken place due to frost attack. Although compressive strength is a measure of durability, to a great extent it is not entirely true that the strong concrete is always a durable concrete. It has been proved that the degree of harshness of the environmental condition to which concrete is exposed over its entire life is equally important. Therefore both strength and durability have to be considered explicitly at the design stage.

ACI Committee 201(2002) defines durability of cement concrete as the ability to resist weathering action, chemical attack, abrasion, or any other process of deterioration. Durable concrete will retain its original form, quality, and serviceability when exposed to its environment. A durable concrete is one that performs satisfactorily under anticipated exposure (working) condition during its life span (Mehta and Monteiro, 2006). Therefore, the materials and mix proportions used should be such as to maintain its integrity and, if applicable, to protect embedded metal from corrosion. One of the main characteristics influencing the durability of concrete is its permeability to the ingress of water, oxygen, carbon dioxide, chloride, sulphate and other potentially deleterious substances, thus resulting in micro and macro-cracks, and voids developed during production and service of concrete structures.

Most of the durability problems in concrete can be attributed to the volume change in the concrete. Volume change in concrete is caused by many factors. The entire hydration process is nothing but an internal volume change, the effect of heat of hydration, the pozzolanic action, the sulphate attack, the carbonation, the moisture movement, all types of shrinkages, the effect of chlorides, corrosion of steel reinforcement and a host of other aspects come under the preview of volume change in concrete (Neville and Brooks, 1993). The internal or external restraints to volume change in concrete results in the cracks. It is the cracks that promotes permeability and thus becomes a part of cyclic action, till such time that concrete deteriorates, degrades, disrupts, and eventually fails (Shetty, 2002).

2.4.2.1. Significance of durability

Even though concrete is a durable material requiring little or no maintenance in normal environment, but when subjected to highly aggressive or hostile environment, it has been found to deteriorate resulting in premature failure of structure or reach a state of requiring costly repairs (Neville and Brooks, 1993). Therefore, when designing a concrete structure, the exposure condition at which the concrete is supposed to withstand is to be assessed in the beginning with good judgment. In case of foundations, the soil characteristics are also required to be investigated. The environment pollution is increasing day by day particularly in urban areas and industrial atmosphere. It was reported by Murdock *et.al.* (1991) that in industrially developed countries over 40% of total resources of the building industries are spent on repairs and maintenance; this is due to the fact that presently, the use of concrete has been extended to more hostile environments, having already used up all good, favorable sites. Even the good materials such as aggregate-sand, are becoming short in supply. No doubt that the cement production is modernized, but sometimes the second grade raw materials such as limestone's containing excess of chloride is being used for pressing economical reasons. Earlier specification of Portland cement permitted a maximum chloride content of 0.05%. Recently, maximum permissible chloride content in cement has been increased to 0.1% (Gupta and Gupta, 2004). This high permissible chloride content in cement demands much stricter durability considerations in other aspects of concrete making practices to keep the total chloride content in concrete within the permissible limits. In other words, considerations for durability of modern concrete constructions assume much more importance, than hitherto practiced.

Mehta and Monteiro (2006) summarized the significance of durability as follows:

a) The escalation in replacement costs of structures and the growing emphasis on the life-cycle cost rather than the first cost are forcing engineers to pay serious attention to durability issues.

b) Conservation of natural resources by making the construction materials last longer is therefore an ecological step.

c) Failure of offshore steel structures has shown that both the human and the economic costs associated with sudden failure of the material of construction can be very high Therefore, the uses of concrete are being extended increasingly to severe environments, such as offshore platforms in the North Sea, and concrete containers for handling liquefied gases at cryogenic temperatures.

2.4.2.2. Strength and durability relationship

By Clients demands, construction industry needs faster development of strength in concrete so that the projects can be completed in time or before time. This demand is catered for by high early strength cement, use of very low W/C ratio through the use of increased cement content and reduced water content as observed by Gambhir (2005). The above steps result in higher thermal shrinkage, drying shrinkage, modulus of elasticity and lower creep coefficient. With higher quantity of cement content, the concrete exhibits greater cracking tendencies because of increased thermal and drying shrinkage. As the creep coefficient is low in such concrete, there will not be much scope for relaxation of stresses. Therefore, high early strength concretes are more prone to cracking than moderate or low strength concrete. Of course, the structural cracks in high strength concrete can be controlled by use of sufficient steel reinforcements, but this practice does not help the concrete durability, as provision of more steel reinforcement, will only result in conversion of the bigger cracks into smaller cracks which are sufficient to allow oxygen, carbon dioxide, and moisture get into the concrete to affect its long term durability.

Alexander (1983), stated that field experience has also corroborated that high early strength concrete are more cracks-prone. According to a study by Bogue and Lerch (1984), the cracks in pier caps have been attributed to the use of high cement content in concrete. A point for consideration is that the high early strength concrete made with modern Portland cement, which is finer in nature, containing higher sulphates and alkalis, when used up to 400 kg/m^3 or more, are prone to cracking. Therefore if long-term service life is the goal, a proper balance between a too high and a too low cement content must be considered. This is where the use of mineral admixtures comes in handy. The high early strength concrete has high cement and low water content, which results in only surface hydration of cement particle, leaving considerable amount of unhydrated core cement grains. This unhydrated core of cement grains has strength in reserve. When micro cracks have developed, the unhydrated core gets hydrated, getting moisture through micro cracks.

The hydration products so generated seal the cracks and restore the integrity of concrete for long time durability.

The micro structure of concrete with very low W/C ratio is much stronger and less permeable. The interconnected networks of capillaries are so fine that water cannot flow any more through them. It is reported that when tested for chloride ion permeability, it showed 10-50 times slower penetration than low strength concrete (Mehta and Monteiro, 2006).

2.4.2.3. Volume change in concrete

Volume change in concrete is caused by many factors. Causes of volume change fully expose the various factors affecting durability which encompasses a wide spectrum of concrete technology. The entire hydration process is nothing but an internal volume change, the effect of heat of hydration, the pozzolanic action, the sulphate action, the carbonation, moisture movement, all types of shrinkages, the effect of chloride, rusting of steel reinforcement and a host of others come under the preview of volume change in concrete.

It can also be viewed that it is the permeability that leads to volume change. The volume change results in cracks. It is the cracks that promote more permeability and thus it becomes a cyclic action, till such time that concrete undergoes deterioration, degradation, disruption and eventual failure (Chastain, 1980).

Understanding the nature of volume changes in concrete is useful in planning or analysing concrete work. If concrete were free of any restraints to deform, normal volume changes would be of little consequence; but since concrete in service is usually restrained by foundations, subgrades, reinforcement, or connecting members, significant stresses can develop. This is particularly true of tensile stresses.

Cracks develop because concrete is relatively weak in tension but quite strong in compression. Controlling the variables that affect volume changes can minimize high stresses and cracking. Tolerable crack widths should be considered in the structural design. Volume change was defined by Powers (1958) as an increase or decrease in volume. Most commonly, the subject of concrete volume changes deals with linear expansion and contraction due to temperature and moisture cycles. But chemical effects such as carbonation shrinkage, sulfate attack, and the disruptive expansion of alkaliaggregate reactions also cause volume changes. In addition, creep is a volume change or deformation caused by sustained stress or load. Equally important is the elastic or inelastic change in dimensions or shape that occurs instantaneously under applied load. For convenience, the magnitude of volume changes is generally stated in linear rather than volumetric units. Changes in length are often expressed as a coefficient of length in parts per million, or simply as millionths. It is applicable to any length unit (for example, m/m or ft/ft); one millionth is 0.000001 m/m (0.000001 in./in.) and 600 millionths is 0.000600 m/m (0.000600 in./in.). Change of length can also be expressed as a percentage; thus 0.06% is the same as 0.000600, which incidentally is approximately the same as 6 mm per 10 m (3⁄4 in. per 100 ft). The volume changes that ordinarily occur in concrete are small, ranging in length change from perhaps 10 millionths up to about 1000 millionths.

2.4.2.4. Permeability of concrete

Theoretically, the introduction of low-permeability aggregate particles into a high-permeability cement paste (especially with high water-cement ratio; pastes at early ages when the capillary porosity is high) is expected to reduce the permeability of the system because the aggregate particles should intercept the channels of flow within the cement paste matrix. Compared to a neat cement paste, therefore, a mortar or a concrete with the same water-cement ratio and degree of maturity should give a lower coefficient of permeability. Test data by Neville and Brooks (1990) indicated that, in practice, this does not happen. The two sets of data clearly show that the addition of aggregate to a cement paste or a mortar increased the permeability considerably; in fact, the larger the aggregate size, the greater the coefficient of permeability. Typically, the permeability coefficients for moderate-strength concrete (containing 38 mm aggregate, 356 kg/m^3 cement, and an 0.5 water-cement ratio), and low-strength concrete used in dams (75 to 150 mm aggregate, 148 kg/m^3 cement, and an 0.75 water-cement ratio) are of the order of 1×10^{-10} and 30×10^{-10} cm/s, respectively. The explanation as to why the permeability of mortar or concrete is higher than the permeability of the corresponding cement paste lies in the micro-cracks normally present in the interfacial transition zone between aggregate and the cement paste. Studies have shown that, the aggregate size and grading affect the bleeding characteristic of a concrete mixture that, in turn, influences the interfacial transition zone (Neville and Brooks, 1993).

During the early hydration period, the interfacial transition zone is weak and vulnerable to cracking from differential strains between the cement paste and the aggregate particles that are induced by drying shrinkage, thermal shrinkage, and externally applied load. The cracks in the interfacial transition zone are too small to be seen by the naked eye, but are larger than most capillary cavities present in the cement paste matrix. Later, the propagation of micro-cracks established the interconnections that become instrumental in increasing the permeability of the system, due to the significance of the permeability to physical and chemical processes of deterioration of concrete, because strength and permeability are related to each other through the capillary porosity.

2.4.2.5. Fire resistance of concrete

Concrete though not a refractory material is incombustible and has good fire-resistant properties. Mehta and Monteiro (2006) confirmed that concrete has a good service record in respect of fire resistance. Fire resistance of concrete structure is determined by three main factors-the capacity of the concrete itself to withstand heat and the subsequent action of water without losing strength unduly, without cracking or spalling; the conductivity of the concrete to heat and coefficient of thermal expansion of concrete. In the case of reinforced concrete, the fire resistance is not only dependent upon the type of concrete but also on the thickness of cover to reinforcement. The fire introduces high temperature gradients and as a result of it, the surface layers tend to separate and spall off from the cooler interior. The heating of reinforcement aggravates the expansion both laterally and longitudinally of the reinforcement bars resulting in loss of bond and loss of strength of reinforcement.

The effect of increase in temperature on the strength of concrete is not much up to a temperature of about 250ºC but above 300ºC, definite loss of strength takes place (Neville, 1993). Hydrated hardened concrete contains a considerable proportion of free calcium hydroxide which loses its water above 400ºC leaving calcium oxide. If this calcium oxide gets wetted or is exposed to moist air, rehydrates to calcium hydroxide accompanied by an expansion in volume. This expansion disrupts the concrete. Portland blast furnace slag cement is found to be more resistant to the action of fire in this regard.

In mortar and concrete, the aggregates undergo a progressive expansion on heating while the hydrated products of the set cement, beyond the point of maximum expansion, shrinks.

These two opposing actions progressively weaken and crack the concrete. The various aggregates used differ considerably in their behavior on heating. Quartz, the principal mineral in sand, granites and gravels expands steadily up to about 573ºC. At this temperature it undergoes a sudden expansion of 0.85% which expansion has a disruptive action on the stability of concrete. The fire resisting properties of concrete is least, if quartz is the predominant mineral in the aggregate.

The best fire resistant aggregates, amongst the igneous rocks are the basalts and dolerities. Limestone expands steadily until temperature of about 900ºC and then begins to contract owing to decomposition with liberation of carbondioxide. Since the decomposition takes place only at a very high temperature of 900ºC, it has been found that dense limestone is considered as a good fire resistant aggregate. Perhaps the best fire resistant aggregate is blast furnace slag aggregate. Broken bricks also form a good aggregate in respect of fire resistance. The long series of tests indicated that even the best fire resistant concretes have been found to fail if concrete is exposed for a considerable period to a temperature exceeding 900ºC, while serious reduction in strength occurs at a temperature of about 600ºC. Concrete does not show appreciable loss of strength up to a temperature of about 300ºC. The loss of strength may be about 50% or more at about 500ºC. This determines the effect of temperature on the relative modulus of elasticity.

2.5. Crude Oil

Crude oil or petroleum is a complex mixture of thousand of organic compounds called hydrocarbon (Fingas, 2001; BPES, 2006). Crude Oil is defined as a mixture of hydrocarbons that exists in a liquid phase in natural underground reservoirs and remains liquid at atmospheric pressure after passing through surface production facilities. It is a naturally occurring liquid that can be distilled or refined to make fuels, lubricating oils, asphalts and other valuable products. It is a hydrocarbon composed mainly of hydrogen and carbon, along with minor impunities like sulphur, nitrogen and oxygen.

Crude oils are complex mixtures containing many different hydrocarbon compounds that vary in appearances and composition from one oil field to another. Crude oils range in consistency from water to tar-like solids, and in colour from clear to black. An “average” crude oil contains about 84% carbon, 14% hydrogen, 1%-3% sulphur and less than 1%

each of nitrogen, naphthenic or aromatic, based on the predominant proportion of similar hydrocarbon molecules.

2.5.1. Nigeria oil coastal area

Nigeria has a coastline of approximately 853 km facing the Atlantic Ocean. This coastline lies between latitude 4^o 10′ to 6^o 20′ N and Longitude 2^o 45′ to 8^o 35′ E. The terrestrial portion of this zone is about 28,000 km^2 in area, while the surface area of the continental Shelf is 46,300 km^2. The coastal area is low lying with heights of not more than 3.0 m above sea level and is generally covered by fresh water swamp, mangrove swamp, lagoonal mashes, tidal channels, beach ridges and sand bars (Dublin- Green *et al*, 1998). The Nigerian coast is composed of four distinct geomorphologic units namely the Barrier-Lagoon complex; the Mud coast; the Actuate Niger delta; and the Strand coast (lbe, 1988). Nigeria is one of the world's largest oil exporters.

2.5.2. Oil spills and its consequences

Oil spills are a frequent occurrence, particularly because of the heavy use of oil and petroleum products in our daily lives (Fingas, 2001). Oil spill is the release of a liquid petroleum hydrocarbon into the environment, and is a form of pollution. The term often refers to marine oil spills, where oil is released into the ocean or coastal waters. The oil may be a variety of materials, including crude oil, refined petroleum products (such as gasoline or diesel fuel) or by- products, ships' bunkers, oily refuse or oil mixed in waste. Hence, spills take months or even years to clean up and thus, oil is also released into the environment from natural geologic seeps on the sea floor. Onabolu *et al*. (1994) observed that oil spills in Nigeria occur due to a number of causes which include: corrosion of pipelines and tankers (accounts for 50% of all spills), sabotage (28%), and oil production operations (21%), with 1% of the spills being accounted for by inadequate or non-functional production equipment. The largest contributor to the total oil spill, corrosion of pipes and tanks, is the rupturing or leaking of production infrastructures that are described as, "very old and lack regular inspection and maintenance. A reason that corrosion accounts for such a high percentage of oil spills is that as a result of the small size of the oilfields in the Niger Delta, there is an extensive network of pipelines between the fields, as well as numerous small networks of flowlines—the narrow diameter pipes that carry oil from wellheads to flow stations—allowing many opportunities for leaks. In onshore areas, most pipelines and flow lines are laid above ground. Pipelines, which have an estimated life span of about fifteen years, are old and susceptible to corrosion. Many of the pipelines are as old as 20 to 25 years. Even Shell admits that "most of the facilities were constructed between the 1960s and early 1980s to the then prevailing standards. Shell operates the Bonny Terminal in Rivers State, which has reportedly been in operation for forty years without a maintenance overhaul; its original lifespan was supposed to be 25 years (Onabolu *et al*., 1994).

Oil spillage has a major impact on the ecosystem into which it is released. Immense tracts of the mangrove forests, which are especially susceptible to oil (this is mainly because it is stored in the soil and re-released annually with inundation), have been destroyed. An estimated 5-10% of Nigerian mangrove ecosystems have been wiped out either by settlement or oil. The rainforest which previously occupied some 7,400 km² of land has disappeared as well. Spills in populated areas often spread out over a wide area, taking out crops and aquacultures through contamination of the groundwater and soils, though the consumption of dissolved oxygen by bacteria feeding on the spilled hydrocarbons also contributes to the death of fishes. In agricultural communities, often a year's supply of food can be destroyed by only a minor leak, debilitating the farmers and their families who depend on the land for their livelihood. Drinking water is also frequently contaminated, and sheen of oil is visible in many localized bodies of water. If the drinking water is contaminated, even if no immediate health effects are apparent, the numerous hydrocarbons and chemicals present in oil are highly carcinogenic. Although, people often do manifest sickness following consumption of polluted water, offshore spills, which are usually much greater in scale, contaminate coastal environments and cause a decline in local fishing production (Nwilo and Badejo, 2004).

The harmful effects of oil spill on the environment are many. Oil kills plants and animals in the estuarine zone. Oil settles on beaches and kills organisms that live there; it also settles on ocean floor and kills benthic (bottom-dwelling) organisms such as crabs. Oil poisons algae disrupt major food chains and decreases the yield of edible crustaceans. It also coats birds, impairing their flight or reducing the insulative property of their feathers, thus making the birds more vulnerable to cold. Oil endangers fish hatcheries in coastal waters and as well contaminates the flesh of commercially valuable fish. In a bid to clean oil spills by the use of oil dispersants, serious toxic effects will be exerted on plankton, thereby poisoning marine animals. This can further lead to food poisoning and loss of lives. Another effect of oil slicks is loss of economic resources to the Government when spilled oil is not quickly recovered, it will be dispersed abroad by the combined action of tide, wind and current (Nwilo and Badejo, 2004; Imoobe and Iroro, 2009).

Control of oil spills is difficult as it requires ad hoc methods and often a large amount of manpower. Oil spills on land are more readily containable if a makeshift earth dam can be rapidly 'bulldozed' around the spill site, before most of the oil escapes. Modern techniques would include pumping the oil from the wreck, like in the prestige oil spill or the Erika oil spill. However, bioremediation was noted as an economical and safe method for cleaning up oil spills and soil contaminated with petroleum hydrocarbons and dangerous organic compounds. The bioremediation process utilizes beneficial microbes, surfactants, micronutrients and bio-stimulants to decompose contaminants transforming them into harmless by-products, i.e. water and carbondioxide. The remediation process can be performed in-situ or ex-situ. The in-situ process is adopted where excavation is impractical and involves either bio-stimulation or bio-augmentation. Bio-stimulation involves aeration and the application of selected micronutrients and bio-stimulants which are only effective when indigenous microbial populations, present in the substrates, are high enough to degrade the contaminants and when these microbes can readily adapt to foreign contaminants. Bio-augmentation involves the application of beneficial microbes that have an affinity towards specific contaminants. Typically, these microbes are suspended by a stabilizing agent and lie dormant in a spore until activated in solution and applied together with micronutrients and bio stimulants.

2.6. Contamination

Contamination, as defined by the US Environmental Protection Agency (2005) is the influx of unwanted materials/substances into a body/medium (soil, water etc) due to spills, industrial waste, soil reaction etc. In view of these, it is pertinent to note that the presence of contaminant (organic or inorganic) greatly influence the quality of soil (which is an essential component of concrete), as they are either attached physically or chemically to the soil particles or trapped in the voids between the particles (US Environmental Protection Agency, 2005)

Soil contamination is caused by the presence of man-made chemicals or other alteration in the natural soil environment. This type of contamination typically arises from the rupture of underground storage tank, application of pesticides, percolation contaminated surface water to subsurface strata, oil and fuel dumping, leaching of waste from landfills or direct discharge of industrial wastes to the soil.

2.6.1. Concrete in hydrocarbon product environment

Research into the effect of constituents of hydrocarbon on the properties of concrete has been on for decades. Biczok (1964) and Lea (1970) observed that the chemical constituents of mineral oils (hydrocarbons) retard the hardening and affect the hydration of fresh concrete resulting in a reduction of long-term strength. Lea (1970) indicated that the effects on hardened concrete were not significant and that the oils do not contain any constituents that react chemically with set and hardened concrete. He did, however, suggested that phenols, creosotes and similar acidic compounds in creosote may have some effect on hardened concrete which was confirmed by Orchard (1971) who reported that creosote causes mild deterioration of hardened concrete. Smith (1985) considered the effects of phenols on concrete by curing 100 mm concrete cubes in phenol solution of varying strengths and observed that though the phenol has caused a reduction gain in strength, the actual strength in all the solutions continued to increase above the 28-day compressive strength of the control. The actual reduction in strength compared with the control varied between 6% and 19% at two years. Dobrowlski (1998) reported that petroleum oils and coal-tar distillates had very slight or no effect on hardened concrete strength and durability. Indeed coal-tar paints and pitches are used in protective coatings to concrete to prevent deterioration by other compounds. Pye and Harrison (1997) opined that the chemical resistance of Portland cement concrete surfaces to mineral oil and organic solvents is good, although oil will cause staining. Wilson *et. al.* (2001) investigated the effects of hydrocarbon contamination on the strength development of foundation concrete. They assessed common substances that originally caused the ground contamination, i.e diesel, lubricating oil and creosote, rather than looking at concentrations of the specific chemicals which make up the compounds. They confirmed that hydrocarbon contamination of concrete affect the long-term strength of in-situ concrete and thereafter recommended allowance of 20% to 25% reduction in long-term strength of fresh concrete. Ham *et. al.* (1999) analysed the physical and chemical properties of concrete specimen soaked in grease for 180 days and tested for strengths and static elastic modulus. They noticed increase in the values of the tested parameters due to grease that penetrated into the concrete and thus fill up pores. Hamad *et. al.* (2003) investigated the effect of used engine oil on properties of fresh and hardened concrete and the results indicated that used engine oil acted as an air-entraining agent by improving the slump and fluidity of the concrete mix, and enhancing the air content of fresh concrete. Reductions in the strength properties of hardened concrete due to the incorporation of oil were not as significant as when a commercial chemical air-entraining admixture was used. Hamad and Rteil (2003) further evaluated the effect of used engine oil on structural behavior of reinforced concrete elements. The beam specimens were subjected to flexure, shear, and bond tests. Results showed that regardless of the mode of failure, used engine oil did not have any significant effect on the ultimate load or load-deflection behavior of the beams. Used engine oil caused small reductions in the ultimate flexural capacity, maximum shear load, and bond splitting resistance. The losses relative to the companion beams with no oil were 2.7, 6 and 6.9%, respectively.

The above researchers worked on petroleum products other than crude oil in their investigations. However, while focusing on crude oil, Blaszczyriski (2002) found that crude oil products with very low neutralization number are the physico-chemical active agents on the concrete. In technical literature, effects of crude oil products on concrete are classified either as non-harmful or only mildly harmful, but there is evidence that serious damage can be caused. In case of physico-chemical environment, usually, physico-chemical bonds are affected and because of that, the process can be reversible sometime. Using three different industrial mineral oils (machine oil, hydraulic oil and turbine oil) in his experiment, Blaszczyriski (2002) observed that the direct reason for the decrease of bond is the progressive degradation of oiled concrete and its adhesion to reinforcement. The friction between cement matrix and reinforcement is influenced by increase of mineral oil viscosity.

2.6.2. Effect of crude oil on concrete

One aspect that is true of all crude oil type is that each has differing amount of sulphur content, which is usually in compound form. Nigerian crude oil has been rated as both sweet and sour crude as a result of sulphur content percentage which is greater or equal to 10% (Kline, 2004). Though sulphur content is expected to be removed during refining, it requires extra processing and records have shown that most of the oil spill in the Niger Delta area is of crude type, thereby endangering aquatic and human lives; and may be cement-based materials. Kline (2004) also showed that sulphurous compounds are aggressive medium for cement based materials. According to his report, concrete deterioration in sulphur pit environment is characterized by the concrete cement paste matrix being chemically modified and no longer exhibiting properties consistent with structural support/containment. Usually, the concrete/mortar mass exposure to sulphurous products normally undergoes chemical reactions that expand the mortar fraction. This expansion always proves fatal to long term concrete durability as it causes increase in solid volume. The formation of ettringite is the root cause of most expansion and disruption of mortar/concrete caused by sulphate solutions. This problem can only be exacerbated by changes in temperature as well as other erosive agents like the sea water.

There are many concrete structures related to oil industry, which are located in marine environment. Generally, the bond strength of repair materials immersed in crude oil decreased compared to that of samples held in a laboratory environment. Based on the obtained results, the bond strength of concrete repair material is decreased by 11% in crude oil environment (Paul and Spry, 1997). Ejeh and Uche (2009) investigated the effect of crude oil spillage on the strength properties of concrete made with ordinary Portland cement (OPC), used in constructions in Nigeria. The results obtained showed that the ordinary Portland cement concrete is susceptible to different aggressiveness of the solutions of crude oil concentrations as they led to low rates of strength development of concrete specimens. Corrosion rate is highest in undiluted crude oil than in the crude oil/water mix as the reductions in compressive strength are in the ratio 23:13 percent. It was also found that the entire media, even the control medium, led to increase in strength of concrete specimens after two months of immersion but the rate of compressive strength development is low in the crude oil and crude oil/water mix. The investigation conducted by Ramzi and Azad (2000) also indicated that at 70% loading, compressive strength of concrete after 60 days of soaking in crude oil was reduced by 12.52% as compared with initial unsoaked strength.

Other researchers concentrated on the effect of contaminated sand on concrete and its use in concrete products. Calabrese et al (1991) examined the effect of petroleum contamination on concrete strength. The compressive and flexural results indicated that, irrespective of the soil type, concrete containing higher Petroleum Contaminated Soil (PCS)/sand replacement ratio develops lower compressive and flexural strengths at early and late stages. The presence of contamination seems to interfere with the water-cement binding reactions, delaying or preventing full hydration of the cement particles. The increase of PCS content (increase in PCS / sand replacement ratio) yields to the presence of more petroleum contaminants that separate the cement particles from water. Hence, for the same total content of cement, a less amount is actually reacting with water to produce the hardened binder. This results in concrete weaker than the control. The strength reduction at each PCS/sand replacement ratio level depends on contaminated concrete, contaminant type and soil type. The increase in contaminated concrete has an adverse effect on the concrete strength. For a particular soil, at 40% PCS/sand replacement ratio, the concrete strength reduced by 10% for the two days compressive strength and 13% for the seven days compressive strength. The results also indicate that sandy soil contaminated with gasoline produces concrete with lower strength than concrete containing a higher concentration of heating oil. This is observed for early and late stages. Ayininuola (2009) investigated the effects of dielsel oil and bitumen contaminated marine sand in concrete and observed a reduction in the compressive strength of concrete cubes when compared with uncontaminated sand concrete. The 28-day compressive strengths of diesel oil and bitumen contaminated concrete cubes were in the range of 96.8 to 77.4% and 76.2 to 26.2% respectively of those of uncontaminated concrete cubes. Ezeldin and Vaccari (1996) conducted an environmental investigation to evaluate the feasibility of using Petroleum (hydrocarbons at levels of 0.5 and 3.0% by weight of benzene) contaminated sand in concrete for exterior, nonresidential construction purposes. They recommended based on the results of the tests conducted that fixation of low hydrocarbon levels within concrete is a technically viable and safe technology for recycling petroleum-contaminated soil. Hassan (2009) used PCS as a fine aggregate substitute in Hot Mix Asphalt concrete (HMA) with a percentage up to 40%, by total aggregate weight and observed a reduction in both the dynamic modulus and tensile strength due to the PCS, though, tensile strength ratio criteria is satisfied for the mixes containing up to 15% PCS. Al-Mutairi and Eid (1997) utilized crude oil contaminated sand to mix asphalt concrete to determine the feasibility of using sand contaminated with oil as feed stock in the production of asphalt construction materials. They recommended, following laboratory tests, the use of crude oil contaminated sand in the construction of secondary roads, road beds, road sub-base, impermeable layers for landfill and contaminated facilities, or as stabilizers for steep embankments. Mansurov *et. al.*(2001) investigated the possibility of producing a cold asphalt concrete mixture from solid waste residue on addition of mineral fillers and proposed a thermal method of separating wastes into organic and mineral parts for processing crude oil sludges and oil-contaminated soils. They succeeded in manufacturing grade BN 90/10 construction asphalt. So far none of the previous researches was focused on the utilization of crude oil contaminated sand wholly in the production of concrete taking into consideration the concentration of the oil in the sand and modeling the effect of the contaminated sand on the fresh and hardened properties of concrete as considered in this research.

2.7. Modelling of Concrete Properties and Optimization

Models are tools designed to represent simplified version of reality (Agbede, 1996). Ogunsola *et. al.* (2006) stated that concrete is a porous, heterogeneous material whose abundant use in numerous applications demands a detailed understanding of its properties. Besides experimental measurements, mathematical models can be useful to investigate its behaviour with respect to frequency, moisture content or other agents. Models of different types have been applied to many aspects of concrete. Khan (2010) developed a predictive model based on experimentally obtained values to predict chloride permeability of High Performance Concrete containing supplementary composites at 7, 28, 90, and 180 days. Sun *et. al.*(2007) adopted a combination of experiments and simulation to model the concrete elastic properties. The model proved to accurately compute the elastic properties of concrete composite by using a differential effective medium theory (D- EMT). Ogunsola *et. al.* (2006) developed models that can be used in electromagnetic compatibility to predict the shielding effectiveness of a concrete structure against external electromagnetic waves. Yeh (1998) provided a methodology for predicting the compressive strength of High Performance Concrete (HPC) and observed that the strength model based on the artificial neural network is more accurate than the model based on regression analysis. Jamil *et. al.* (2009) adapted artificial neural network in the development of neural network simulator model for workability (measured by slump) and compressive strength (measured by compressive test) for HPC incorporating silica fume, fly ash and rice husk ash. Al-Qadi *et.al*. (2009) carried out statistical models to model the influence of key mixture parameter (cement, water to powder ratio, fly ash and super plasticizer) on hardened properties affecting the performance of Self Compacting Concrete. Franklin (2010) addresses the problem of the design of suitable model concrete mixes for the investigation of the punching strength of post-tensioned concrete flat slabs. Carstensen (2011) extended existing models for the ambient condition of concrete to elevated temperatures by applying the material properties at a given elevated temperature to the current formulation. Several other mathematical and statistical models have been used to predict a property or properties of concrete when modified by either varying any of its constituents or the addition of a foreign material to investigate the effect of such material on the properties of concrete. Among several mathematical models used for concrete is the Response Surface Methodology (RSM) and it has been found very useful particularly when it has to do with design of experiment and optimization.

RSM consists of a group of empirical techniques devoted to the evaluation of relations existing between a cluster of controlled experimental factors and the measured responses, according to one or more selected criteria (Cornell, 1990; Mayer and Montgometry, 1995; Montgometry, 2001). Prior knowledge and understanding of the process and the process variables under investigation is important for achieving a realistic model. RSM provides an approximate relationship between a true response y and p design variables, which is based on the observed data from the process or system (Lepadatu *et al*., 2005, 2006). The response is generally obtained from real experiments or computer simulations and the true response y is the expected response. Murali and Kandasamy (2009) observed that RSM is a set of techniques that encompasses: designing of a set of experiments for adequate and reliable measurement of the true mean response;

determining the mathematical model with best fit; finding the optimum set of experimental factors that produces maximum and minimum values of the response, and representing the direct and interactive effect of the process parameters. Marinela and Lepadatu (2008) used a statistical investigation to analyze data from mixture experiment design and involve regression models to determine the response surface polymer concrete. And from the statistical analysis carried out, it was observed that all factors have an important influence on the mechanical characteristics of polymer concrete; the polymer percentage obtained satisfies the requirement of low cost and high strength. Al Qadi *et. al.*(2009) predicted workability and hardened properties of Self-Compacting Concrete (SCC) via statistical modeling the influence of key mixture parameter (cement, water to powder ratio, fly ash and super plasticizer) on hardened properties affecting the performance of SCC. Full quadratic models that show high correlations were developed.

Murali and Kandasamy (2009) carried out an experimental program in which RSM was employed to optimize a four-component concrete containing fly-ash subjected to six performances criteria. The four key mixture constituents used in the models included cement, fly-ash, and high range water reducer and water binder ratio. The modeled response that included the compaction factor, compressive strength, split tensile strength and flexural strength at 28 days. The derived models are valid for a wide range of mixtures with ranges of water binder ratio of 0.28-0.44, cement content of 400 to 600 kg/m3, fly-ash 0 to 10% (by weight of mass cement and HRWR dosage of 1 to 3% (by weight of mass cement). Similarly, RSM was considered in this research based on its proven efficiency in modeling concrete properties due to modification of the constituents. Specifically, a software package for RSM-Design Expert, was adopted to carry out the modeling.

CHAPTER THREE

METHODOLOGY

3.1. Materials

3.1.1. Cement

The cement used for the investigation was the Type I normal Ordinary Portland Cement that conforms to BS 12 and was obtained in 50 kg bags from retailers in Ibadan.

3.1.2. Water

Potable water supplied by the University of Ibadan water supply unit was used for concreting and curing of samples. The water aided the hydration of cement which resulted in the setting and hardening of the concrete (BS 3148).

3.1.3. Coarse aggregate

Since the cubes were 100 x 100 x 100 mm in size, the nominal maximum size must not exceed 20 mm size of coarse aggregate. Crushed aggregate from Ladson quarry in Ibadan, with nominal size of 10 mm in accordance to BS 882 (1993) was used.

3.1.4. Fine aggregate

A tipper load of sand was obtained in Ibadan, through F.M. construction company Ltd.

3.1.5. Crude oil

The crude oil was obtained in gallons from Bomu oil field in Rivers state, Nigeria.

3.1.6. Contaminated sand

Samples of contaminated sands were obtained from three different crude oil polluted sites for preliminary analysis. This was intended to determine the grading of the soil of the area and the percentage crude oil contamination of the soil in order to serve as a basis for choosing the sand type and the percentage crude oil contamination for the research. The three sites are located at Bodo-city, Bomu, and B-Dere in Gokana LGA of River state (Plates 3.1 to 3.3). The samples were obtained at an average depth of 1000 mm below the ground level and then transported in sacks to the laboratory.

3.2. Sample Preparation

3.2.1. Aggregate

The coarse and fine aggregates were air dried to obtain saturated surface dry condition to ensure that water to cement ratio was not affected. The sand was sieved through 10 mm mesh in order to increase the zone of the fine aggregate thus making it finer.

3.2.2. Contaminated sand

The samples were pulverized using scoop (Plate 3.4), air dried and labelled to differentiate among different sites samples. Samples were subsequently taken for Total Petroleum Hydrocarbon (TPH) test. CS was used as prefix for each sample while numbers 1 to 3 were used to designate the site where the sample was taken from while block letters A, B, and C where used to differentiate the three specimens obtained from each sample. Thus a specimen labelled CS 1A implies specimen A taken from sample obtained from B-Dere (1).

3.2.3. Contamination of sand with crude oil

Following the result of the TPH test, the sieved uncontaminated fine aggregate was divided into seven equal parts and each part was contaminated with crude oil in 2.5%, 5%, 10%, 15%, 20%, and 25% by weight of the fine aggregate. The uncontaminated part was left for the production of control samples.

Plate 3.1: Oil Spill Location at B-Dere

Plate 3.2: Oil Spill Location at Bomu

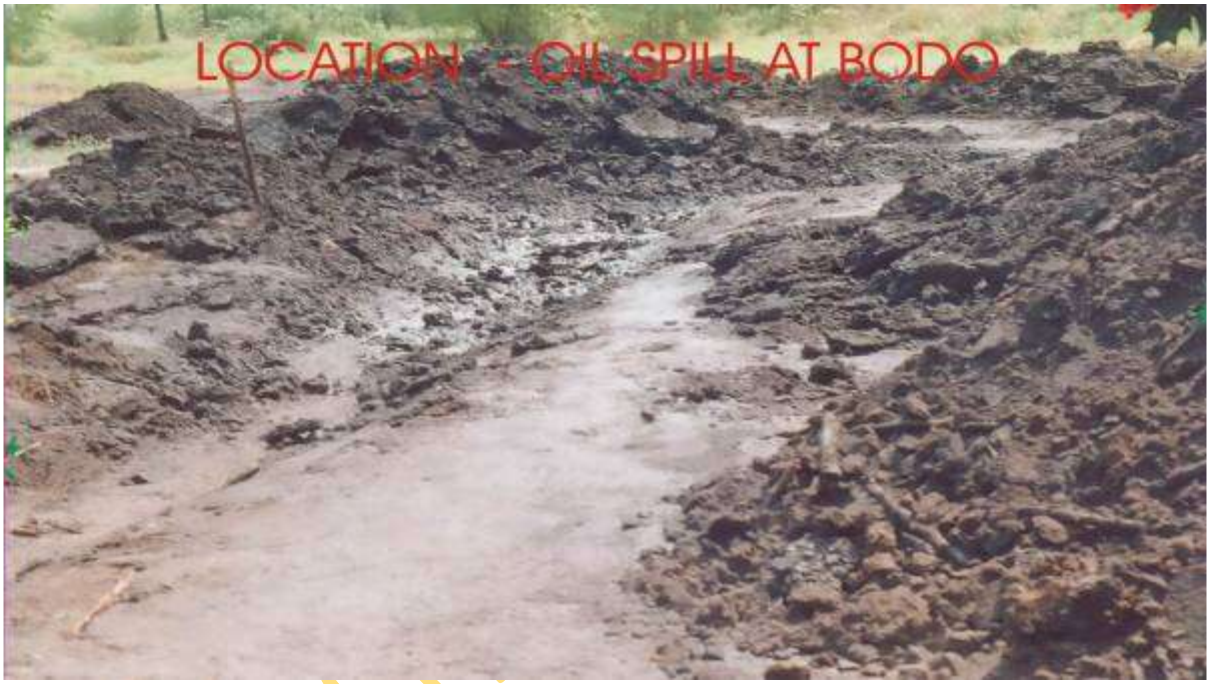


Plate 3.3: Oil Spill Location at Bodo

Plate 3.4: Preparing Soil Sample for TPH Test

3.3. Materials Testing

3.3.1. Cement

Being a manufactured product, the properties of the cement as supplied by the manufacturer was considered for this research.

3.3.2. Water

Water sample was collected and tested for chloride, sulphate, alkalis and total solids at the analytical laboratory of the department of Civil Engineering, University of Ibadan.

3.3.3 Aggregates

The granite, sand and the contaminated sand from polluted sites were graded using dry sieve analysis (Plate 3.6).

The sieve analysis was used to determine the grain size distribution curve of samples by passing them through a stack of sieves of decreasing mesh opening sizes and by measuring the weight retained on the sieve in accordance to BS 812 PT 103.1 (1989).

The percentages retained and passing were calculated as follows:

$$\text{Percentage retained} = \frac{\text{weight of retained soil mass}}{\text{total weights of soil sample}} \times 100\% \qquad \text{....................(3.1)}$$

Percentage passing = 100 – cumulative sum of percentage retained

Using the grain size distribution obtained for the fine aggregate, the coefficient of uniformity (C_u) and the coefficient of curvature (C_c) were calculated as stated below.

$$C_u = D_{60} / D_{10} \qquad \text{...................... (3.2)}$$

$$C_c = (D_{30})^2 / (D_{60} \text{ X } D_{10}) \qquad \text{...................... (3.3)}$$

Where D_{60} = grain diameter at 60% finer

D_{30} = grain diameter at 30% finer

D_{10} = grain diameter at 10% finer

3.3.4. Extraction of crude oil

Total Petroleum Hydrocarbon (TPH) in the contaminated samples from polluted sites was determined using gravimetry, following saponification in methanolic-KOH, extraction by n-Hexane, and separation via liquid chromatography. The test was carried out at the analytical laboratory of the department of Chemistry, University of Ibadan. The TPH in the samples was requred to serve as guide in the quantity of crude oil needed for the artificial contamination of clean sand to simulate the COCS for the experiment.

A sample of the crude oil was tested for classification. The specific gravity and the viscosity tests were carried out at the department of Petroleum Engineering laboratory, University of Ibadan.

3.4. Concrete Mix Design

A design mix was employed to enable the proportioning of available materials to produce concrete of desired strength (Day, 1992). Hence, to select the correct proportions of cement, fine and coarse aggregates, and water to produce concrete having the specified properties, the British method of concrete mix design, popularly referred to as the Department of Environment (DOE) United Kingdom was adopted in this study.

3.4.1. British method of concrete mix design

STAGE 1

Characteristic strength = 13.5 N/mm^2 @ 7 days (Proportion Defective 5%)

Grade of concrete = M20

$f_t = f_c + (K * S)$

f_t = Target mean strength

f_c = Characteristic strength

K = Statistical coefficient known as tolerance factor, using K = 1.65

S = Standard deviation, using S = 4.0 N/mm^2

$f_t = 13.5 + 1.65(4) = 20.1$ N/mm^2

Cement Type – Ordinary Portland Cement

Aggregate Type: Coarse - crushed

Fine – crushed

Since it is a plain concrete, W/C ratio maximum = 0.50

STAGE 2

Maximum size of coarse aggregate = 10mm

Using slump = 25 – 50mm

Free water content = 200 kg/m^3

STAGE 3

Cement content = 200/ 0.5 = 400 kg/m^3

STAGE 4

Relative density of aggregate = 2.7

Concrete density = 2400 kg/m^3

Total aggregate content = 2400 – 200 – 400 = 1800 kg/m^3

STAGE 5

Grading of fine aggregate (% passing 600µm) = 38%

Proportion of fine aggregate = 40%

Fine aggregate content = 1800 x 0.40 = 720 kg/m^3

Coarse aggregate content = 1800 – 720 = 1080 kg/m^3

Mix ratio: Cement**:** Fine aggregate**:** Coarse aggregate

400/400	720/400	1080/400
1	**1.8**	**2.7**

Proportions of the mix design determined using the British method is presented in Table 3.1.

3.5. Production of Concrete

Following the result of the above mix design, a mix ratio of 1 : 1.8 : 2.7 at a water-to-cement ratio (w/c) of 0.5 was arrived at for all mixes. Materials were weighed on air dry basis. Batching of the mix was carried out according to the proportion presented in Table 3.1. The quantity of concrete prepared in each batch was at least 10% in excess of the required quantity. The constituent materials were thoroughly mixed manually at ambient temperature such that each particle of aggregate in fresh concrete was well coated with the cement paste.

Table 3.1.: Mix Proportion of Materials

Crude Oil Contamination (%)	Cement (Kg/m^3)	Water (Kg/m^3)	Fine aggregate (Kg/m^3)	Coarse aggregate (Kg/m^3)	Crude oil content (Kg/m^3)
Control (0)	400	200	720	1080	-
2.5	400	200	720	1080	18
5	400	200	720	1080	36
10	400	200	720	1080	72
15	400	200	720	1080	108
20	400	200	720	1080	144
25	400	200	720	1080	180

3.6. Concrete Test Procedures

Tests were carried out on both fresh and hardened concrete in order to investigate the effect of the Crude Oil Contaminated Sand on the engineering properties of concrete.

3.6.1. Tests on fresh concrete

Tests carried out on the properties of freshly mixed concrete include the following: slump, compacting factor, unit weight, and flow table tests. All tests on the properties of freshly mixed concrete were conducted immediately after the mixing and in accordance with the appropriate BS 1881 specifications.

3.6.1.1. Slump test

This test is useful for finding the variations in the uniformity of a mix of given nominal proportions and specifies procedure for determining the consistency of concrete where the nominal maximum size of the aggregate does not exceed 38.0 mm. The test was conducted on each of the contaminated samples (Plates 3.5a and b) as well as the control, at the concrete laboratory of the department of Civil Engineering, University of Ibadan and in accordance with the procedure stated in BS 1881, PT 102 (1983).

Procedure:

The mould for the slump test is the frustum of a cone, 300 mm high. The base is 200 mm diameter and is placed on a smooth surface with the smaller opening of 100 mm diameter at the top.

The container was filled with concrete in three layers. Each layer was tamped 25 times with a standard 16 mm diameter steel rod, rounded at the end, and the top surface was strucked off by means of a screeding and rolling motion of the tamping rod. The mould was firmly held against its base during the entire operation. This was facilitated by handles or foot-rest brazed to the mould. Immediately after filling, the cone was slowly lifted and the unsupported concrete slumped.

The decrease in the height of the centre of the slump concrete was called slump and was measured to the nearest 5 mm. In order to reduce the influence of the variation in the surface friction on slump, the inside of the mould and its base were moistened at the beginning of every test. Prior to lifting of the mould, the area immediately around the base of the cone was cleared of concrete which may have dropped accidentally.

3.6.1.2. Compacting factor test

This test measures the degree of compaction resulting from the application of a standard amount of work (British Cement Association, 1993; Shetty, 2002; Gupta and Gupta, 2004). The apparatus (Plate 3.6a) used was obtained from the concrete laboratory of the department of Civil Engineering, University of Ibadan. It consists essentially of two hoppers, each of the shape of a frustum of a cone and one cylinder. The hoppers are hinged on a vertical frame one above the other. The hoppers have hinged doors at their bottoms. The inside surfaces of the hoppers are polished to reduce friction. The dimensions of the hoppers mould and the distances between them are as stated below:

- Upper hopper

Top diameter=254 mm
Bottom diameter=127 mm
Height=279 mm

- Lower hopper

Top diameter=229 mm
Bottom diameter=127 mm
Height=229 mm

The distance between the two hoppers and between the lower hopper and the cylinder = 203 mm

The test was conducted (Plates 3.6b) in accordance with the procedure stated in BS 1881 PT 103 (1983) for each of the contaminated mixes and the control.

Plate 3.5 a. Measuring of the Slump of a Contaminated Concrete Mix in Progress

b. The Slump of a Contaminated Concrete Mix**.**

Procedure:

The cylinder was weighed empty, set in position and covered. Concrete as mixed was put into the top hopper gently to fill approximately, but no consolidation was given. It was then allowed to fall into the second hopper by release of the top flap. When settled in the second hopper, the cylinder was uncovered and the second flap opened. The cylinder fills and some concrete spills over. Consolidation is only by gravity.

The excess concrete was cut off by two trowels working inward and the full cylinder then removed and weighed. The net weight was obtained. The cylinder was then emptied, and refilled in layers approximately 50 mm deep and heavily rammed or preferably vibrated (if of low workability) and completely filled. The objective was to remove all air voids after reweighing; the second net weight was calculated.

The compacting factor was obtained as the ratio of the actual density obtained during the test to the density of fully compacted concrete.

The compacting factor, (CF) =1st net weight/2nd net weight

This is a fraction and the higher its value the more workable; and the lower, the less workable. Compacting factor is always less than one (BS 1881 Part 103: 1993; British Cement Association, 1993).

3.6.1.3. Flow table test

This method gives an indication of the concrete consistency and cohesiveness and also proneness to segregation by measuring the spread of a pile of concrete subjected to jolting. This test is of greatest value with regard to segregation. However it gives a good assessment of consistency of stiff, rich and cohesive concrete mixes. The flow table test gives satisfactory results for concrete of the consistencies for which slump test may be used.

Apparatus: The test requires two apparatuses as follows:

1. Mould: A mould in the form of a frustum of cone of base diameter 250 mm, top diameter 170 mm and height 120 mm. The internal surface of the mould should be smooth. It should also be provided with two handles. A tamping rod 600 mm long and 16 mm diameter having one end rounded is also needed for rodding the concrete.

2. Flow table: It is a 760 mm square brass top table. It is mounted in such a way that it can be jolted by a drop of 13 mm. This table is bolted to a concrete or wooden base having a height of 400 mm and weighing not less than 140 kg.

Both the flow table and the mould were fabricated purposely for this research (Plates 3.7a and b). The test was conducted in accordance with the procedure stated in BS 1881 PT 105 (1983) for each of the contaminated mixes and the control.

Procedure:

To perform the test, the cone mould was placed at the centre of the plate and filled in two layers, each of which was compacted with a tamping rod. The plate was lifted with the attached handle a distance of 40 mm and then dropped a total of 15 times. The horizontal spread of the concrete was measured. Resistance to segregation can be assessed qualitatively: in concrete mixes that are susceptible to segregation, the paste will tend to separate from the coarse aggregate around the perimeter of the concrete mass.

3.6.2. Tests on hardened concrete

Tests were also conducted on hardened concrete to investigate the effect of Crude Oil Contaminated Sand on the engineering properties of concrete. Tests on hardened concrete were categorized into two: strength tests and durability tests.

3.6.2.1. Strength tests

Compressive and flexural strength tests were conducted on contaminated samples as well as the control samples.

Plate 3.6a. The Compacting Factor Apparatus Ready for Use

b. Compacting Factor Test in Progress

(a)

Plate 3.7a: Flow Table (Locally fabricated) Test in Progress

b. Spread of Concrete Being Measured in a Flow Table Test in Progress

3.6.2.1.1 Compressive strength test

The cubes produced were of size 100 mm x 100 mm x 100 mm. The filling of the mould was in three layers and were manually compacted using 16 mm diameter metal rod at 25 strokes per layer (BS 1881: Part 1, 1983). Following this, 147 concrete cubes comprising of 21 controls and 126 crude oil contaminated specimens were produced. The cubes were demoulded after 24 hrs of casting and cured in a water container (BS 1881: Part 111, 1983). The compressive strength gained was observed at ages 3, 7, 14, 28, 56, 84, and 168 days (BS 1881-116, 1983). The compressive test was conducted at Segun-Labiran & Associates, Consulting Civil & Structural Engineers material laboratory (Plate 3.8). The compressive strengths of the tested samples were obtained from the following relationship:

$$\text{Compressive Strength} = P/A \ (\text{N/mm}^2)$$

Where:

P = Ultimate compressive load on concrete (kN)

A = Surface area in contact with the platens (mm^2)

3.6.2.1.2. Flexural strength (Modulus of Rupture) test

100 mm x 100 mm x 500 mm timber formwork and steel moulds were used for the casting of both contaminated and control samples of unreinforced concrete beams. Three specimens each were cast per percentage of crude oil contamination and control. Thus a total of 21 beam samples (18 contaminated, 3 uncontaminated-control beams) were cast for the experiment. The samples were cured in water, separating the contaminated samples from the control, for 28 days after which they were weighed and tested for flexure in a Universal Testing Machine (UTM) (Plates 3.9a and b). Single/central point loading method of flexural test was adopted and was carried out at the material laboratory of Polytechnic Ado-Ekiti in accordance to EN 12390-5 (2000). Both the crushing load and the point of fracture from each support ends were determined.

Plate 3.8. Cube in a Compression Machine Ready for Crushing

The flexural strength of the resulting concrete beam using central point loading test was determined as

$$F_{cf} = (3 \text{ x } F \text{ x } l)/(2xd_1xd_2^2)$$

Where F_{cf} is the flexural strength of concrete

F is the maximum crushing load on beam

$l = 3d = 300$ mm

$d_1 = d_2 = 100$ mm

⇨ $3xl/(2xd_1xd_2^2) = 3x300/(2x100^3) = 4.5x10^{-4}$ (mm^{-2})

⇨ $\mathbf{F_{cf} = 4.5x10^{-4} F (N/mm^2)}$

3.6.2.2. Durability tests

The ability of the COCS concrete to resist any process of deterioration-durability, was investigated via water absorption, linear shrinkage, electrical resistivity and fire resistance tests. The control samples were also subjected to the same tests for comparison purpose.

3.6.2.2.1. Water absorption test

The test for water absorption of concrete was performed to determine the rate of water absorption of a given concrete mix exposed to different environmental conditions and draw inference from such results on the durability of the concrete mix.

The test was conducted on 21 (3 control and 18 contaminated samples), 100 mm concrete cubes and were then subjected to the test in accordance with BS 1881 Part 122 (1983). The test was carried out at the materials laboratory of the department of Civil Engineering, University of Ibadan.

Plate 3.9 a. Concrete Beams after Curing Ready for Weighing

b. Concrete Beams in Universal Machine being inspected prior to Flexural Test

3.6.2.2.2. Shrinkage test

Drying shrinkage is defined as the contracting of a hardened concrete mixture due to the loss of capillary water. This shrinkage causes an increase in tensile stress, which may lead to cracking, internal warping, and external deflection, before the concrete is subjected to any kind of loading. The behavior of COCS concrete in relation to shrinkage needs to be examined and thus its consideration among the tests conducted. The ASTM C 157 test for shrinkage allows the use of either 100 by 100 mm (4 inch) or 75 by 75 mm (3 inch) concrete cubes depending on the maximum aggregate size. For a maximum aggregate size of 25 mm (1 inch), either size of concrete cubes may be used, since rate and magnitude of shrinkage are influenced by specimen size, any specification based on ASTM C 157 must include the specimen size. Thus 100 mm cubes were considered in this test.

The mould preparation was done as in reference to paragraph 3.6 of ASTM C 157, and also casting of 21 (3 control and 18 contaminated samples) 100 mm concrete cubes in reference to paragraph 3.7 ASTM C 157. As per the code requirement, the samples were cured in lime-saturated water for 27 days and other procedures were followed accordingly.

3.6.2.2.3. Surface resistivity indication of concrete's ability to resist chloride ion penetration

This non-destructive laboratory test method determines the electrical resistivity of water-saturated concrete and provides a rapid indication of its resistance to the penetration of chloride ions. The test result is a function of the electrical resistance of the specimen.

According to the AASHTO T XXX-08, Surface resistivity meter (0 to 100 kΩ-cm range, resolution of 0.1 kΩ-cm and an accuracy of +/- 3% of reading) with a Wenner linear four-probe array, was used to measure the resistivity of 200 mm nominal length and 100 mm nominal diameter cylinderical moulds meeting the requirements of ASTM C-470 were the major apparatuses used to conduct the test. A total of 21 (3 control and 18 contaminated samples) cylindrical concrete samples were cast for the test with three samples cast for each of the percentage contamination and in accordance to ASTM C-192 or ASTM C-31. All specimens were moist cured in accordance to ASTM-192. Using the resistivity metre locally fabricated for this research, an AC potential difference was applied in the outer pins of the Wenner array generating current flow in the concrete. The potential difference generated by this current was measured by the two inner probes. The current used and the potential obtained along with the area affected were used to calculate the resistivity of the concrete in Ohms-cm. Resistivity of the concrete specimens to the flow of current were measured following the procedure stated in AASHTO T XXX-08 and the average readings for the different categories were recorded and used to characterize the penetrability of the specimens.

3.6.2.2.4. Fire Resistance

The test was conducted on 21 (3 control and 18 contaminated samples), 100 mm concrete cubes in accordance with IS:519-1959. The test examined the effect of elevated temperature of 200^0C on COCS concrete cubes as percentages of crude oil contamination increases. The preparation of the mould, casting, curing and monitoring of the compressive strength of the heated samples were as discussed under section 3.6.2.1.1.

The compressive test was conducted at SEGUN-LABIRAN & ASSOCIATES consulting Civil & Structural Engineers material laboratory.

3.7. Experimental Control

To ensure reliability of the test results, some measures were taken to ensure that alternatives adopted as substitutes to any of the recommended equipment or apparatus for tests produced results similar to the expected ones assuming the appropriate specifications were followed.

3.7.1. Casting of concrete samples:

Timber moulds were used for both concrete cubes and beams for compressive strength and flexural strength tests respectively. This was against the recommended steel materials in the British Standard. Thus, for the two cases, the steel moulds were used to cast samples, three each, for cubes and beams and cured for 28 days. The compressive test and flexural strength test were conducted on the cubes and beams respectively and subsequently compared with that of timber mould samples.

Also, all the precautions stated along-side the different tests in the standards were strictly adhered to during the testing operations. For slump test, the workability of a concrete mix changes with time due to the hydration of the cement and, possibly, loss of moisture. Tests on different samples were, therefore, carried out at a constant time interval after mixing in order to obtain comparable results.

3.8. Development of Models

Statistical models were carried out to establish the influence of the percentage crude oil contamination of sand on fresh and hardened properties of COCS concrete. Such responses included compressive strength, flexural strength, chloride resistivity, water absorption, slump, campacting factor, and flow. Response Surface Methodology (RSM) was adopted in developing the models using Design Expert-8.0.5.2 software package. A model was developed for compressive strength to allow for the variation of strength with curing age while other models were developed to predict other parameters. The design summary for compressive strength model and models for others are as stated in sections 3.8.1 and 3.8.2 respectively.

3.8.1. Design summary for compressive strength model

The design parameters for modelling compressive strength are as stated below. Similarly the experimental factor input and measured response input for compressive strength model development are presented in Tables 3.2 and 3.3 respectively.

Study Type	Response Surface	**Runs**	49
Design Type	Central Composite	**Blocks**	No Blocks
Design Model	Quadratic	**Build Time (ms)**	4.45
Factor A:	Crude Oil Contamination (%)	**Factor B:**	Curing Age (Days)

3.8.2. Design summary for other properties

Similarly, the experimental factors input and measured responses input of other properties' model development are presented in Tables 3.4 and 3.5 respectively.

Table 3.2. Experimental Factor Input for Compressive Strength

Factor	***Type***	***Sub-Type***	***Actual Value***		***Coded Value***		***Mean***	***Standard Deviation***
			Min.	***Max.***	***Min.***	***Max.***		
A	Numeric	Continuous	0.00	25.00	-1.00	1.00	11.07	8.65
B	Numeric	Continuous	3.00	168.00	-1.00	1.00	51.43	54.69

Table 3.3. Measured Response Input for Compressive Strength

Response	Name	Units	Obs	Analysis	Min.	Max	Mean	Std. Dev.	Ratio	Trans.	Model
Y1	Compr. Strength	N/mm^2	49	Polynomial	0.83	40.3	13.86	10.37	48.55	Log_{10}	Sixth

Table 3.4. Experimental Factor Input for Other Properties

Resp-onse	**Name**	**Units**	**Type**	**Sub-type**	**Actual Values**		**Coded Values**		**Mean**	**Std. Dev.**
					Min	**Max**	**Min**	**Max**		
A	Crude Oil	%	Numeric	Cont.	0.00	25.00	-1.00	1.00	10.11	9.52

Table 3.5. Measured Response Input for Other Properties

Response	**Name**	**Units**	**Min.**	**Max.**	**Mean**	**Std. Dev.**	**Ratio**	**Model**
Y1	Slump	mm	30	200	106.429	61.3538	6.6667	Quadratic
Y2	C.F.	Ratio	0.45	0.85	0.6686	0.1536	1.8889	Linear
Y3	Flow	%	15	85	284.286	58.4828	1.6087	Inverse Fifth
Y4	Flex St.	N/mm^2	0.113	5.865	3.298	2.2701	51.9027	Inverse Sqrt Quartic
Y5	Perm.	Kg	0	0.15	0.0557	0.05740	N/A	Sqrt Quadratic
Y6	L. S.	mm	0.02	0.09	0.0543	0.0263	4.5	Sqrt Fifth
Y7	Resist.	KΩ-cm	25.07	32.31	28.7857	2.5347	1.2888	Linear

3.9. Mix Proportioning for Enhanced Strength COCS Concrete

The purpose of mix proportioning is to obtain a product that will perform according to certain predetermined requirements (Hansen and Demaro, 1997), the most essential requirements being the workability of fresh concrete and the strength and durability of the hardened concrete. This exercise followed the outcome of the investigation of the effect of COCS on the fresh and hardened properties of concrete. The concrete constituents were re-proportioned using the COCS (5 and 10% contaminations) with the aim of finding an appropriate mix that would produce desired compressive strength relative to that of uncontaminated concrete. The water cement ratio was reduced from 0.5, used for the previous experiment, to 0.45, 0.42, 0.38, and 0.35. For the sake of workability, a super plasticizer – CONPLAST-SP 430, was added to mixes of w/c of 0.38 and 0.35. The four different mixes were designed using British method-DOE (See section 3.4.1 of this thesis) and the material proportion schedule is presented in Table 3.6. A total of 108 (12 controls and 96 contaminated samples with varying w/cs) samples, 100 x 100 x 100 mm cubes were cast and cured for ages 3, 7, 14, and 28 days. The compressive strength of the cubes were determined at the curing ages.

Table 3.6. Mix Proportion of Materials

Water/ Cement Ratio	Material Quantities (Kg/m^3)				Plasticizer (L/ m^3)	Plastic Density (Kg/m^3)
	Cement	Sand	Granite	Water		
0.5	400	720	1080	200	-	2400
0.45	444	710	1066	200	-	2420
0.42	488	686	1031	205	-	2410
0.38	500	690	1050	190	7.50	2430
0.35	500	710	1065	175	10.00	2450

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Results of Preliminary Studies

4.1.1. Sieve analysis

The results of particle size grading of the contaminated samples, and the uncontaminated fine and coarse aggregates are presented in Figs. 4.1 to 4.5. The grading curves of all the fine aggregate samples fell within the fine aggregate grading envelope as specified in BS 812: Part 103 (1989). From the particle size distribution curve of the uncontaminated fine aggregate (Fig. 4.4), it was deduced that the fine aggregate consist of 12% fine, 65% medium and 23% coarse sand. It possesses coefficient of uniformity (C_u) of 4.3 and coefficient of curvature (C_c) of 0.74 which shows that the fine aggregate is well graded.

The coarse aggregate when analysed had more than 80% of its particle fell within 13.2 mm and 6.7 mm sieve sizes. This conformed to the specification by BS 1881 PT 108 (1983) that for a cube size of 100 x 100 x 100 mm, the nominal size of aggregate must not exceed 20 mm. Also, Fig. 4.5 shows that the coarse aggregate is of the normal size of graded aggregate based on BS 812: Part 103 specification. This can be used for normal concrete works.

4.1.2. Result of Total Petroleum Hydrocarbon (TPH)

The results of TPH analysis of the soil samples obtained from the three polluted sites are presented in Table 4.1 below. The results showed that samples from B-Dere have the highest average percentage crude oil contamination of 14.1%, Bodo has 10.1% contamination while Bomu has lowest value of 8.6%. Based on this result, the percentage contamination by weight of sand for the research was set at 2.5%, 5.0%, 10.0%, 15.0%, 20.0%, and 25.0%.

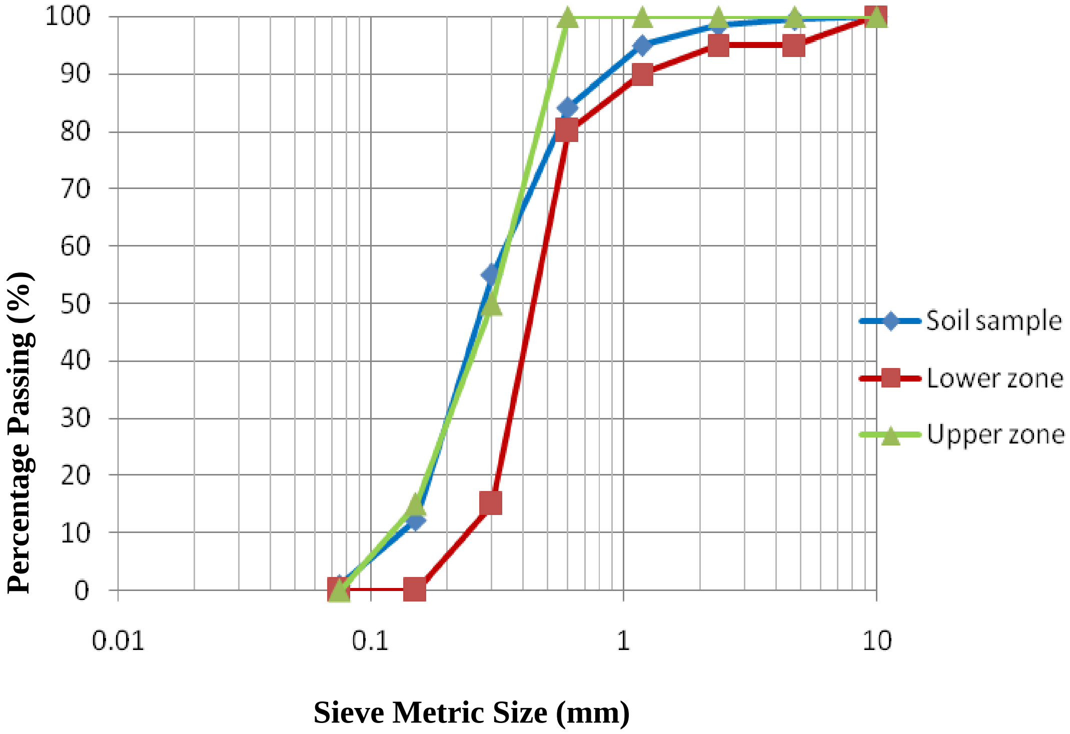


Fig. 4.1. Particle Size Distribution Curve of Sand from Bodo Spill Location.

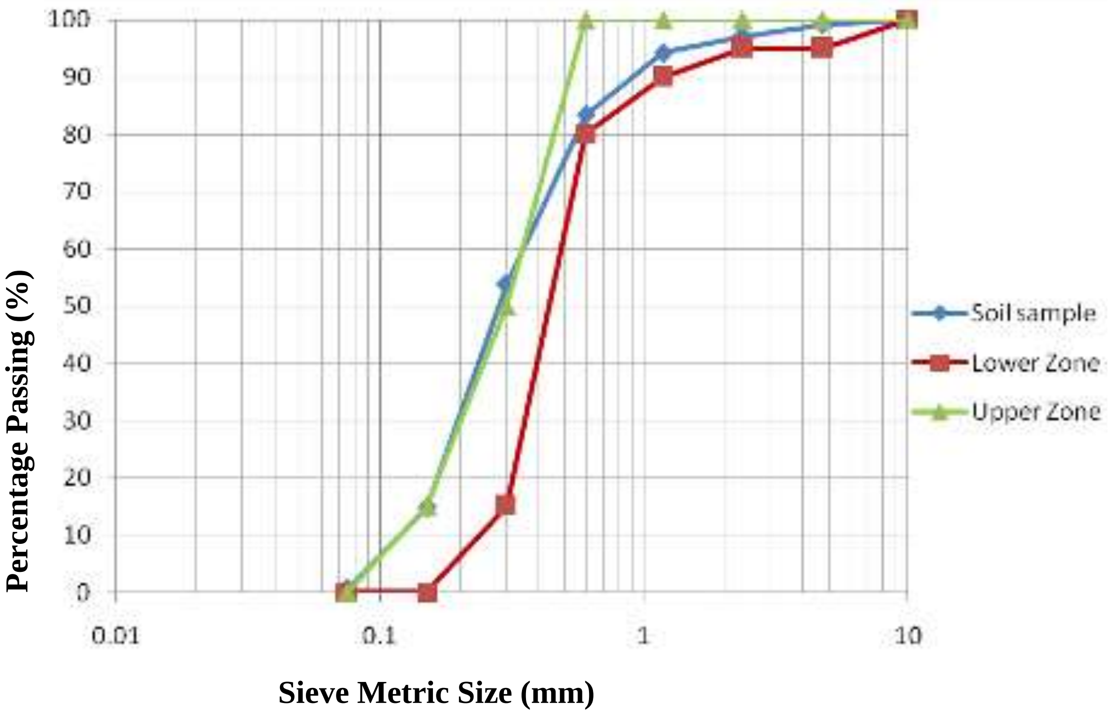


Fig. 4.2. Particle Size Distribution Curve of Sand from Bomu Spill Location.

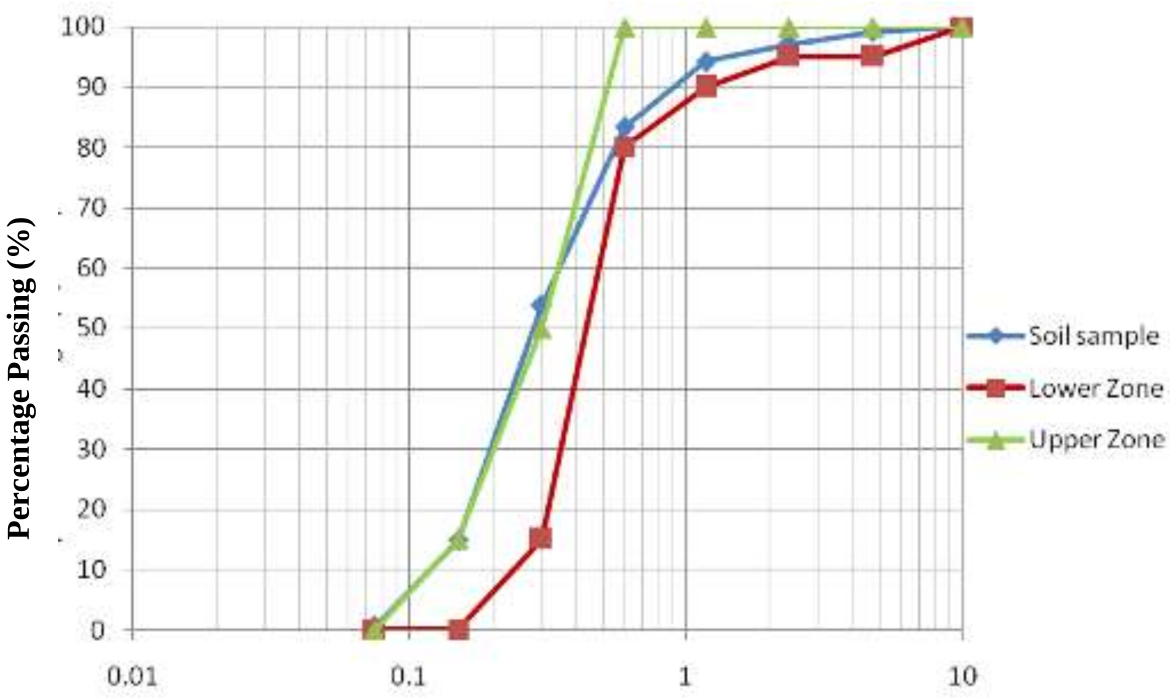


Fig. 4.3. Particle Size Distribution Curve of Sand from B-Dere Spill Location.

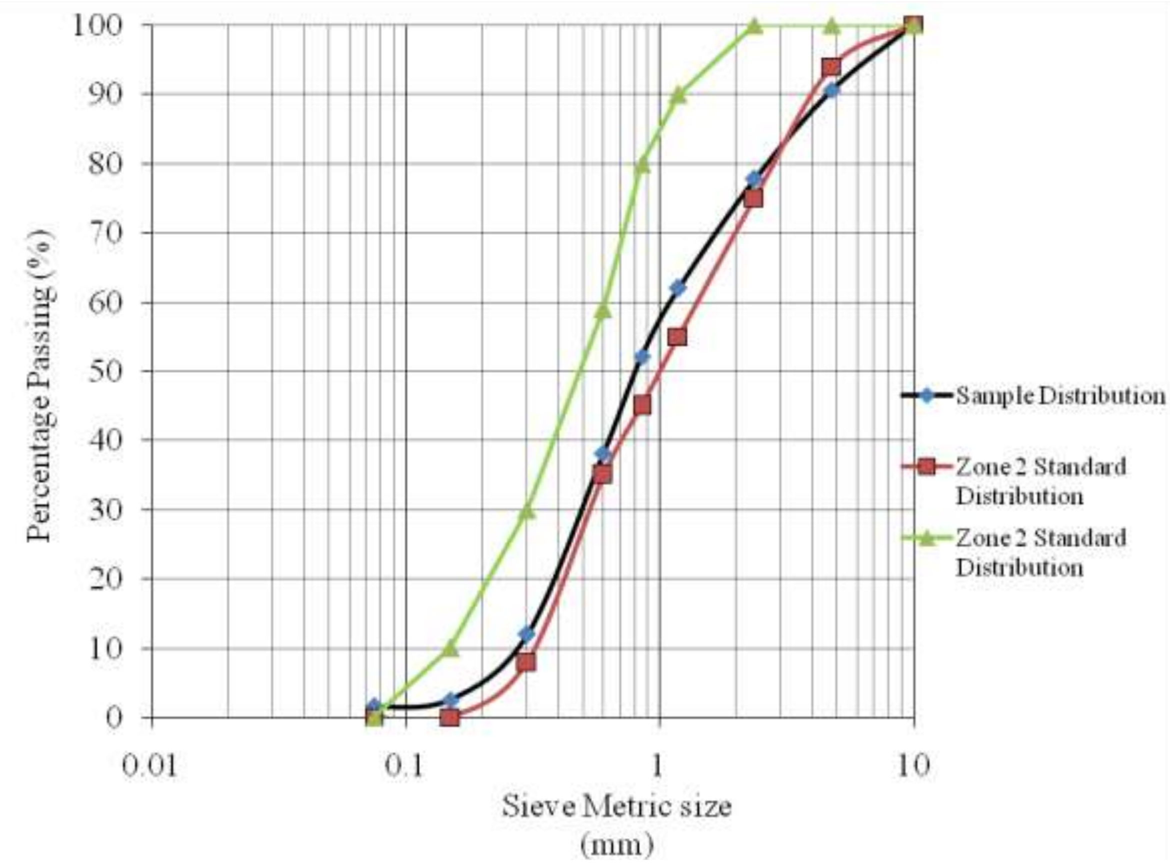


Fig. 4.4. Particle Size Distribution Curve of Uncontaminated Fine Aggregate

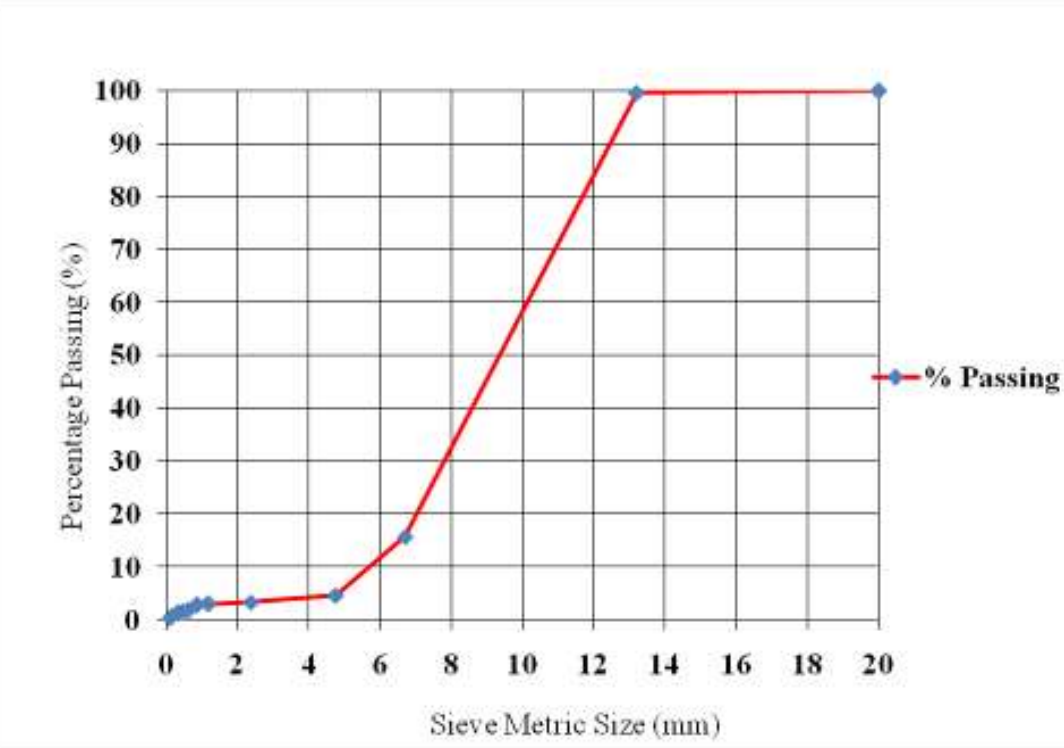


Fig. 4.5: Particle Size Distribution Curve of Coarse Aggregate

Table 4.1. TPH Test Results

S/N	***Sample Location***	***ID/Code***	***TPH (%)***	***AVG (%)***
1	B-DERE	CS1A	15.4	14.1±1.30
2		CS1B	12.8	
3		CS 1C	14.1	
4	BOMU	CS 2A	8.43	8.6±0.15
5		CS 2B	8.68	
6		CS 2C	8.69	
7	BODO	CS 3A	10.23	10.1±0.14
8		CS 3B	9.96	
9		CS 3C	10.11	

4.2. Results and Discussions of Tests on Concrete Samples

The results of the different tests conducted on both fresh and hardened concrete to investigate the effect of crude oil contaminated sand on the properties of concrete are as presented in the following sections. Similarly, the corresponding impacts of COCS, based on the test results, on concrete are inferred.

4.2.1. Results of tests on fresh concrete

4.2.1.1. Slump test

The slump values obtained for each of the samples are as presented in Table 4.2 below. When compared with the control sample's slump value of 30, the contaminated samples have greater values that increase with increase in percentage contamination of sand with crude oil. The slump value increases from 55 for 2.5% contamination to 200 for 25%. This implies that the addition of crude oil to sand will improve the workability of concrete, the slump values corresponding to medium-high workability levels. It is, however, obvious that increasing crude oil contamination beyond 25% will further increase the slump till it ultimately become too wet and thus result into a collapse slump.

4.2.1.2. Compacting factor test

Though the test is more suitable for low workability concrete having a slump of less than 10, applying the test to the samples further revealed that COCS concrete samples have higher compacting factor and thus higher workability when compared with the control sample. The compacting factors of the contaminated samples increased with increase percentage contamination (Table 4.3). The very low workability implied by the results is due to the fact that the samples are not of the dry mix for which the test is most suitable.

4.2.1.3. Result of Flow Table test

The flow test is most suitable for very high workability concrete with a slump of more than 175, applying the test to all the samples, however, clearly established that the presence of crude oil in the mix truly improves the workability. While the flow rate of the control mix was 15% (Table 4.4), a contamination of 2.5% crude oil in sand increased the flow rate by 3% and this trend increases as the crude oil percentage increases. Hence, 25%

Table 4.2. Results of Slump Test

Crude oil Contamination (%)	***Slump (mm)***	***Degree of workability***
0	30	Low
2.5	55	Medium
5.0	75	Medium
10.0	95	Medium
15.0	120	High
20.0	170	High
25.0	200	High

Table 4.3. Results of Compacting Factor Test

Crude Oil Contamination (%)	***Compacting Factor***	***Remark***
0	0.45	Very Low
2.5	0.48	Very Low
5.0	0.65	Very Low
10.0	0.70	Very Low
15.0	0.75	Very Low
20.0	0.80	Very Low
25.0	0.85	Low

Table 4.4. Results of Flow Table Test

Crude Oil Contamination (%)	***Initial Concrete Diameter (mm)***	***Final Average Concrete Diameter (mm)***	***Flow Rate (%)***	***Remark (Flow Rate)***
Control	200	230	15	Low
2.5	200	235	18	Low
5.0	200	240	20	Low
10.0	200	250	25	Low
15.0	200	330	65	Medium
20.0	200	335	68	Medium
25.0	200	370	85	High

contamination produced a flow rate of 85%, a value far more than that of the control value.

4.2.2. Effect of COCS on the fresh properties of concrete

Fresh concrete is defined as workable and consistent when the concrete can be transported, placed, compacted and finished sufficiently easily and without segregation. When the sand with different percentages of crude oil contamination were mixed to produce the contaminated concrete samples, the property at the concrete fresh state differ from the control sample. The three tests conducted on the concrete samples at the fresh state established that COCS concrete is more workable than the uncontaminated mix. The presence of crude oil in the mix acted as a plasticizer improving the fluidity and almost doubling the slump of the concrete mix at 2.5% contamination. Also, crude oil plasticize fresh concrete mixtures by reducing the surface tension of water and thus reduces the quantity of water required for cement hydration. This implies that COCS concrete is more easily transported, placed and compacted when compared with the uncontaminated concrete.

4.3. Results and Discussions of Tests on Hardened Concrete

4.3.1. Strength test results

4.3.1.1. Compressive strength test results

The results of the compressive strength test are depicted in Fig. 4.6 (see details in Appendix A.). The compressive strength for all the samples increased with time but at different rate. The control sample maintains the highest compressive strength values over time while the values for the contaminated samples decreased with increase in crude oil contamination but increases with time. The percentage reduction in compressive strength of COCS concrete in relation to the control is expressed graphically in Fig. 4.6 to show the level of strength loss. The average of the percentage strength reduction indicated that about 18% of the strength was lost when the soil was contaminated with 2.5% crude oil while almost 90% of the strength was lost due to 25% contamination (Fig. 4.7).

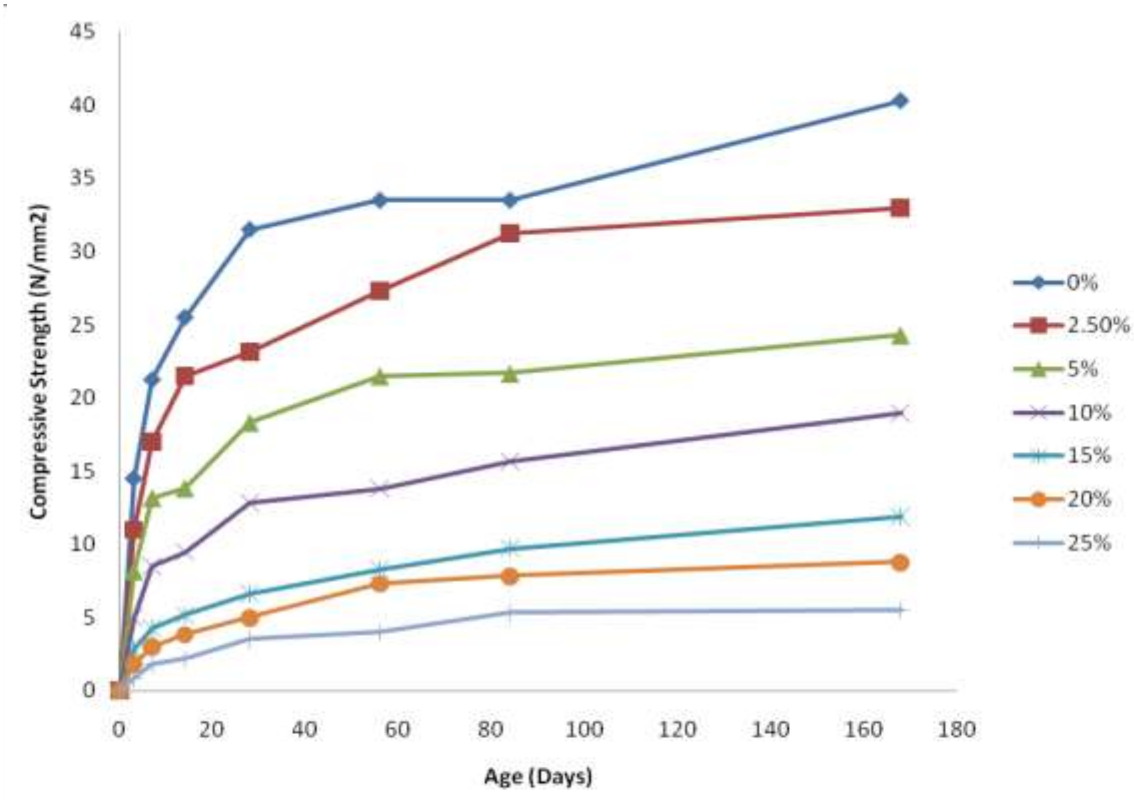


Fig. 4.6: Compressive Strength Development of Concrete

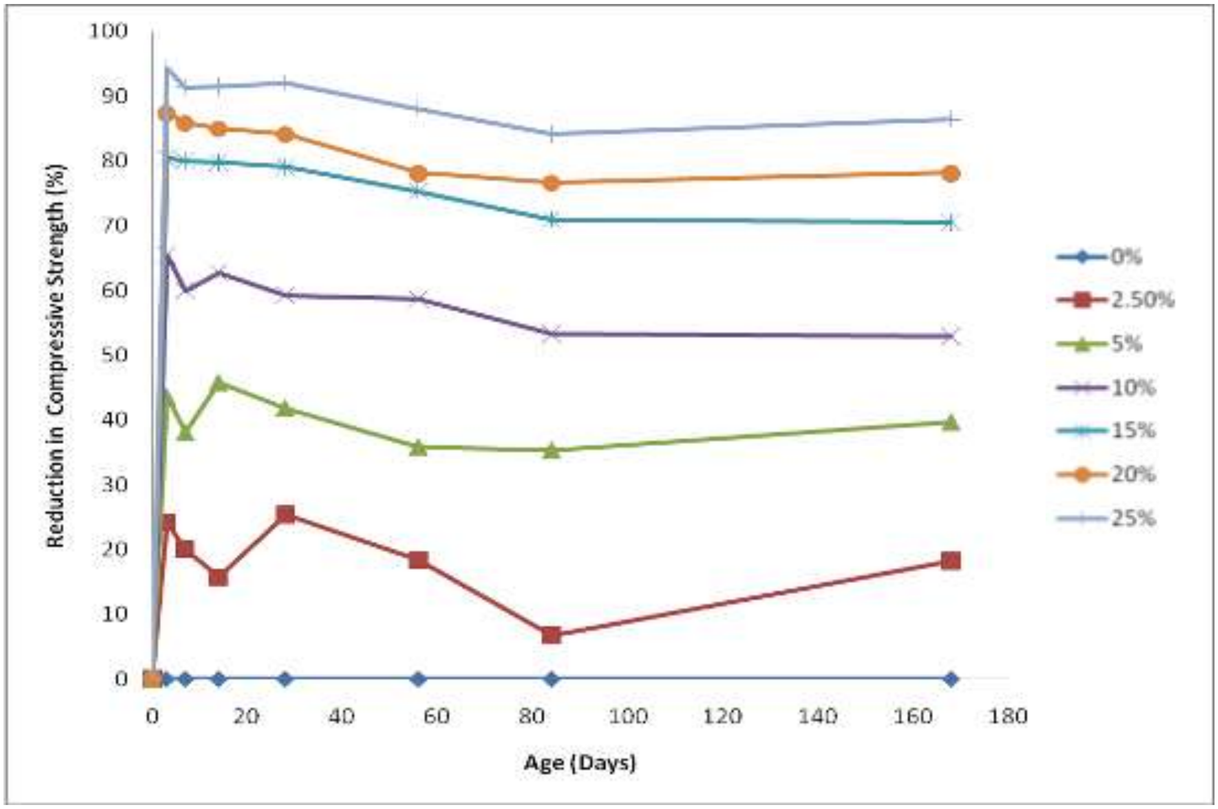


Fig. 4.7. Percentage Reduction of Compressive Strength of Concrete Cubes

4.3.1.2 Flexural strength test results

The results of the flexural strength tests (Table 4.5) indicated a negative effect of COCS on the flexural strength of concrete. The results are similar to that of the compressive strength in that the flexural strength reduces with increase in crude oil percentage contamination. Thus the control sample had the highest value of 5.87 N/mm^2 while the highest percentage contamination gave the lowest value of 0.11 N/mm^2. The presence of crude oil in the sand of concrete will reduce its flexural strength.

4.3.2 Effect of COCS on the Strength of Concrete

The effect of COCS was negative on both the compressive and flexural strengths of concrete. The values of the control maintained a consistent increase in compressive strength as the curing age increases. This is not surprising as the strength of cement-based materials cured in water with no contamination increases with age. The crude oil contaminated concrete cubes also increases but at lower rate of strength development. The reduction in strength can be related to the varying percentages of crude oil contamination in the concrete which may lead to loss of water content/moisture and preventing water from entering the concrete cube when curing in water which has effect on the hydration of cement present in the concrete cubes. The contamination of fine aggregate with crude oil which forms part of the microstructure of the matrix of concrete may have caused dilation of the gel and weakening of the cohesive forces in the paste and hence low strength development of the concrete cubes cast with COCS. The outcome of this research as per compressive strength reduction is in agreement with the findings of past researchers (Onabolu, 1989; Ramzi, 2000; Ejeh and Uche, 2009); on the adverse effect of hydrocarbons on concrete.

The large losses in compressive strength imply that crude oil percentages above 10% would not be suitable for most structural applications where high compressive strengths are required (Ajagbe et al., 2011). However, this type of concrete could be used in low-strength-concrete applications e.g. sidewalks, sandcrete blocks, etc. Due to the low strength of COCS concrete which would not be acceptable for reinforced concrete in most cases, the research was thereafter extended to improve on the strengths of 5% and 10%

contaminated COCS concrete by reducing the water cement ratio and the addition of plasticizer to assist the concrete in workability at low water/cement ratio.

4.3.3 Durability test results

4.3.3.1. Water absorption test result

The water absorption characteristic of the COCS concrete is as shown in Table 4.6. The increase in the dimensions and weight of the samples clearly showed that water was absorbed by the concrete samples but in varying quantity. While the control sample absorbed the highest volume of water, the quantity of water absorbed by COCS concrete samples reduced as the percentage of crude oil increases and this implies that COCS concrete offer resistance to the penetration of water. The outcome of the tests is better explained by the fact that water and oil are immiscible and thus the presence of crude oil in the concrete repels water and thus prevented it from penetrating. In porous solids, water is known to be the cause of many types of physical processes of degradation and as a vehicle for transport of aggressive ions; water can also be a source of chemical processes of degradation. Also, the physical-chemical phenomena associated with water transport in porous solids are controlled by the permeability of the solid (Mehta and Monteiro, 2006). This behavior of COCS concrete makes it more durable than the uncontaminated concrete since there would be resistance to aggressive chemicals or elements, such as chloride, from penetrating into the concrete thus protecting the reinforcement in reinforced concrete from corrosion.

4.3.3.2 Shrinkage test results

With reference to Table 4.7, the linear shrinkage of the sample was much on the control when compared with contaminated samples. The 25% crude oil contamination was least affected by shrinkage. Shrinkage is one of the detrimental properties of concrete, which affects its long-term strength and durability. Volume change in concrete results into the formation of unsightly cracks and is one of the most objectionable defects particularly in floors and pavements. Shrinkage particularly contributes to the formation crack. Therefore, the presence of crude oil in the fine aggregate of the concrete has limited its

Table 4.5. Flexural Strength Test Results

Contamination (%)	***Avg. Weight (kg)***	***Flexural Strength (N/mm^2)***
0	11.97	5.87
2.5	11.87	4.82
5.0	10.98	4.70
10.0	11.73	4.53
15.0	11.55	2.57
20.0	11.57	0.50
25.0	11.51	0.11

Table 4.6. Water Absorption Test Result

Crude oil Contamination (%)	***Change in Dimension (∆L) in cm***			***Weight Difference (Kg)***
	Length	***Breadth***	***Depth***	
0	0.13	0.12	0.12	0.15
2.5	0.10	0.08	0.08	0.12
5	0.06	0.05	0.05	0.05
10	0.04	0.04	0.04	0.04
15	0.03	0.03	0.03	0.02
20	0.01	0.02	0.02	0.01
25	0.00	0.01	0.01	0.00

Table 4.7. Shrinkage Test Results

Crude oil Contamination (%)	*Change in Dimension (ΔL) in cm*		
	Length	*Breadth*	*Depth*
0	0.10	0.08	0.09
2.5	0.08	0.07	0.08
5	0.07	0.06	0.07
10	0.05	0.05	0.06
15	0.04	0.04	0.05
20	0.03	0.03	0.03
25	0.01	0.02	0.02

volume change and hence the shrinkage. It could be said that COCS concrete is more durable than uncontaminated concrete when subjected to similar conditions of shrinkage.

4.3.3.3 Concrete Electrical Resistivity test results

Likewise, the same observation was made for the concrete electrical resistivity test as a rapid indication of its resistance to the penetration of chloride ions. The control mix of concrete cylinders made with uncontaminated sand offered least resistance to the passage of electric current ranging from about 24.00 to 25.50 KΩ-cm, which can be compared with International Standard Surface Resistivity Penetrability (Table 4.8). The control mix of concrete cylinder made with uncontaminated sand show a trend of about 21 – 37 KΩ-cm, indicating a low chloride ion penetrability. Similarly, the contaminated samples displayed lower chloride penetration when compared with the control. The chloride ion penetrability reduces with increase in crude oil percentage contamination (Table 4.9).

4.3.3.4 Fire Resistance test result

The compressive strength of sample cubes subjected to elevated temperature of 200ºC was used as an indication of the fire resistance of the samples. Significant decrease in compressive strength of heated concrete cubes were observed with increased in percentage contamination. The compressive strength decreased from 21.2 N/mm^2 (control) to 3.33 N/mm^2 for 15% contamination (See Table 4.10) . By these results, fire resistance of concrete decreases as the crude oil contamination level in the fine aggregate increases. This is not unconnected with the fact that crude oil is a fuel that can on its own aid ignition of fire. It specifically increases the heat within the concrete which resulted into the reduction of the concrete strength.

Table 4.8. Chloride Ion Penetrability Based

Chloride Ion Penetrability	***Surface Resistivity Test***	
	100 mm X 200 mm Cylinder (KΩ-cm) a = 1.5	***150 mm X 300 mm* Cylinder (KΩ-cm) a = 1.5**
High	**< 12**	< 9.5
Moderate	**12 -21**	9.5 – 16.5
Low	**21 – 37**	16.5 – 29
Very Low	**37 – 254**	29 – 199
Negligible	**>254**	>199

a = Wenner probe tip spacing

AASHTO: T XXX-08

Table 4.9. Concrete Surface Resistivity Test Results

Crude oil Contamination (%)	***Surface Resistivity Test (KΩ-cm)***	***Chloride Ion Penetrability***
0	25.07	Low
2.5	27.22	Low
5.0	28.05	Low
10.0	28.38	Low
15.0	28.66	Low
20.0	31.81	Low
25.0	32.31	Low

Table 4.10. Compressive Strength of Heated (200˚C) COCS Concrete Cubes

Crude oil Contamination (%)	***Specimen***	***Crushing Load (N)***	***Compressive Strength (N/mm^2)***	***Average Compressive Strength (N/mm^2)***
0.0	A1	215	21.5	21.17±1.04
	A2	220	22.0	
	A3	200	20.0	
2.5	B1	170	17.0	17.33±0.29
	B2	175	17.5	
	B3	175	17.5	
5.0	C1	138	13.8	13.77±0.25
	C2	140	14.0	
	C3	135	13.5	
10.0	D1	100	10.0	11.17±1.26
	D2	125	12.5	
	D3	110	11.0	
15.0	E1	35	3.5	3.33±0.29
	E2	35	3.5	
	E3	30	3.0	
20.0	F1	29.1	2.9	2.7±0.34
	F2	28.9	2.9	
	F3	23.3	2.3	
25.0	G1	12.1	1.2	1.1±0.10
	G2	1.05	1.1	
	G3	1.04	1.0	

4.3.4 Effect of COCS on the durability of concrete

Unlike the effect of COCS on the strength of hardened concrete, the durability tests conducted in this research showed clearly that the effect of crude oil in the sand of the concrete improves the resistance of the COCS concrete to water and chloride penetrability. These two attributes greatly increases the durability of the concrete by preventing the corrosion of steel and other substances that may affect the durability of concrete. The use of COCS concrete can thus be extended to the production of concrete products wherein the absorption of water affects the aesthetics as is the case in roof tiles, and reduces the passage of water in liquid retainning structures such as septic tank etc. In addition, the reduction of water absorption by COCS concrete makes it a better choice as damp proof courses in a water logged area to reduce seepage.

The low fire resistance of the COCS concrete will not compromise the durability of the concrete when adopted in the liquid retainning structures and damp proof courses as suggested above. Furthermore, the exhibition of good durability properties by the COCS confirmed the recommendations by Al-Mutairi and Eid (1997) of the suitability of the material for use in the production of asphalt concrete mixes for use in secondary roads, road beds, impermeable layers for landfill and containment facilities, or as stabilizers for steep embarkments.

4.4 Mathematical Models

The result of the derived models in this research is presented, along with the correlation coefficients and the relative significance.

4.4.1. Compressive strength model

The response surface methodology was used to investigate the effect of some parameters (crude oil contamination and curing age) on the compressive strength of concrete. The experimental values for compressive strength at 3, 7, 14, 28, 56, 84 and 168 days under different crude oil contamination percentages are presented in Table 4.11 . The model summary statistics of linear, 2FI (Two Factors Interaction), quadratic, cubic, quartic, fifth and sixth polynomials are presented in Table 4.12. Statistical analysis for compressive strength at the curing ages and different contamination percentages indicated that the model (sixth order polynomial) with coefficient of correlation R^2 equal to 0.9982 was adequate, possessing less significant lack of fit than other models and its thus the best one fit. The final model, after a base 10 logarithmic transformation, for the compressive strength as determined by the above analysis is presented below.

$$\mathrm{Log}_{10}(\textbf{Compressive Strength}) = 0.73288+9.07341E\text{-}003*A+0.14930*B-0.030193*A^{2}-0.013114*B^{2}+6.07861E\text{-}003*A^{3}+5.28517E\text{-}004*B^{3}-5.35718E\text{-}004*A^{4}-9.78501E\text{-}006*B^{4}+2.130221E\text{-}005*A^{5}+9.97399E\text{-}007*B^{5}-3.11650E\text{-}007*A^{6}-2.24025E\text{-}010*B^{6} \quad \text{...(Eqtn. 4.1)}$$

Fig. 4.9 show the correlation between measured and predicted models while Fig. 4.10 shows the non-linear response surface interactions between the factors.

4.4.2. Models for other properties

The input parameters and the model types for the slump, compacting factor, flow, flexural strength, permeability, linear shrinkage and chloride resistivity of the COCS concrete are shown in Table 4.13. Similarly, the model equations and the R^2 values for each of the responses are presented in Table 4.14. Statistical analysis for slump and compacting factor was best described by linear type model while a model based on the inverse of flow values gave a R^2 of 1.000. Linear model also described permeability and resistivity better while a transformation of the inverse of the square root of flexural strength improved the R^2 to 0.9950.

Based on the correlation observed between the measured and the predicted models for all the factors, the models can be used to navigate the design space. Thus the fresh and hardened properties of concrete when made with COCS can be predicted by the developed models. Further details on the statistical analyses of the models are contained in appendix B.

Table 4.11. Input Details Showing Factors and Response

Order	*Factor A: Contamination (%)*	*Factor B: Curing Age (Days)*	*Response 1: Compressive Strength (N/mm^2)*
1	0.00	3.00	14.50
2	0.00	7.00	21.25
3	0.00	14.00	25.50
4	0.00	28.00	31.50
5	0.00	56.00	33.50
6	0.00	84.00	33.50
7	0.00	168.00	40.30
8	2.50	3.00	11.00
9	2.50	7.00	17.00
10	2.50	14.00	21.50
11	2.50	28.00	23.17
12	2.50	56.00	27.33
13	2.50	84.00	31.25
14	2.50	168.00	33.00
15	5.00	3.00	8.17
16	5.00	7.00	13.17
17	5.00	14.00	13.83
18	5.00	28.00	18.33
19	5.00	56.00	21.50
20	5.00	84.00	21.67
21	5.00	168.00	24.30
22	10.00	3.00	5.00
23	10.00	7.00	8.50
24	10.00	14.00	9.50
25	10.00	28.00	12.83
26	10.00	56.00	13.83

Table 4.11. Input details Showing Factors and Response (Cont'd).

Order	**Factor A: Contamination (%)**	**Factor B: Curing Age (Days)**	**Response 1: Compressive Strength (N/mm^2)**
27	10.00	84.00	15.67
28	10.00	168.00	19.00
29	15.00	3.00	2.83
30	15.00	7.00	4.25
31	15.00	14.00	5.17
32	15.00	28.00	6.61
33	15.00	56.00	8.27
34	15.00	84.00	9.73
35	15.00	168.00	11.90
36	20.00	3.00	1.83
37	20.00	7.00	3.00
38	20.00	14.00	3.83
39	20.00	28.00	5.00
40	20.00	56.00	7.33
41	20.00	84.00	7.83
42	20.00	168.00	8.80
43	25.00	3.00	0.83
44	25.00	7.00	1.83
45	25.00	14.00	2.17
46	25.00	28.00	3.50
47	25.00	56.00	4.00
48	25.00	84.00	5.33
49	25.00	168.00	5.50

Table 4.12. Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted	Predicted	PRESS	
Linear	0.13	0.8947	0.8902	0.8788	0.91	
2FI	0.13	0.9031	0.8966	0.8800	0.90	
Quadratic	0.087	0.9565	0.9514	0.9421	0.44	
Cubic	0.063	0.9793	0.9745	0.9664	0.25	
Quartic	0.051	0.9881	0.9833	0.9758	0.18	
Fifth	0.043	0.9930	0.9880	0.9723	0.21	
Sixth	0.026	0.9982	0.9959	0.9764	0.18	Suggested

Response 1: Compressive Strength Transform: Base 10 Log Constant: 0

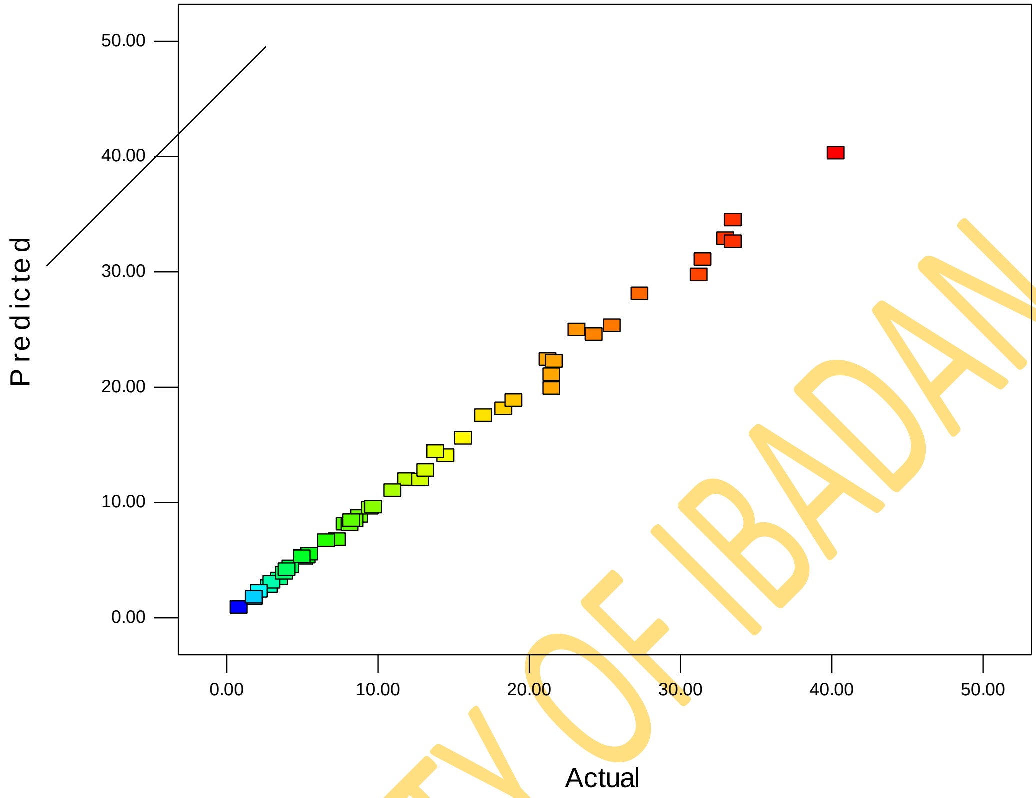


Fig. 4.9. Comprssive Strength Measured Values Vs Predicted Values

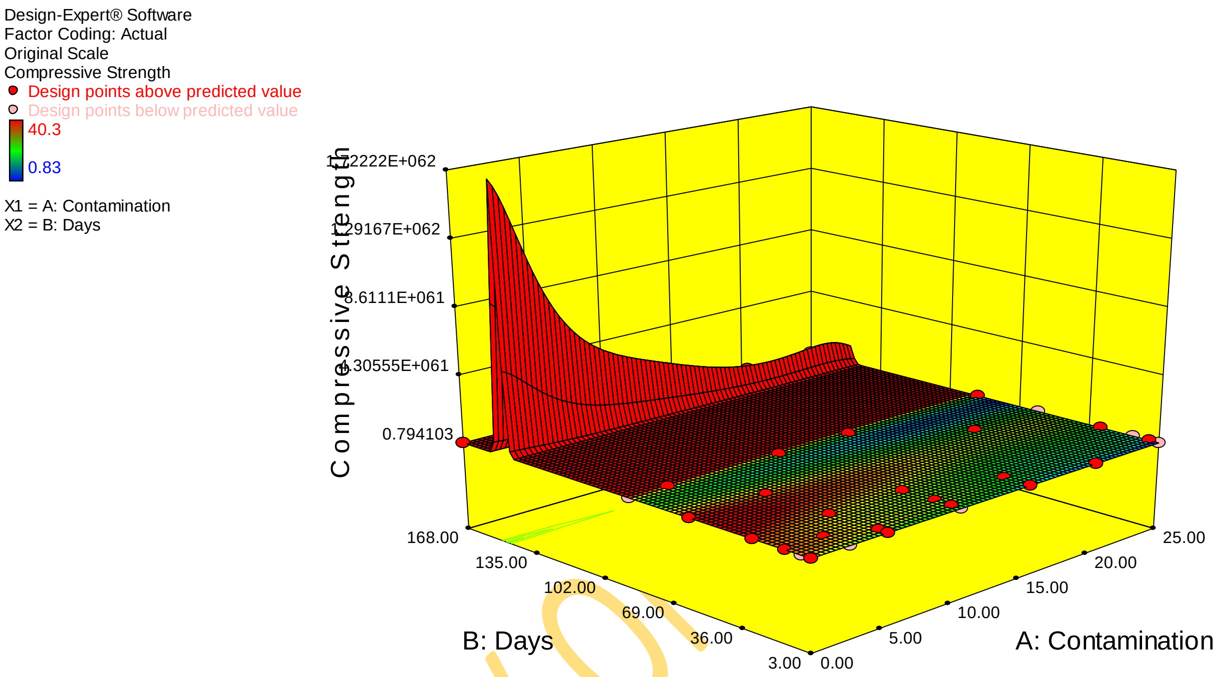


Fig. 4.10. Response Surface for Desirability Effects of Variables Interactions

Table 4.13. Input Parameters for the Responses and the Model Type

Response	**Name**	**Units**	**Min.**	**Max.**	**Mean**	**Std. Dev.**	**Ratio**	**Model**
Y1	Slump	mm	30	200	106.429	61.3538	6.6667	Quadratic
Y2	C.F.	Ratio	0.45	0.85	0.6686	0.1536	1.8889	Linear
Y3	Flow	mm	230	370	284.286	58.4828	1.6087	Inverse Fifth
Y4	Flex St.	N/mm^2	0.113	5.865	3.298	2.2701	51.9027	Inverse Sqrt Quartic
Y5	Perm.	Kg	0	0.15	0.0557	0.05740	N/A	Sqrt Quadratic
Y6	L. S.	mm	0.02	0.09	0.0543	0.0263	4.5	Sqrt Fifth
Y7	Resist.		25.07	32.31	28.7857	2.5347	1.2888	Linear

Table 4.14. Statistical Models for Other Responses

Response	Model Equation	R^2
Slump	$Y1 = 51.73293+3.36976A+0.10685A2$	0.9535
C.F.	$Y2 = 0.53075+0.013626A$	0.8323
Flow	$1/Y3 = 4.34772E\text{-}003-4.04052E\text{-}004A+1.45468E\text{-}004A^2-1.80853E\text{-}005A^3+8.63682E\text{-}007A^4-1.40548E\text{-}008A^5$	1.000
Flexural Strength	$1/\sqrt{Y4} = 0.41581+0.11320A+0.021411A^2+1.20874E\text{-}003\ A^3-1.47846E\text{-}005\ A^4$	0.995
Permeability	$\sqrt{Y5} = 0.32287-0.011316A-4.45260E\text{-}005\ A^2$	0.8721
Linear Shrinkage	$\sqrt{Y6} = 0.3003-0.072901A+0.016220\ A^2-1.45447E\text{-}003\ A^3+5.65235E\text{-}005\ A^4-8.01463E\text{-}007\ A^5$	1.000
Resistivity	$Y7 = 26.52368+0.22365A$	0.8230

4.5. Mix Proportioning Compressive Strength Test Result

Compressive strength test for the four different mixes with COCS was carried out at 3, 7, 14 and 28 days with the intention of improving the compressive strength of COCS concrete when the contamination by crude oil does not exceed 10%. The results of the test are presented in Table 4.15. It was observed from the result that the compressive strength of the mixes increases with decrease in water cement ratio. Thus the maximum values at 28 days for 5% and 10% contamination for 0.35 water/cement ratio are 28.33 N/mm^2 and 26.77 N/mm^2 respectively. The designed mix ratios and the corresponding 28 days compressive strengths are shown in Table 4.16. The least 28 days strength for 10% contamination was 21 N/mm^2 obtained at water/cement ratio of 0.45. Thus a mix ratio of 1: 1.6 : 2.4 at 0.45 water/cement ratio could be used for reinforced concrete to resist tension provided the crude oil contamination does not exceed 10% by weight of the fine aggregate.

Table 4.15. Compressive Strength for Different Mix Proportions

Crude Oil Contamination (%)	Water/Cement Ratio	Compressive Strength (N/mm^2)			
		3 Days	7 Days	14 Days	28 Days
5	0.5*	8.17	13.17	13.83	18.33
	0.45	10.67	15.67	20.67	23.67
	0.42	11.69	16.67	23.00	25.67
	0.38	14.00	23.50	24.00	27.33
	0.35	18.00	21.33	25.33	28.33
10	0.5*	5.00	8.50	9.50	12.83
	0.45	10.33	15.00	19.00	21.00
	0.42	11.67	16.00	22.33	23.67
	0.38	13.50	18.33	22.67	25.00
	0.35	13.50	19.67	24.33	26.67

*From previous experiment

Table 4.16. Designed Mix Ratios and their 28 days Compressive Strength

S/N	*Design Mix Ratio*	*W/C Ratio*	*Compressive Strength (N/mm^2) @ 28 days*	
			5%	*10%*
1	**1 : 1.8 : 2.7**	0.5	18.33	12.83
2	**1 : 1.6 : 2.4**	0.45	23.67	21.00
3	**1 : 1.4 : 2.1**	0.42	25.67	23.67
4*	**1 : 1.38 : 2.1**	0.38	27.33	25.00
5*	**1 : 1.42 : 2.13**	0.35	28.33	26.67

*CONPLAST SP-430 -Super plasticizer added.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The effect of Crude Oil Contaminated Sand on the fresh and hardened concrete was investigated in this research. The consistency and workability of COCS concrete were evaluated through slump, compacting factor and flow table tests while the hardened properties were estimated by assessing the compressive and flexural strengths; water absorption, linear shrinkage, electrical resistivity and fire resistance tests. The findings of the research are stated below:

(i). The presence of crude oil in the fine aggregate of concrete improved the rheological behaviour of the concrete thus making the concrete more workable. It was confirmed that hydrocarbons adversely affect the hydration of fresh concrete and thus retard the strength gain.

(ii). The compressive strength of the COCS concrete was reduced beyond 50% when the fine aggregate was contaminated by crude oil to more than 10% by weight of the sand. The flexural strength of the COCS concrete was greatly affected particularly at 20% to 25% contamination.

(iii). COCS concrete exhibited better resistance to water and chloride penetration when compared to the uncontaminated concrete. Similarly, the COCS concrete shrink less compared to the control sample.

(iv). COCS concrete exhibited poor fire resistance relative to the uncontaminated concrete. The COCS concrete is suitable for use in low strength structures or generally where durability requirement outweighed that of strength.

(v). Mathematical models were developed for compressive strength and other properties (flexural strength, slump, compacting factor, flow, water absorption, chloride resistivity, and linear shrinkage) of COCS concrete at 0.5 water/cement ratio.

(vi). At 0.45 water/cement ratio, a strength of 21 N/mm^2 was obtained at 10% crude oil contamination. This is a suitable strength for reinforced concrete structures. Further reduction in water/cement ratio will increase the strength accordingly, a table of compressive strength at 3, 7, 14 and 28 days for different mix proportions was provided.

5.2 Recommendation for further Studies

Further studies in the following areas would improve the use of contaminated soils in the polluted sites in the Niger Delta area

a. A research should be conducted on the use of COCS for sandcrete block production.

b. More durability tests should be conducted on the COCS concrete over a longer period of time than considered in this research.

c. The possibility of using locally available material as admixture such as metakaolin, to improve the strength of the COCS concrete should be investigated.

REFERENCES

ACI Committee, 2003. Guide for the silica fume in concrete. ACI Manual of Concrete Practices, l. 96, 234 R-1 to 46.

ACI 1990. Cement and concrete terminology. ACI 116R-90. American Concrete Institute, Detroit, USA.

ACI Committee 201, 2002. Guide to durable concrete. ACI Manual of Concrete Practice, Detroit, USA.

ACI Committee 211, 2002. Guide for proportioning low slump concrete. ACI Manual of Concrete Practice, Detroit, USA.

Agbede O. A. 1996. Ground water modelling-an overview. *Journal of Mining and Geology*. 32. 2: 105-112.

Ajagbe W. O., Omokehinde S. O., Agbede O. A., and Alade G. A. 2011. Effect of crude oil impacted sand on compressive strength of concrete. *Construction and Building Materials* 26. 1: 9-12.

Alexander, K. M. 1983. A study of concrete strength and mode of fracture in terms of matrix, bond and aggregate strengths. Tewksbury Symposium on Fracture, University of Melbourne, 25-34.

Al-Mutairi, N. M. 1995. Kuwait oil-based pollution: effect on building material. *Journal of Materials in Civil Engineering* 7. 3: 154 – 160.

Al-Mutairi, N. M. and Eid, W. K. 1997. Utilization of oil-contaminated sands in asphalt concrete for secondary roads. *Materials and structures*. 30: 497-505.

Al Qadi, A. N. S., Nasharuddin, K., Al-Mattarneh, H and AL-Kadi, Q. N. S.. 2009. Statistical Models for Hardened Properties of Self-Compacting Concrete. *American J. of Engineering and Applied Sciences* 2 (4): 764-770

ASTM 1993. Standard definitions and terms relating to concrete and concrete aggregates. American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA.

ASTM C125-93. American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA.

ASTM C143-78, Test for slump of Portland Cement Concrete. American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA.

Ayininuola, G. M. 2009. Influence of diesel oil and bitumen on compressive strength of concrete. *Journal of Civil Engineering (IEB)*, 37(1) 65-7.1

Badejo, O.T. and Nwilo, P.C. 2004. Management of oil spill dispersal along the Nigerian coastal areas, Department of Surveying and Geoinformatics, University of Lagos. pp. 1

Biczok, I. 1964. Concrete corrosion and concrete protection. Publishing House of the Hungarian Academy of Sciences, Budapest. In. Wilson, S.A., Langdon, N.J. & Walden, P.J. 2001. The effects of hydrocarbon contamination on concrete strength. *Proceedings of the Institution of Civil Engineers. Geotechnical Engineering.* 149. 3:189–193.

Blaszczynski, T. Z. 2002. Reinforced concrete structures in crude oil products environment. *Proceedings of the Foundations of Civil and Structural Engineering*, Poznan University of Technology. 2.

Bogue, R. H. and Lerch, W. 1984. *Hydration of portland cement compounds: Industrial and Engineering Chemistry*. Easton, Pa.

BP Educational Services (BPES), 2006. Oil refining and products. Energy Business Booklet, BP International Ltd. Retrieved April 15, 2011 from http/www.bp.com/bpes.

Building Research Establishment 212 (BRE), 1991.Construction of new buildings on gas-contaminated land. Garston, Watford.

British Cement Association, 2001. Computer aided learning for concrete. Version 2.3.

British Precast 2003. Sustainable development in the cement and concrete sector. Project summary. pp. 3.

British Standard Institution 1985. Methods of determination of particle size distribution.

BS 3148 (1980). Methods of test of water for making concrete. London. British Standards Institution.

BS 1881: Part 1 1983. Method for making test cubes from fresh concrete. London. British Standard Institution.

BS 1881: Part 116 1983. Method for determination of compressive strength of concrete cubes. London. British Standard Institution.

BS 812: Part 1 1975. Methods for sampling and testing of mineral aggregates, sands and fillers: sampling, shape, size and classification. London. British Standard Institution.

BS 812: Part 103. 1989. Method of determination of particle size distribution. London. British Standard Institution.

BS 812: Part 2. 1995. Method of determination of density. London. British Standard Institution.

BS 882: 1983. Aggregates from natural sources for concrete. London. British Standard Institution.

Calabrese, E.J., Kostecki, P.T. and Bonazountas, M. 1991. *Hydrocarbon contaminated soils*. Vol. II. CRC Press.

Carstensen, J. V. 2011. Materialmodelling of reinforced concrete at elevated temperatures. M.Sc. thesis, department of Civil Engineering, the Technical University, Denmark. Pp124.

Cement and Concrete Association, 1979. Concrete Practice. Pp 61

Chastain, W. E. 1980. Performance of concrete pavement on granular sub-base. Highway Research Board Bull. 52.

Cornell, J. A. 1990. How to apply response surface methodology. 8. ASQC. Wisconsin.

Cox, I. 2002. Innovative housing development goes underground. Concrete Quarterly. Winter 2002/2003 ed. 203.

Craig, C.F. 2006. How oil refining works. How stuff works. Retrieved Nov. 19, 2006, from http://science.howstuffworks.com/oil-refining.

Day, K. W. 1992. Concrete mix design, quality control and specification. 2nd ed. E & FN Spon

Dobrowolski, J. A. 1998. *Concrete construction handbook.* 4th ed. New York: McGraw-Hill.

Domone, P. L. 2003. Advanced concrete technology-concrete properties. J. Newman and B. S. Choo Eds. Elsevier Ltd.

Dublin-Green, W. F., Nwankwo, J. N. and Irechukwu, D. O. 1998. Effective regulation and mangement of HSE issues in the petroleum industry. *SPE International*

Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Caracas, Venezeula, 7-10 June, 1998. Paper No. SPE 40/26.

Duggal, S. K. 1997. *Building Materials*. 2nd Ed. New Age International.

Ejeh, S. P. and Uche, O. A. U. 2009. Effect of crude oil spill on compressive strength of concrete materials. *Journal of Applied Science Research* 1756, 61.

EN 12390-5: 2000. Testing hardened concrete-part 5: flexural strength of test specimens.

Energy Information Association 1998. Refining and simple distillation. Retrieved Nov. 18, 2006, from http://www.eia.doe.gov/.

Ezeldin, H. S. and Vaccari, D. A. 1996. Organic Emissions from Petroleum-Contaminated Soil Fixed in Concrete. *Journal of Soil Contamination*, 5(1):35–52

Etxeberria, M., Vazquez, E., Mari, Antonio R., and Barra, M. 2004. Influence of amount of recycled coarse aggregates and production process on properties of recycled aggregate concrete. Department of Construction Engineering, Faculty of Civil Engineering, Universitat Politécnica de Catalunya (UPC), Barcelona, Spain.

Fingas, M. 2001. *The basics of oil spill clean up*. 2nd Ed. London: Lewis Publishers. 191-208.

Franklin, S. O. 2010. Modelling of the compressive and tensile strength relationship of concrete in studies on the punching phenomenon in prestressed flat slabs. *Journal of Applied Sciences Research*, 6(3): 205-211.

Gambhir, M. L. 2005. *Concrete Technology*. 3rd ed. New Delhi: Tata McGraw-Hill Company Ltd. 147 – 175.

Garvin, S. L. and Lewry, A. J. 1996. The Performance of Contaminated Land. In Concrete in the Service of Mankind-Concrete for Environment Enhancement and Protection, Conference Proceedings, University of Dundee, Scotland, 24-26 June. E & FN Spon, London.

Gupta *et al* 1982. A multidimensional finite element code for the analysis of coupled fluid, energy and solute transport. Battelle Pacific Northwest Laboratory PNL 2939, EPA Contract 68-03-3116

Gupta, B. L. and Gupta, A. 2004. *Concrete technology.* Delhi: Standard publishers Distributors.

Hamad, B. S., Rteil, A. A. and El-Fadel, M. 2003. Effect of used engine oil on properties of fresh and hardened concrete. *Construction and Building Materials* 17 311–318

Hamad, B. S.and Rteil, A. A. 2003, Effect of used engine oil on structural behavior of reinforced concrete elements. *Construction and Building Materials* 17 203 – 211.

Ham, Y., Lin, J., Lee, J., and Kim, S. 1999. Properties of grease-soaked concrete in containment building. *Transactions of the 15th International Conference on Structural Mechanics in Reactor Technology (SMiRT-15)*, Seoul, Korea, August 15 – 20, 49 -56.

Hansen, M. R. and Demaro J. R. 1997. HPC mixture proportion optimization for precast concrete using statistical. *Proceedings of the international symposium on HPC*, New Orleans: Lousiane.

Hassan, H. F. 2009. Evaluation of Petroleum-Contaminated Soil effect on the properties of hot-mix asphalt concrete using dynamic modulus |E*| and indirect tensile tests. Advanced Testing and Characterization of Bituminous Materials. Taylor & Francis Group, London. 497 - 505

Ibe, A. C., 1988. Coastline erosion in Nigeria. University of Ibadan Press.

Imoobe, T. O. T. and Iroro T. 2009. Ecological restoration of oil spill sites in the Niger Delta, Nigeria. *Journal of Sustainable Development in Africa* 2. 2.

IS: 6461 Pt VII. 1973. Glossary of terms relating to cement concrete: Part VII Mixing, Laying, Compaction, Curing, and Other Construction Aspects.

Jamil, M., Zain, M. F. M., and Basri, H. B. 2009. Neural network simulator model for optimization in high performance concrete mix design. European Journal of Scientific Research. Vol.34 No.1, pp.61-68.

Khan, M. I. 2010. Chloride ingress resistant concrete: high performance concrete containing supplementary composites. *International Journal of Civil & Environmental Engineering IJCEE-IJENS*. Vol:10 No: 04, pp. 41-47.

Kline, T. R. 2004. Sulfur pit assessment and repair strategies, structural preservation systems Inc, Houston, Texas.

Kulkarni,V. R. 2009. Exposure classes for designing durable concrete. *The Indian Concrete Journal*, 23-43.

Lamond, J. F., and Pielert, J. H. 2006. *Significance of tests and properties of concrete and concrete making materials*. ASTM international, West Conshohocken, PA.

Lea, F. M. 1970. *The chemistry of cement and concrete*. 3rd ed. London: Edward Arnold (Publishers) Ltd. In. Wilson, S.A., Langdon, N.J. & Walden, P.J. 2001. The effects of hydrocarbon contamination on concrete strength. *Proceedings of the Institution of Civil Engineers. Geotechnical Engineering*. 149. 3: 189 – 193. Retrieved Nov. 18, 2006, from http://www.thomastelford.com/journals.

Lepadatu, D. C. *et al*., 2005. Optimization of springback bending process using FEM and response surface methodology. *Int. J. Adv. Manuf. Tech*., 27: 40-47.

Lepadatu, D. C. *et al*., 2006. Statistical Investigation of Die Wear in Metal Extrusion Process. Int. J. Adv. Manuf. Tech., 28: 272-278.

Leschine, T. M., McGee J. and Gaunt, R. 1993. Federal on-scene coordinator's report T/V *Exxon Valdez* Oil Spill, vol. I. Department of Transportation, Springfield, Virginia.

Mamlouk, M. S. and Zaniewski, J. P. 2011. *Materials for civil and construction engineers*. Third ed. New Jersey :Prentice Hall.

Mansurov, Z. A., Ongarbaev, E. K., and Tuleutaev, B. K. 2001. Contamination of soil by crude oil and drilling muds. Use of Wastes by Production of Road Construction Materials. *Chemistry and technology of fuels and oils*. Vol. 37, Issue 6. Pp 441 – 443.

Marinela, B. and Lepadatu, D. 2008. Mechanical characteristics investigation of polymer concrete using mixture design of experiments and response surface method. *Journal of applied sciences* 8 (12): 2242- 2249.

Mayer, R. H. and Montgomery, D. C. 1995. Response surface methodology process and product optimization using design of experiments. New York: Wiley.

Mehta, P. K. and Monteiro, P. J. M. 2006. *Concrete: Microstructure, Properties, and Materials*. 3rd ed. New York: McGraw-Hill Company Ltd.

Microsoft Encarta, 2008. Concrete, microsoft corporation.

Microsoft Encarta. 2009. Concrete, microsoft corporation.

Miflin, H. 2000. The American heritage dictionary of the english language, 4th ed. Houghton Mifflin Company.

Mindess, S. and Young, J. F. 1981. *Concrete*. 1st ed. N. J.: Prentice-Hall Inc. 118-119.

Montgomery, D. C. 2001. Design and analysis of experiments. 5th Ed. USA: John Wiley & Sons.

Murali, T. M. and Kandasamy, S. 2009. Mix proportioning of high performance self-compacting concrete using response surface methodology. *The Open Civil Engineering Journal*, 3: 93-97.

Murdock, L. J., Brook, K. M. and Dewar, J. D. 1991. *Concrete: materials and practice*. 6th ed. Edward Arnold.

NDES, 1997. Environmental and socio-economic characteristics. 1. Niger Delta Environmental Survey ERML, Ikoyi Lagos, pp. 268.

Nielsen, M. P. and Hoang, L. C. 2010. *Limit analysis and concrete plasticity*. Third ed. CRC Press Inc. 796

Newman, J. B. 2003. *Advanced concrete technology: constituent materials*. J. Newman and B. S. Choo. Eds .Elsevier Ltd.

Newman, J. B. 2003. *Advanced concrete technology: concrete properties*. J. Newman and B. S. Choo. Eds .Elsevier Ltd.

Newman, J. B. 2003. *Advanced concrete technology: processes*. J. Newman and B. S. Choo. Eds .Elsevier Ltd.

Newman, J. B. 2003. *Advanced concrete technology: testing and quality*. J. Newman and B. S. Choo. Eds .Elsevier Ltd.

Neville, A.M. and Brooks, J. J. 1990. *Concrete technology*. Revised ed. Singapore: Longman Group UK Limited.

Neville, A.M. and Brooks, J. J. 1993. *Concrete technology*. ELBS ed. Singapore : Longman Publishers Ltd.

Neville, A.M. 1981. *Properties of concrete.* Third ed. Longman.

Neville, A.M. 1993. *Properties of concrete.* ELBS ed. of third Edition. Longman.

Neville, A.M. 1999. *Properties of concrete.* Fourth Edition. Longman.

Nigerian Environmental Study/Action Team (NEST) 1991. Threatened environment: a national profile. Ibadan, 288 pp.

Nwilo, P.C. and Badejo, O.T. 2004. Management of oil spill dispersal along the Nigerian coastal areas. Department of Surveying and Geoinformatics, University of Lagos Retrieved 15 September 2011, from http://www.oceandocs.net/handle/1834/267.

Nwilo, P.C. and Badejo, O.T. 2008. Impacts of oil spills along the Nigerian coast. *Niger Delta Today*, 24 October 2008. Retrieved 15 Sptember 2011, from pttp://nigerdeltatoday.wordpress.com/2008/10/24/mpacts-of-oil-spills-along-the-nigerian-coast.

Ogunsola, A., Reggiani, U., and Sandrolini, L. 2006. Modelling shielding properties of concrete. 17th International Zurich Symposium on Electromagnetic Compatibility. 84 - 87.

Onabolu O. A. 1989. Some properties of crude oil soaked concrete exposure at ambient temperature. *ACI Materials Journal*: 150-158

Onabolu, G. *et al*. 1994. Offshore structures. ELBS ed. Nigeria: Longman Publishers Ltd.

Orchard, D. F. 1971. *Concrete technology- properties of materials*. 11, 4th ed. London: Applied Science publishers In Wilson, S.A., Langdon, N.J. & Walden, P.J. 2001. The effects of hydrocarbon contamination on concrete strength. *Proceedings of the Institution of Civil Engineers. Geotechnical Engineering*. 149. 3: 189 – 193. Retrieved Nov. 18, 2006, from http://www.thomastelford.com/journals.

Ossevorth, R., 2009. Concrete Theory: The cement mason's quick fix survival guide to concrete theory. Retrieved May 10, 2011 from www.cementmanson.com/cement Masons Guide to Concrete Theory.pdf.

Power, T. C., 1958. The physical structure and engineering properties of concrete. *Bulletin 90*, Portland Cement Association, Skokie II.

Paul, E. and Spry, O. 1997. Aggressive underground environment. *Proceedings of International Conference on Environment Protection*, University of Dundee, United Kingdom. 2. (4):57–68.

Pye, P. W. and Harrison. H. W. 1997. BRE building elements, floors and flooring, performance, diagnostics, maintenance, repair and the avoidance of defects. Building Research Establishment, Construction Research Communications Ltd., London.

Ramachandran, V. S., Malhotra, V.M., Jolicoeur, C. and Spiratos, N. 2001. Superplasticizers: properties and applications in concrete. CAMNET, Ottawa, Canada.

Ramzi, B. A. and Azad, A. M. 2000. Compressive and tensile strength of concrete loaded in crude oil. *Engineering Journal of the University of Qatar* 13: 18.

Reynolds, C. E. and Steedman, J. C. 1994. *Reinforced concrete designers' handbook*. 10th ed. London: E & FN Spon,.

Scott, J.S. 1991. *Penguin dictionary of civil engineering*. 4th ed. London : the Penguin Group. 88.

Shetty, M. S. 2002. *Concrete technology: theory and practice*. 5th ed. India: Rajendra Ravindra Printers. Ingraffea, A. R. (Eds). Martinius Nijhoff Publishers, Dordrecht, The Neiderlands.

Slate, F. O. and Hover, K. C. 1984. Fracture mechanics of concrete: material characterisation and testing. Carpinteri, A. and Ingr

Smith, M. A. 1985. The effect of phenol upon concrete. Magazine of Concrete Research. 133: 234-237.

Soroka, I. 1993. *Concrete in hot environments*. Modern Concrete Technology series. 139.

Sun, Z., Garboczi, E. J. and Shah, S. P. 2007. Modelling the elastic properties of concrete composites: experiment, differential effective medium theory, and numerical simulation. Cement and concrete composite 29,pp. 22- 38.

Tanigawa, Y., Mori, H., and Watanabe, K. 1990. Computer simulation of consistency and rheology tests of fresh concrete by viscoplastic finite element method. *Properties of fresh concrete proceedings of the RILEM colloquium.*

Tattersall, G.H. 1991. *Workability and quality control of concrete*. London: E & FN Spon.

Tattersall, G.H. and Banfill, P. F. G. 1983. *The rheology of fresh concrete*. Pitman:London.

Troxell, G. F. 1988. *Composition and properties of concrete*. 2nd ed. ELBS Macmillan.

U. S. Energy Information 2004. Crude oil and petroleum products. Retrieved Dec. 2, 2008, from http://en.wikipedia.org/wiki/concrete

U.S. Bureau of Reclamation, 1975. Concrete manual. 8th ed. Denver, Colorado.

U.S. Environmental Protection Agency 2005. Emission facts: average carbon dioxide emissions resulting from gasoline and diesel. Retrieved March 16, 2009 from http://www.epa.gov.otaq/climate/420f05001.htm.

Vandegrift, D. and Schindler, A. 2006. The effect of test cylinder size on the compressive strength of sulfur capped concrete specimens. Highway and research centre and department of civil engineering: Auburn University.

Wegian, F. M. 2010. Effect of seawater for mixing and curing on structural concrete. *The EIS Journal Part A: Civil and Structural Engineering*. 3. 4: 235-243.

Weiner, A.; Berg, C.; Gerlach, T.; Grunblatt, J.; Holbrook, K.; Kuwanda, M. 1997. The exxon valdez oil spill: habitat protection as a restoration strategy. *Restoration Ecology* **5**(1): 44- 55.

Wikipedia. 2005. Concrete materials and structures. Retrieved Dec. 2, 2008, from http://en.wwikipedia.org/wiki/concrete.

Wikipedia. 2006: Concrete, cement and masonry- "Truth be Told". Everything necessary to know about concrete. Retrieved Nov.21, 2008, from http://en.wikipedia.org/concrete.

Wikipedia. 2009. Concrete and its properties. Everything necessary to know about concrete. Retrieved March. 30, 2009, from http://en.wikipedia.org/wiki/Concrete.

Wilby, C.B. 1991. Concrete materials and structures. Revised edition. Press Syndicate of The University of Cambridge.

Wilson, S.A., Langdon, N.J. & Walden, P.J. 2001. The effects of hydrocarbon contamination on concrete strength. *Proceedings of the Institution of Civil Engineers. Geotechnical Engineering*. 149. 3: 189 – 193. Retrieved Nov. 18, 2006, from http://www.thomastelford.com/journals.

Wong, Y. L., Yu, X., Poon, C. S., and Anson, M. 2000. Damage to PFA concrete subject to high temperatures. *Proceedings of International symposium on high performance concrete-workability, strength and durability*. Hong Kong, 1093 – 1100.

Yeh, I. C; 1998. Modeling of Strength High – Performance Concrete using Artificial Neutral Network. *Cement and Concrete Research* 28 (12) 1797- 1808.

APPENDIX A

Density/ Compressive Strength of both Contaminated and Uncontaminated Concrete

Contamination	Age (Days) 3		7		14		28		56		84		168	
	Density	Compr Srength	Density	Compr. Srength	Density	Compr. Srength	Density	Compr. Srength	Density	Compr. Srength	Density	Compr. Srength	Density	Compr. Srength
150x150 0%							2479.01	31						
100x100 0%	2416.67	14.5	2533.33	21.25	2433.33	25.5	2416.67	31.5	2383.33	33.5	2583.33	33.5		40.3
2.50%	2466.67	11	2533.33	17	2383.33	21.5	2433.33	23.17	2400	27.33	2533.33	31.25		33
5%	2366.67	8.17	2500	13.17	2400	13.83	2550	18.33	2350	21.5	2433.33	21.67		24.3
10%	2350	5	2400	8.5	2400	9.5	2433.33	12.83	2350	13.83	2400	15.67		19
15%	2233.33	0.83	2366.67	3	2333.33	4.5	2400	5.4	2216.67	7.33	2333.33	8.33		9.3
20%	2300	1.83	2333.33	3	2233.33	3.83	2383.33	5	2233.33	7.33	2366.67	7.83		8.8
25%	2233.33	0.83	2316.67	1.83	2266.67	2.17	2316.67	3.5	2200	4	2300	5.33		5.5

APPENDIX B :
MODELLING COMPRESSIVE STRENGTH AND OTHER PROPERTIES OF COCS CONCRETE USING RESPONSE SURFACE METHODOLOGY (RSM) VIA DESIGN-EXPERT 8.5.0.3 SOFTWARE

COMPRESSIVE STRENGTH

Run Order		% Contamination	Days	Compressive Strength (N/mm^2)
15	1	0.00	3.00	14.5
17	2	0.00	7.00	21.25
38	3	0.00	14.00	25.5
2	4	0.00	28.00	31.5
46	5	0.00	56.00	33.5
7	6	0.00	84.00	33.5
12	7	0.00	168.00	40.3
42	8	2.50	3.00	11
25	9	2.50	7.00	17
32	10	2.50	14.00	21.5
29	11	2.50	28.00	23.17
13	12	2.50	56.00	27.33
43	13	2.50	84.00	31.25
19	14	2.50	168.00	33
36	15	5.00	3.00	8.17
45	16	5.00	7.00	13.17
48	17	5.00	14.00	13.83
5	18	5.00	28.00	18.33
10	19	5.00	56.00	21.5
27	20	5.00	84.00	21.67
35	21	5.00	168.00	24.3
9	22	10.00	3.00	5
21	23	10.00	7.00	8.5
14	24	10.00	14.00	9.5
24	25	10.00	28.00	12.83
23	26	10.00	56.00	13.83
49	27	10.00	84.00	15.67
26	28	10.00	168.00	19
3	29	15.00	3.00	2.83
22	30	15.00	7.00	4.25
18	31	15.00	14.00	5.17
47	32	15.00	28.00	6.60667
39	33	15.00	56.00	8.27
41	34	15.00	84.00	9.72667
11	35	15.00	168.00	11.9
37	36	20.00	3.00	1.83
16	37	20.00	7.00	3
20	38	20.00	14.00	3.83
40	39	20.00	28.00	5
4	40	20.00	56.00	7.33
8	41	20.00	84.00	7.83
6	42	20.00	168.00	8.8
31	43	25.00	3.00	0.83
28	44	25.00	7.00	1.83
34	45	25.00	14.00	2.17
1	46	25.00	28.00	3.5
44	47	25.00	56.00	4
30	48	25.00	84.00	5.33
33	49	25.00	168.00	5.5

Design Summary

Study Type	Response Surface	**Runs**	49
Design Type	Central Composite	**Blocks**	No Blocks
Design Model	Quadratic	**Build Time (ms)**	4.45

Factor	**Name**	**Units**	**Type**	**Subtype**	**Min.**	**Max.**	**Coded**	**Values**	**Mean**	**Std. Dev.**
A	Conta.	%	Numeric	Contin.	0.00	25.00	-1.000=0.00	1.000=25.00	11.07	8.65
B	Days	No	Numeric	Contin.	3.00	168.00	-1.000=3.00	1.000=168.00	51.43	54.69

Resp.	**Name**	**Units**	**Obs**	**Analysis**	**Min**	**Max**	**Mean**	**Std. Dev.**	**Ratio**	**Trans**	**Model**
Y1	Compr. Str.	N/mm^2	49	Polynomia	l0.83	40.3	13.8599	10.371	48.5542	None	Sixth

Response 1 Compressive Strength

ANOVA for Response Surface Sixth Model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Squar**	**F Value**	**p-value Prob > F**
Model	5146.02	27	190.59	239.74	< 0.0001 significant
A-Cont.	*48.05*	*1*	*48.05*	*60.44*	*< 0.0001*
B-Days	*4.55*	*1*	*4.55*	*5.72*	*0.0262*
AB	*0.60*	*1*	*0.60*	*0.75*	*0.3964*
A^2	*1.45*	*1*	*1.45*	*1.83*	*0.1910*
B^2	*4.53*	*1*	*4.53*	*5.70*	*0.0264*
A^2B	*0.060*	*1*	*0.060*	*0.075*	*0.7869*
AB^2	*1.82*	*1*	*1.82*	*2.29*	*0.1453*
A^3	*4.07*	*1*	*4.07*	*5.12*	*0.0344*
B^3	*4.77*	*1*	*4.77*	*5.99*	*0.0232*
A^2B^2	*0.19*	*1*	*0.19*	*0.24*	*0.6298*
A^3B	*0.16*	*1*	*0.16*	*0.20*	*0.6610*
AB^3	*3.34*	*1*	*3.34*	*4.20*	*0.0530*
A^4	*10.42*	*1*	*10.42*	*13.11*	*0.0016*
B^4	*2.72*	*1*	*2.72*	*3.43*	*0.0783*
A^3B^2	*0.51*	*1*	*0.51*	*0.64*	*0.4333*
A^2B^3	*0.019*	*1*	*0.019*	*0.024*	*0.8789*
A^4B	*0.19*	*1*	*0.19*	*0.24*	*0.6328*
AB^4	*1.61*	*1*	*1.61*	*2.03*	*0.1691*
A^5	*5.71*	*1*	*5.71*	*7.18*	*0.0140*
B^5	*4.71*	*1*	*4.71*	*5.93*	*0.0239*
A^3B^3	*1.44*	*1*	*1.44*	*1.81*	*0.1926*
A^4B^2	*2.59*	*1*	*2.59*	*3.26*	*0.0853*
A^2B^4	*1.20*	*1*	*1.20*	*1.51*	*0.2333*
A^5B	*0.076*	*1*	*0.076*	*0.095*	*0.7608*
AB^5	*2.66*	*1*	*2.66*	*3.34*	*0.0818*
A^6	*12.18*	*1*	*12.18*	*15.33*	*0.0008*
B^6	*4.97*	*1*	*4.97*	*6.26*	*0.0207*
Residual	16.70	21	0.80		
Cor Total	5162.72	48			

The Model F-value of 239.74 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, B^2, A^3, B^3, A^4, A^5, B^5, A^6, B^6 are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy),
model reduction may improve your model.

Std. Dev.	0.89	R-Squared	0.9968
Mean	13.86	Adj R-Squared	0.9926
C.V. %	6.43	Pred R-Squared	0.9518
PRESS	248.98	Adeq Precision	58.606

The "Pred R-Squared" of 0.9518 is in reasonable agreement with the "Adj R-Squared" of 0.9926.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 58.606 indicates an adequate signal. This model can be used to navigate the design space.

Coefficient		**Standard**	**95% CI**	**95% CI**		
Factor	**Estimate**	**df**	**Error**	**Low**	**High**	**VIF**
Intercept	16.73	1	1.78	13.02	20.44	
A-Contamination	-15.82	1	2.03	-20.05	-11.59	122.07
B-Days	234.83	1	98.20	30.61	439.04	2.612E+005
AB	11.03	1	12.74	-15.47	37.53	2977.80
A^2	-7.72	1	5.71	-19.59	4.16	281.85
B^2	1168.63	1	489.32	151.03	2186.24	2.173E+006
$A^2 B$	2.11	1	7.69	-13.89	18.11	699.27
AB^2	62.80	1	41.52	-23.54	149.14	26601.93
A^3	14.54	1	6.42	1.18	27.90	842.57
B^3	1680.80	1	686.52	253.11	3108.48	1.149E+007
$A^2 B^2$	5.27	1	10.77	-17.13	27.67	775.11
$A^3 B$	3.63	1	8.16	-13.34	20.61	839.27
AB^3	50.34	1	24.55	-0.72	101.40	8527.89
A^4	55.64	1	15.37	23.68	87.60	2456.79
B^4	-177.90	1	96.11	-377.77	21.98	94128.07
$A^3 B^2$	-1.50	1	1.87	-5.40	2.40	37.42
$A^2 B^3$	-1.12	1	7.28	-16.27	14.02	527.00
$A^4 B$	0.99	1	2.05	-3.27	5.26	43.24
AB^4	-59.31	1	41.65	-145.93	27.31	22490.72
A^5	-12.85	1	4.80	-22.83	-2.88	426.40
B^5	-1909.99	1	784.40	-3541.24	-278.74	1.397E+007
$A^3 B^3$	-7.25	1	5.38	-18.44	3.95	281.15
$A^4 B^2$	6.01	1	3.33	-0.91	12.92	74.37
$A^2 B^4$	-13.16	1	10.72	-35.45	9.14	714.89
$A^5 B$	1.50	1	4.88	-8.64	11.65	270.51
AB^5	-64.52	1	35.30	-137.92	8.89	15454.69
A^6	-40.93	1	10.46	-62.68	-19.19	1232.64
B^6	-997.25	1	398.69	-1826.38	-168.12	1.685E+006

Final Equation in Terms of Coded Factors:

Compressive Strength $=+16.73-15.82 *A+234.83 * B+11.03 *A*B-7.72 *A^2+1168.63* B^2+2.11* A^2*B+62.80 *A*B^2+14.54 * A^3+1680.80 *B^3+5.27 *A^2*B^2+3.63 *A^3*B+50.34 * A*B^3+55.64 *A^4-177.90* B^4-1.50 *A^3*B^2-1.12 * A^2*B^3+0.99*A^4*B-59.31*A*B^4-12.85 *A^5-1909.99 * B^5-7.25*A^3*B^3+6.01 *A^4*B^2-13.16 *A^2*B^4+1.50 *A^5*B-64.52 * A * B^5-40.93 *A^6-997.2 *B^6$

Response 1 Compressive Strength Transform: None

Diagnostics Case Statistics

Standard Order	Actual Value	Predicted Value	Studentized Residual	Leverage	Internally Studentized Residual	Externally Residual	Influence on Fitted Value DFFITS	Cook's Distance	Run Order
1	3.50	3.50	7.964E-004	0.762	0.002	0.002	0.003	0.000	46
2	31.50	30.70	0.80	0.647	1.514	1.565	* 2.12	0.150	4
3	2.83	2.30	0.53	0.500	0.834	0.828	0.828	0.025	29
4	7.33	7.07	0.26	0.559	0.441	0.432	0.487	0.009	40
5	18.33	17.92	0.41	0.412	0.603	0.594	0.497	0.009	18
6	8.80	8.65	0.15	0.965	0.896	0.892	* 4.71	0.799	42
7	33.50	34.18	-0.68	0.873	-2.129	-2.346	* -6.14	* 1.11	6
8	7.83	7.87	-0.036	0.726	-0.078	-0.076	-0.124	0.001	41
9	5.00	5.72	-0.72	0.480	-1.121	-1.128	-1.084	0.041	22
10	21.50	20.93	0.57	0.433	0.855	0.849	0.743	0.020	19
11	11.90	12.33	-0.43	0.862	-1.298	-1.321	* -3.30	0.376	35
12	40.30	40.32	-0.022	0.975	-0.161	-0.157	-0.991	0.037	7
13	27.33	27.88	-0.55	0.444	-0.831	-0.824	-0.736	0.020	12
14	9.50	9.84	-0.34	0.365	-0.485	-0.476	-0.361	0.005	24
15	14.50	14.59	-0.094	0.690	-0.189	-0.185	-0.276	0.003	1
16	3.00	3.40	-0.40	0.425	-0.589	-0.580	-0.499	0.009	37
17	21.25	21.03	0.22	0.445	0.333	0.326	0.292	0.003	2
18	5.17	4.92	0.25	0.383	0.361	0.353	0.279	0.003	31
19	33.00	32.68	0.32	0.707	0.656	0.647	1.006	0.037	14
20	3.83	3.53	0.30	0.417	0.437	0.429	0.363	0.005	38
21	8.50	8.77	-0.27	0.369	-0.381	-0.373	-0.285	0.003	23
22	4.25	4.57	-0.32	0.381	-0.453	-0.444	-0.348	0.005	30
23	13.83	14.10	-0.27	0.497	-0.428	-0.419	-0.417	0.006	26
24	12.83	11.82	1.01	0.401	1.466	1.510	1.236	0.051	25
25	17.00	17.01	-0.014	0.364	-0.019	-0.019	-0.014	0.000	9
26	19.00	18.38	0.62	0.792	1.530	1.584	* 3.09	0.318	28
27	21.67	22.82	-1.15	0.539	-1.897	-2.033	* -2.20	0.150	20
28	1.83	2.16	-0.33	0.468	-0.500	-0.491	-0.461	0.008	44
29	23.17	24.78	-1.61	0.413	-2.350	-2.671	* -2.24	0.139	11
30	5.33	5.36	-0.028	0.962	-0.160	-0.156	-0.781	0.023	48
31	0.83	0.82	8.837E-003	0.778	0.021	0.021	0.038	0.000	43
32	21.50	20.76	0.74	0.380	1.055	1.057	0.828	0.024	10
33	5.50	5.52	-0.018	0.998	-0.508	-0.499	* -12.24	* 5.55	49
34	2.17	1.79	0.38	0.582	0.667	0.658	0.776	0.022	45
35	24.30	24.92	-0.62	0.625	-1.131	-1.139	-1.470	0.076	21
36	8.17	7.59	0.58	0.441	0.872	0.867	0.770	0.021	15
37	1.83	1.53	0.30	0.578	0.516	0.507	0.593	0.013	36
38	25.50	25.92	-0.42	0.502	-0.675	-0.666	-0.669	0.016	3
39	8.27	8.45	-0.18	0.499	-0.293	-0.286	-0.285	0.003	33
40	5.00	5.57	-0.57	0.504	-0.911	-0.907	-0.915	0.030	39
41	9.73	9.52	0.20	0.583	0.354	0.347	0.410	0.006	34
42	11.00	11.60	-0.60	0.454	-0.911	-0.907	-0.828	0.025	8
43	31.25	29.54	1.71	0.495	2.707	3.274	* 3.24	0.257	13
44	4.00	4.02	-0.022	0.878	-0.072	-0.070	-0.189	0.001	47
45	13.17	12.07	1.10	0.349	1.535	1.590	1.165	0.045	16
46	33.50	33.30	0.20	0.746	0.434	0.426	0.730	0.020	5
47	6.61	6.66	-0.050	0.425	-0.074	-0.073	-0.062	0.000	32
48	13.83	14.74	-0.91	0.345	-1.255	-1.274	-0.925	0.030	17
49	15.67	15.70	-0.029	0.580	-0.051	-0.049	-0.058	0.000	27

* Exceeds limits

Current Transform: None

Box-Cox Power Transformation

Constant k	**95% CI Low**	**95% CI High**	**Best Lambda**	**Rec. Transform**
0.000	-1.000E-002	0.44	0.21	Log

Transformation:

Response 1: Compressive Strength Transform: Base 10 Log Constant: 0

Fit Summary (detailed tables shown below)

Sequential Source	**Lack of Fit p-value**	**p-value**	**Adjusted R-Squared**	**Predicted R-Squared**	
Linear	< 0.0001		0.8902	0.8788	
2FI	0.0549		0.8966	0.8800	
Quadratic	< 0.0001		0.9514	0.9421	
Cubic	< 0.0001		0.9745	0.9664	
Quartic	0.0014		0.9833	0.9758	
Fifth	0.0149		0.9880	0.9723	
Sixth	< 0.0001		0.9959	0.9764	Suggested

Sequential Model Sum of Squares [Type I]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Mean vs Total	48.48	1	48.48			
Linear vs Mean	6.74	2	3.37	195.51	< 0.0001	
2FI vs Linear	0.063	1	0.063	3.88	0.0549	
Quadratic vs 2FI	0.40	2	0.20	26.35	< 0.0001	
Cubic vs Quadratic	0.17	4	0.043	10.74	< 0.0001	
Quartic vs Cubic	0.067	5	0.013	5.09	0.0014	
Fifth vs Quartic	0.037	6	6.110E-003	3.25	0.0149	
Sixth vs Fifth	0.039	7	5.567E-003	8.56	< 0.0001	Suggested
Residual	0.014	21	6.505E-004			
Total	56.01	49	1.14			

"Sequential Model Sum of Squares [Type I]": Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Model Summary Statistics

Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	0.13	0.8947	0.8902	0.8788	0.91	
2FI	0.13	0.9031	0.8966	0.8800	0.90	
Quadratic	0.087	0.9565	0.9514	0.9421	0.44	
Cubic	0.063	0.9793	0.9745	0.9664	0.25	
Quartic	0.051	0.9881	0.9833	0.9758	0.18	
Fifth	0.043	0.9930	0.9880	0.9723	0.21	
Sixth	0.026	0.9982	0.9959	0.9764	0.18	Suggested

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

Response 1 Compressive Strength
Transform: Base 10 Log Constant: 0
ANOVA for Response Surface Sixth Model
Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	7.52	27	0.28	428.18	< 0.0001significant
A-Contamination	0.058	1	0.058	89.60	< 0.0001
B-Days	0.022	1	0.022	33.65	< 0.0001
AB	7.435E-005	1	7.435E-005	0.11	0.7386
A^2	2.312E-003	1	2.312E-003	3.55	0.0733
B^2	0.022	1	0.022	34.31	< 0.0001
A^2B	4.733E-004	1	4.733E-004	0.73	0.4033
AB^2	5.622E-005	1	5.622E-005	0.086	0.7716
A^3	0.010	1	0.010	15.86	0.0007
B^3	0.024	1	0.024	36.37	< 0.0001
A^2B^2	7.734E-004	1	7.734E-004	1.19	0.2879
A^3B	4.348E-004	1	4.348E-004	0.67	0.4228
AB^3	3.007E-004	1	3.007E-004	0.46	0.5040
A^4	7.907E-003	1	7.907E-003	12.16	0.0022
B^4	0.012	1	0.012	18.48	0.0003
A^3B^2	7.486E-005	1	7.486E-005	0.12	0.7378
A^2B^3	7.276E-004	1	7.276E-004	1.12	0.3023
A^4B	3.817E-004	1	3.817E-004	0.59	0.4522
AB^4	3.076E-005	1	3.076E-005	0.047	0.8299
A^5	0.012	1	0.012	18.44	0.0003
B^5	0.023	1	0.023	35.89	< 0.0001
A^3B^3	5.157E-005	1	5.157E-005	0.079	0.7810
A^4B^2	1.192E-003	1	1.192E-003	1.83	0.1902
A^2B^4	1.983E-003	1	1.983E-003	3.05	0.0954
A^5B	3.617E-004	1	3.617E-004	0.56	0.4641
AB^5	1.482E-004	1	1.482E-004	0.23	0.6380
A^6	0.010	1	0.010	15.80	0.0007
B^6	0.025	1	0.025	38.36	< 0.0001
Residual	0.014	21	6.505E-004		
Cor Total	7.53	48			

The Model F-value of 428.18 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, B^2, A^3, B^3, A^4, B^4, A^5, B^5,
A^6, B^6 are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	0.026	R-Squared	0.9982
Mean	0.99	Adj R-Squared	0.9959
C.V. %	2.56	Pred R-Squared	0.9764
PRESS	0.18	Adeq Precision	86.018

The "Pred R-Squared" of 0.9764 is in reasonable agreement with the "Adj R-Squared" of 0.9959.

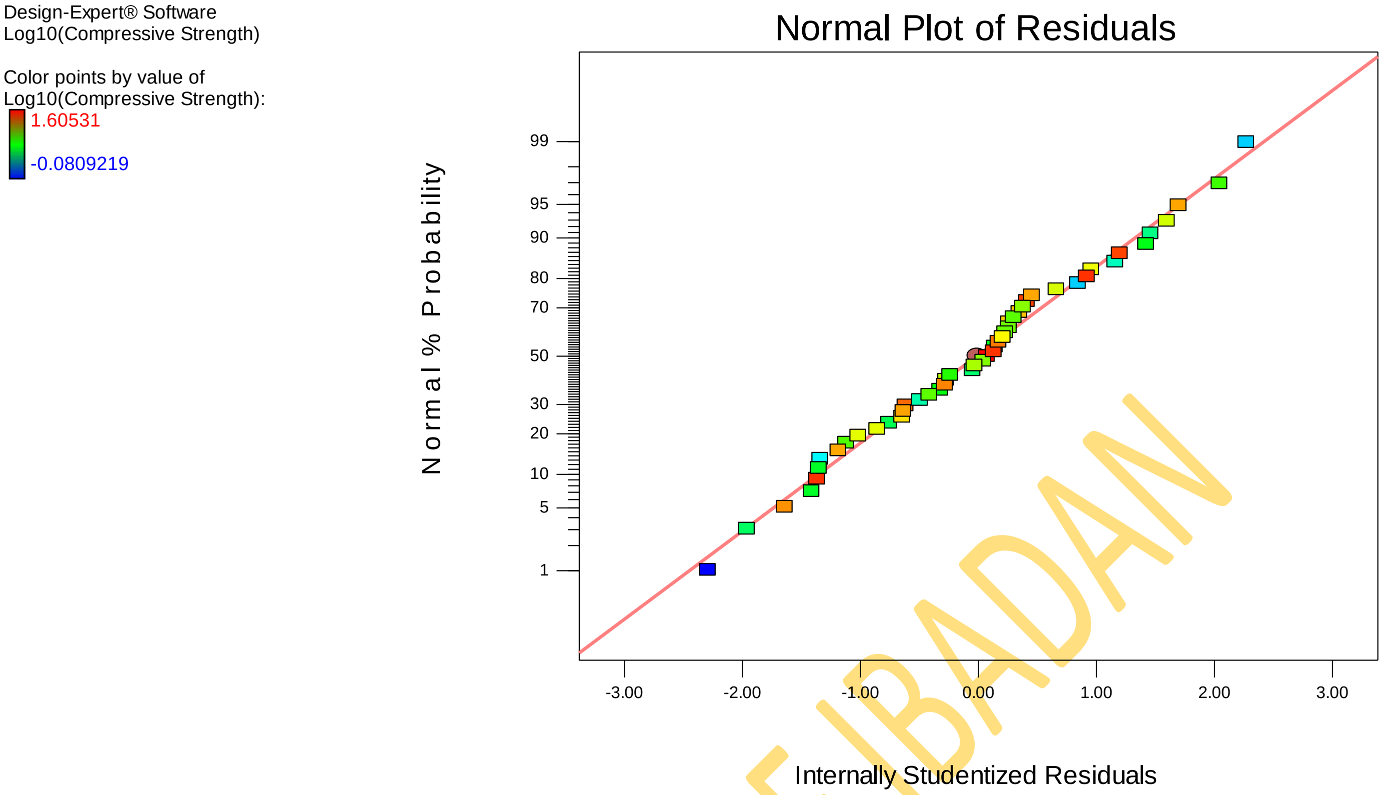
"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 86.018 indicates an adequate signal. This model can be used to navigate the design space.

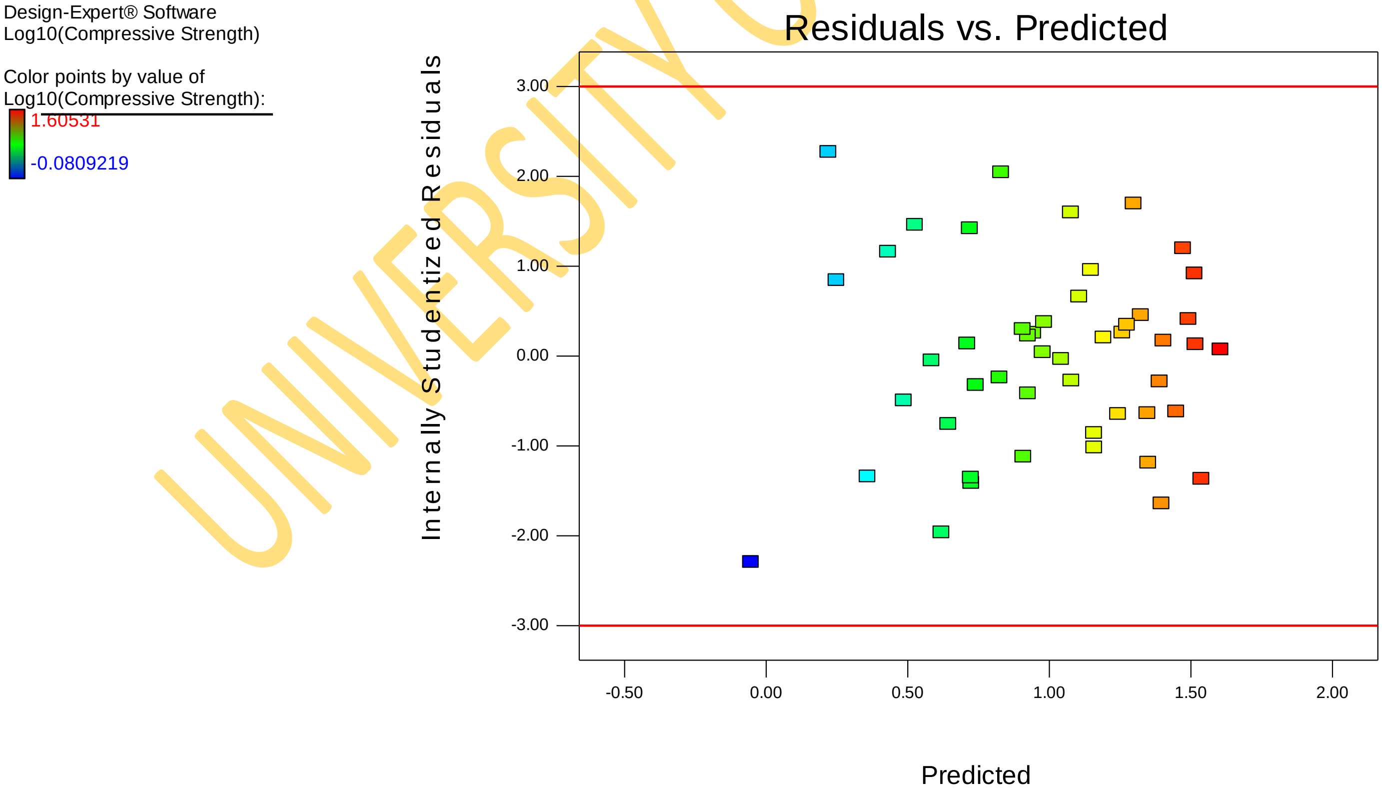
Coefficient **Standard** **95% CI** **95% CI**

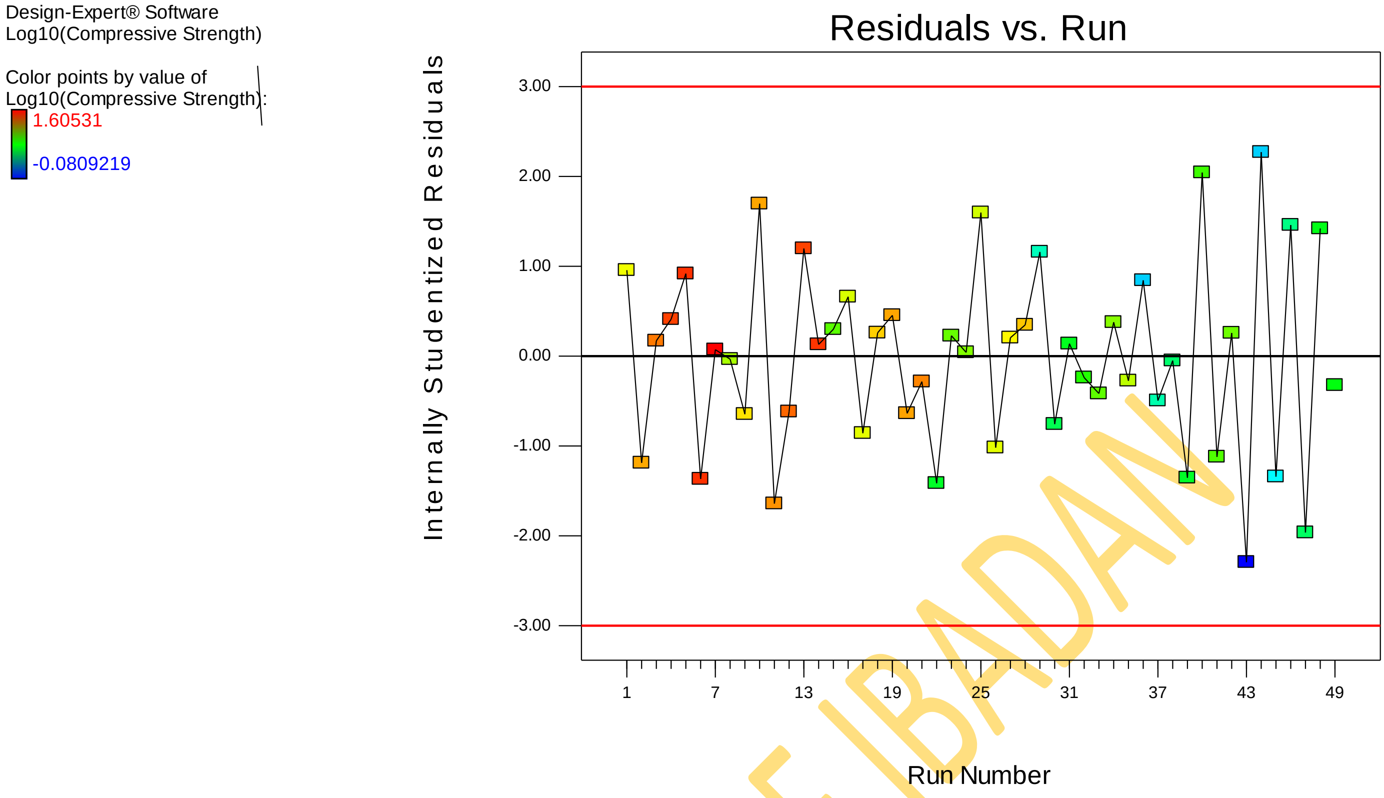
Factor	Estimate	df	Error	Low	High	VIF
Intercept	1.37	1	0.051	1.26	1.47	
A-Contamination	-0.55	1	0.058	-0.67	-0.43	122.07
B-Days	16.29	1	2.81	10.45	22.14	2.612E+005
AB	0.12	1	0.36	-0.63	0.88	2977.80
A^2	-0.31	1	0.16	-0.65	0.032	281.85
B^2	81.98	1	14.00	52.87	111.09	2.173E+006
$A^2 B$	0.19	1	0.22	-0.27	0.65	699.27
AB^2	-0.35	1	1.19	-2.82	2.12	26601.93
A^3	0.73	1	0.18	0.35	1.11	842.57
B^3	118.42	1	19.64	77.58	159.26	1.149E+007
$A^2 B^2$	0.34	1	0.31	-0.30	0.98	775.11
$A^3 B$	-0.19	1	0.23	-0.68	0.29	839.27
AB^3	-0.48	1	0.70	-1.94	0.98	8527.89
A^4	1.53	1	0.44	0.62	2.45	2456.79
B^4	-11.82	1	2.75	-17.53	-6.10	94128.07
$A^3 B^2$	-0.018	1	0.054	-0.13	0.093	37.42
$A^2 B^3$	-0.22	1	0.21	-0.65	0.21	527.00
$A^4 B$	0.045	1	0.059	-0.077	0.17	43.24
AB^4	0.26	1	1.19	-2.22	2.74	22490.72
A^5	-0.59	1	0.14	-0.87	-0.30	426.40
B^5	-134.42	1	22.44	-181.08	-87.76	1.397E+007
$A^3 B^3$	0.043	1	0.15	-0.28	0.36	281.15
$A^4 B^2$	0.13	1	0.095	-0.069	0.33	74.37
$A^2 B^4$	-0.54	1	0.31	-1.17	0.10	714.89
$A^5 B$	0.10	1	0.14	-0.19	0.39	270.51
AB^5	0.48	1	1.01	-1.62	2.58	15454.69
A^6	-1.19	1	0.30	-1.81	-0.57	1232.64
B^6	-70.64	1	11.40	-94.35	-46.92	1.685E+006

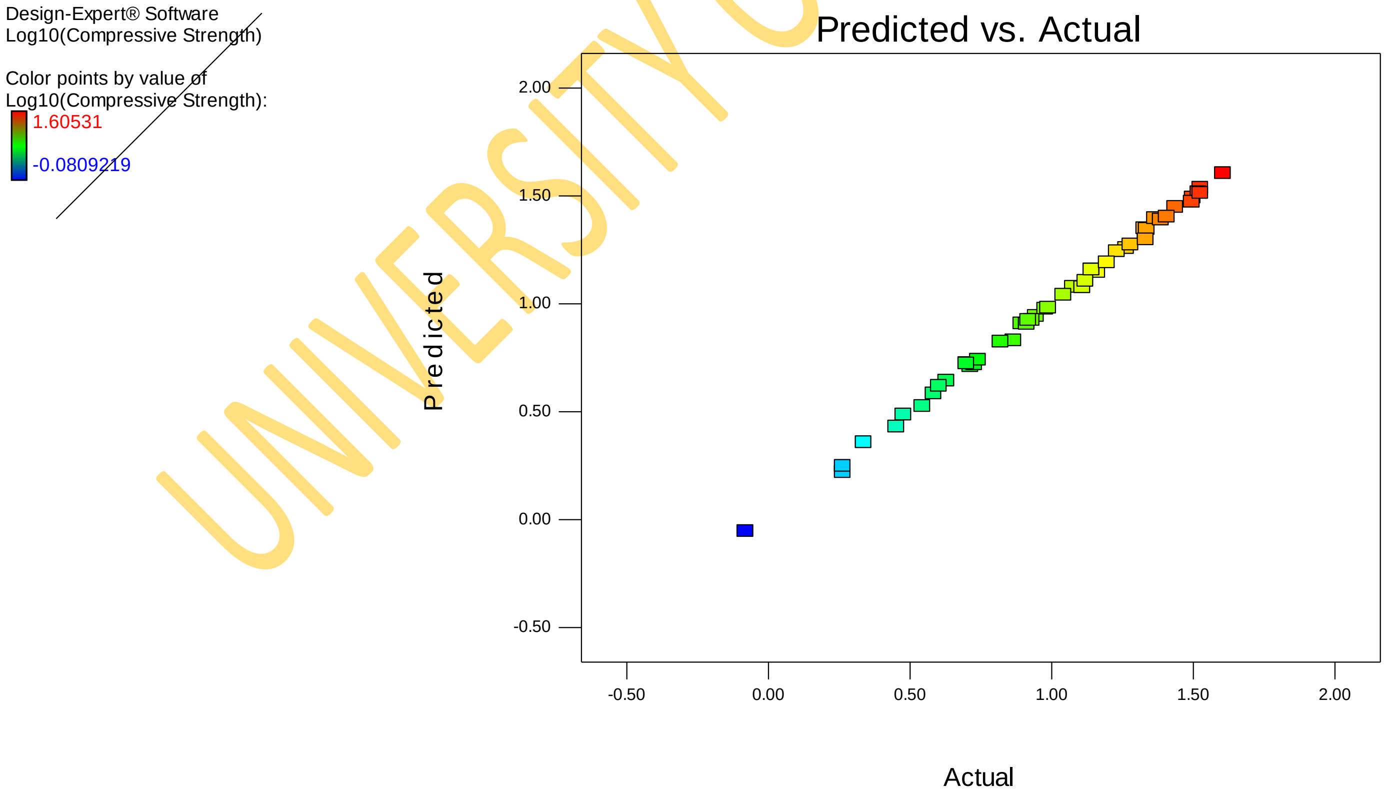
Final Equation in Terms of Coded Factors:

Log10(Compressive Strength) $= +1.37-0.55 * A+16.29 * B+0.12 * A * B-0.31 * A^2+81.98 * B^2+0.19 * A^2 * B-0.35 * A * B^2+0.73 * A^3+118.42 * B^3+0.34 * A^2 * B^2-0.19 * A * B-0.48 * A * B^3+1.53 * A-11.82 * B^4-0.018 * A^3 * B^2-0.22 * A^2 * B^3+0.045 * A^4 * B+0.26 * A * B^4-0.59 * A^5-134.42 * B^5+0.043 * A^3 * B^3+0.13 * A^4 * B^2-0.54 * A^2 * B^4+0.10 * A^5 * B+0.48 * A * B^5-1.19 * A^6-70.64 * B^6$


Design-Expert® Software
Log10(Compressive Strength)
Color points by value of
Log10(Compressive Strength):
1.60531
-0.0809219
Normal Plot of Residuals
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-3.00
-2.00
-1.00
0.00
1.00
2.00
3.00
Internally Studentized Residuals


Design-Expert® Software
Log10(Compressive Strength)
Color points by value of
Log10(Compressive Strength):
1.60531
-0.0809219
Residuals vs. Predicted
Internally Studentized Residuals
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
-0.50
0.00
0.50
1.00
1.50
2.00
Predicted

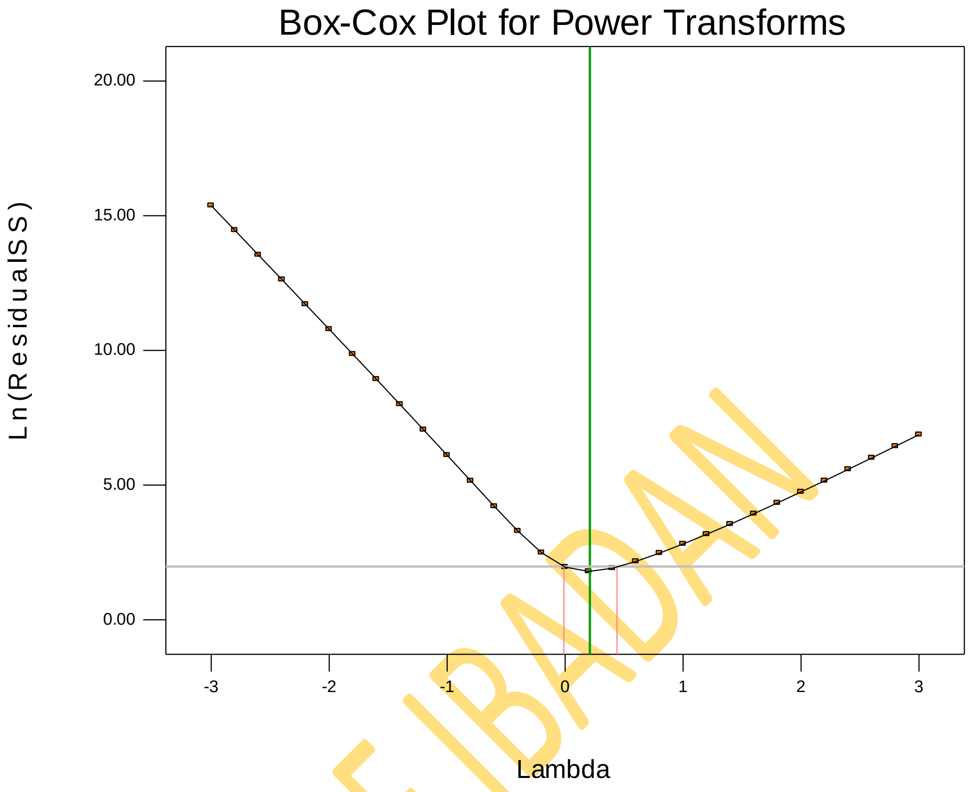

Design-Expert® Software
Log10(Compressive Strength)
Color points by value of
Log10(Compressive Strength):
1.60531
-0.0809219
Residuals vs. Run
Internally Studentized Residuals
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
1
7
13
19
25
31
37
43
49
Run Number


Design-Expert® Software
Log10(Compressive Strength)
Color points by value of
Log10(Compressive Strength):
1.60531
-0.0809219
Predicted vs. Actual
Predicted
2.00
1.50
1.00
0.50
0.00
-0.50
-0.50
0.00
0.50
1.00
1.50
2.00
Actual

Design-Expert® Software
Log10(Compressive Strength)

Lambda
Current = 0
Best = 0.21
Low C.I. = -0.01
High C.I. = 0.44

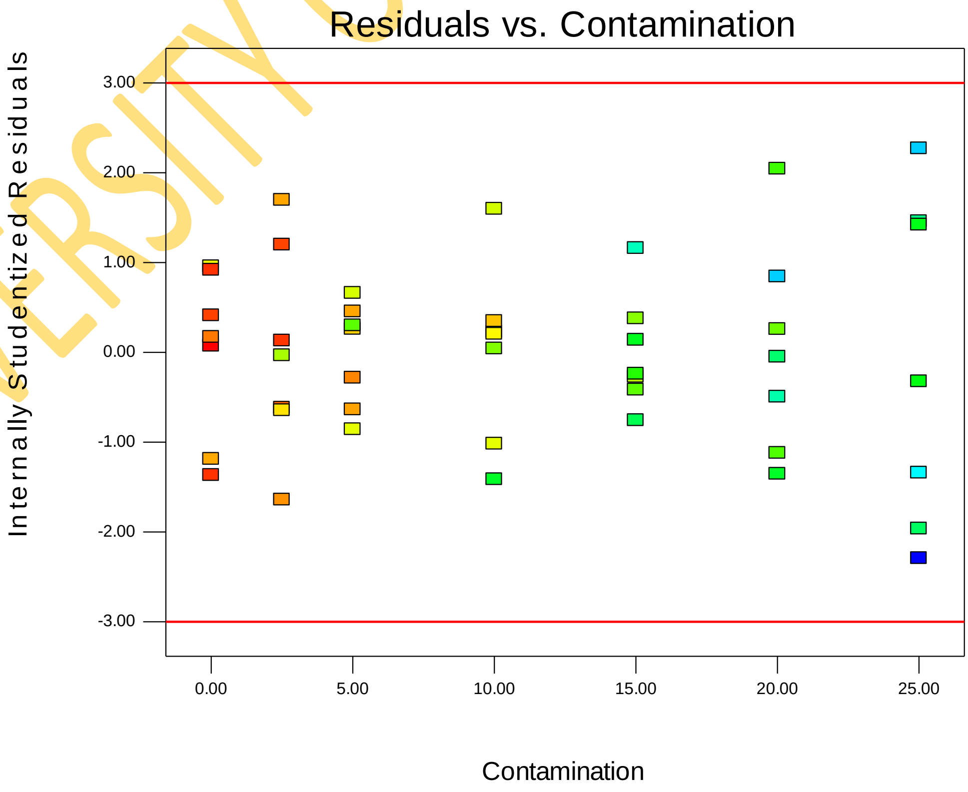
Recommend transform:
Log
(Lambda = 0)

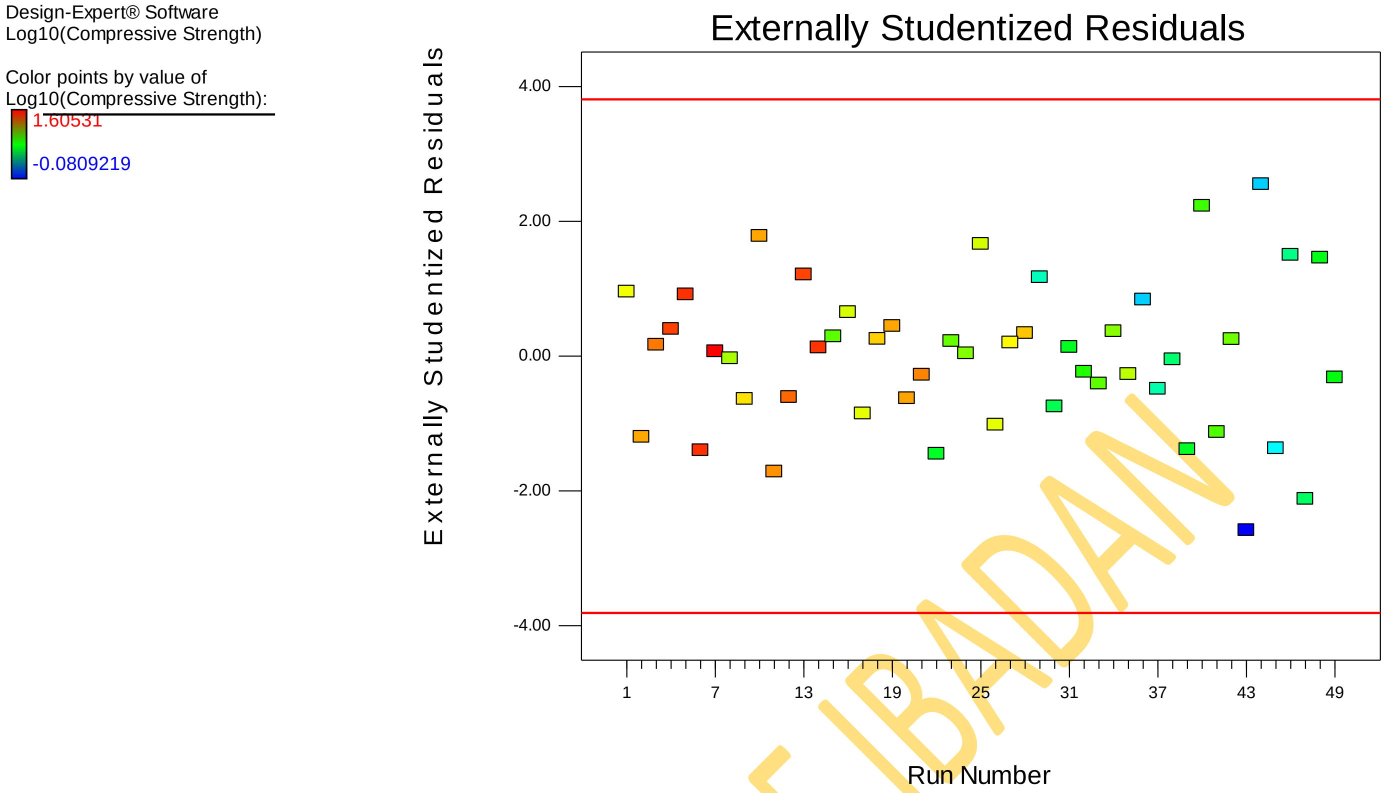


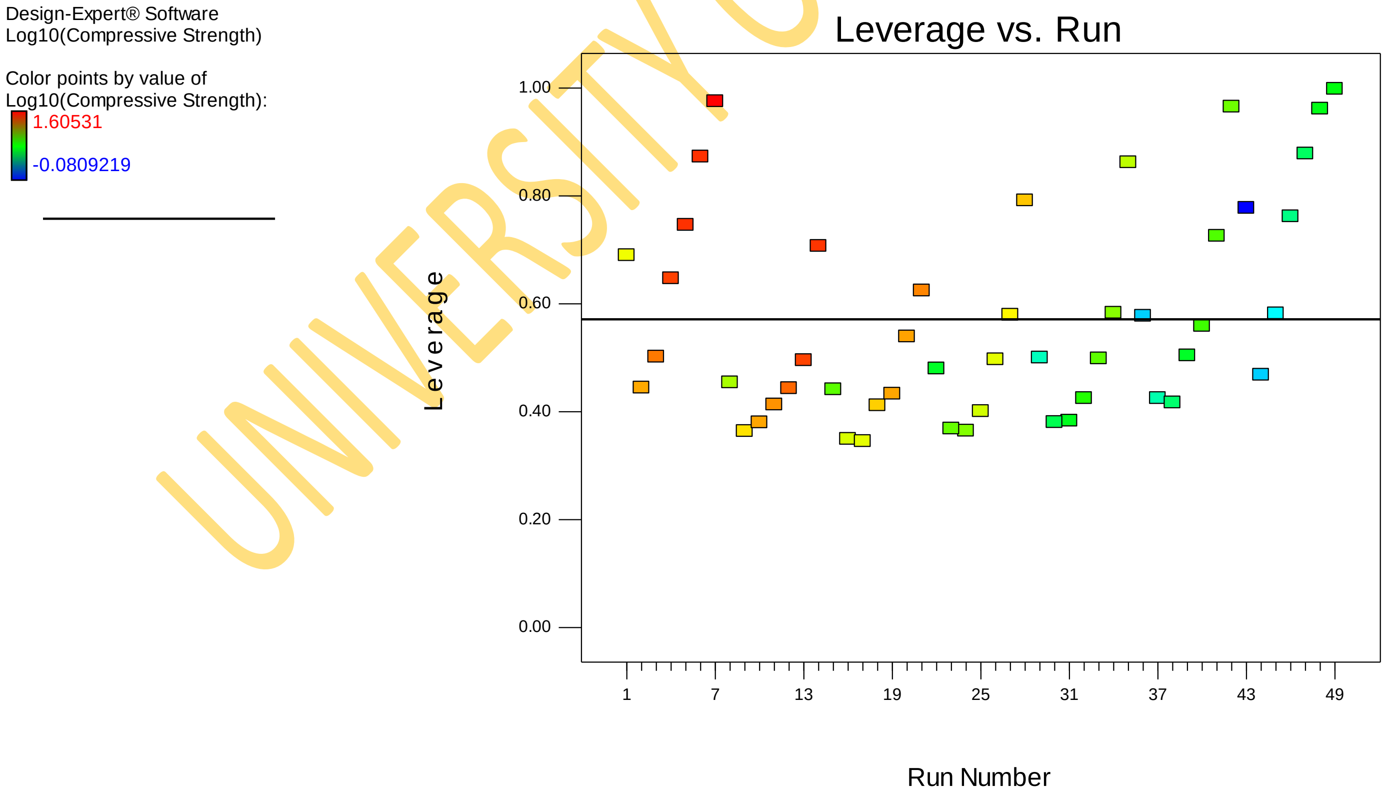
Design-Expert® Software
Log10(Compressive Strength)

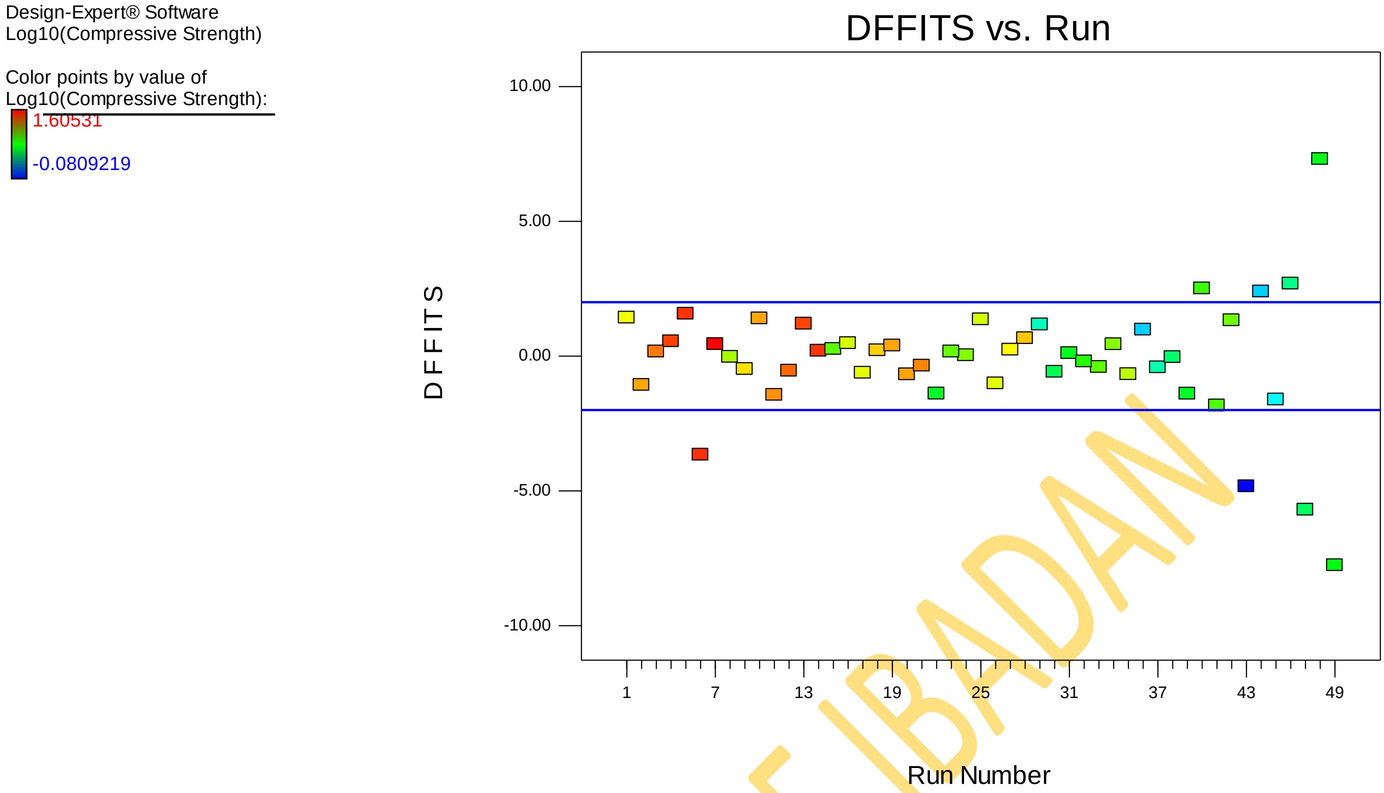
Color points by value of
Log10(Compressive Strength):
1.60531

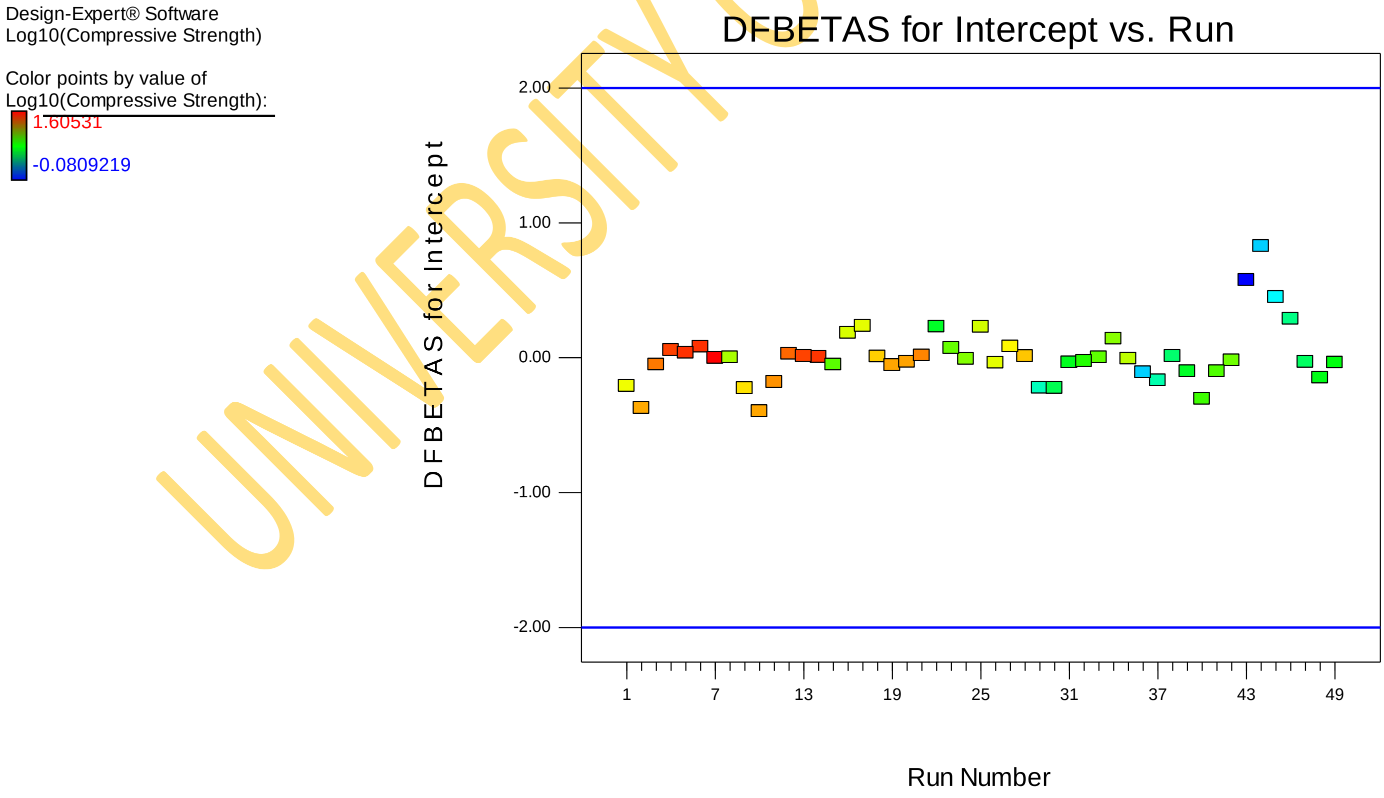
-0.0809219

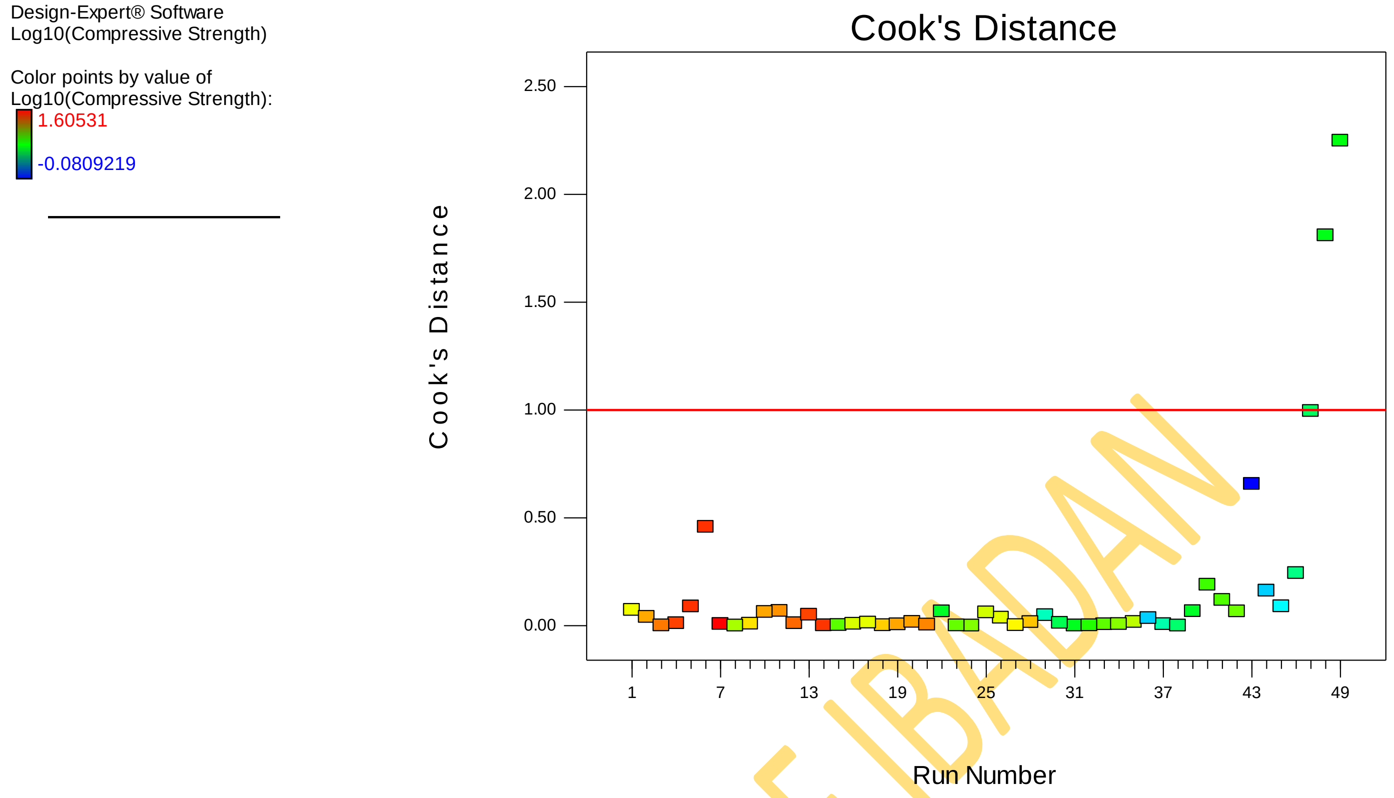



Design-Expert® Software
Log10(Compressive Strength)
Color points by value of
Log10(Compressive Strength):
1.60531
-0.0809219
Externally Studentized Residuals
Externally Studentized Residuals
4.00
2.00
0.00
-2.00
-4.00
1
7
13
19
25
31
37
43
49
Run Number


Design-Expert® Software
Log10(Compressive Strength)
Color points by value of
Log10(Compressive Strength):
1.60531
-0.0809219
Leverage vs. Run
Leverage
1.00
0.80
0.60
0.40
0.20
0.00
1
7
13
19
25
31
37
43
49
Run Number


Design-Expert® Software
Log10(Compressive Strength)
Color points by value of
Log10(Compressive Strength):
1.60531
-0.0809219
DFFITS vs. Run
DFFITS
10.00
5.00
0.00
-5.00
-10.00
1
7
13
19
25
31
37
43
49
Run Number


Design-Expert® Software
Log10(Compressive Strength)
Color points by value of
Log10(Compressive Strength):
1.60531
-0.0809219
DFBETAS for Intercept vs. Run
DFBETAS for Intercept
2.00
1.00
0.00
-1.00
-2.00
1
7
13
19
25
31
37
43
49
Run Number



Response 1 Compressive Strength Transform: Base 10 Log Constant: 0.000

Diagnostics Case Statistics

Standard Order	Actual Value	Predicted Value	Internally Studentized Residual	Leverage	Externally Studentized Residual	Influence on Fitted Value Residual	DFFITS	Cook's Distance	Run Order
1	0.54	0.53	0.018	0.762	1.459	1.502	* 2.69	0.244	46
2	1.50	1.49	6.224E-003	0.647	0.411	0.403	0.545	0.011	4
3	0.45	0.43	0.021	0.500	1.160	1.170	1.171	0.048	29
4	0.87	0.83	0.035	0.559	2.044	2.228	* 2.51	0.189	40
5	1.26	1.26	5.086E-003	0.412	0.260	0.254	0.213	0.002	18
6	0.94	0.94	1.224E-003	0.965	0.258	0.252	1.330	0.066	42
7	1.53	1.54	-0.012	0.873	-1.367	-1.397	* -3.66	0.458	6
8	0.89	0.91	-0.015	0.726	-1.121	-1.128	-1.835	0.119	41
9	0.70	0.72	-0.026	0.480	-1.414	-1.451	-1.394	0.066	22
10	1.33	1.32	8.723E-003	0.433	0.454	0.446	0.390	0.006	19
11	1.08	1.08	-2.594E-003	0.862	-0.274	-0.268	-0.670	0.017	35
12	1.61	1.61	2.890E-004	0.975	0.072	0.071	0.445	0.007	7
13	1.44	1.45	-0.012	0.444	-0.618	-0.608	-0.543	0.011	12
14	0.98	0.98	8.455E-004	0.365	0.042	0.041	0.031	0.000	24
15	1.16	1.15	0.014	0.690	0.958	0.956	1.426	0.073	1
16	0.48	0.49	-9.575E-003	0.425	-0.495	-0.486	-0.418	0.006	37
17	1.33	1.35	-0.023	0.445	-1.187	-1.199	-1.073	0.040	2
18	0.71	0.71	2.785E-003	0.383	0.139	0.136	0.107	0.000	31
19	1.52	1.52	1.802E-003	0.707	0.131	0.127	0.198	0.001	14
20	0.58	0.58	-9.679E-004	0.417	-0.050	-0.049	-0.041	0.000	38
21	0.93	0.92	4.610E-003	0.369	0.227	0.222	0.170	0.001	23
22	0.63	0.64	-0.015	0.381	-0.756	-0.748	-0.587	0.013	30

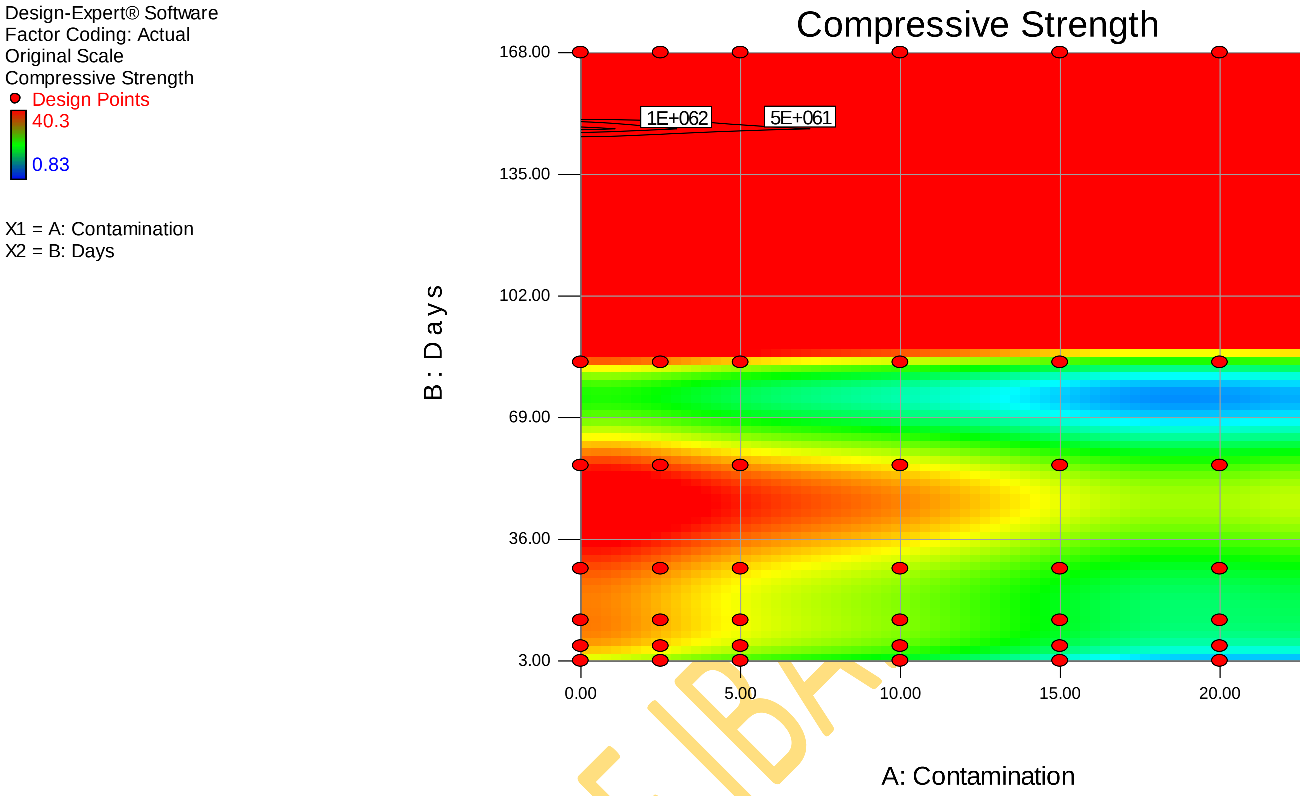
23	1.14	1.16	-0.018	0.497	-1.018	-1.019	-1.013	0.037	26
24	1.11	1.08	0.032	0.401	1.597	1.663	1.361	0.061	25
25	1.23	1.24	-0.013	0.364	-0.645	-0.636	-0.481	0.009	9
26	1.28	1.27	4.044E-003	0.792	0.347	0.340	0.662	0.016	28
27	1.34	1.35	-0.011	0.539	-0.636	-0.627	-0.678	0.017	20
28	0.26	0.22	0.042	0.468	2.270	2.551	* 2.39	0.162	44
29	1.36	1.40	-0.032	0.413	-1.641	-1.715	-1.439	0.068	11
30	0.73	0.72	7.099E-003	0.962	1.422	1.459	* 7.31	* 1.81	48
31	-0.081	-0.053	-0.028	0.778	-2.293	-2.584	* -4.83	0.657	43
32	1.33	1.30	0.034	0.380	1.696	1.782	1.396	0.063	10
33	0.74	0.74	-3.366E-004	0.998	-0.324	-0.317	* -7.76	* 2.25	49
34	0.34	0.36	-0.022	0.582	-1.341	-1.369	-1.615	0.089	45
35	1.39	1.39	-4.427E-003	0.625	-0.283	-0.277	-0.357	0.005	21
36	0.91	0.91	5.712E-003	0.441	0.300	0.293	0.261	0.003	15
37	0.26	0.25	0.014	0.578	0.843	0.837	0.979	0.035	36
38	1.41	1.40	3.080E-003	0.502	0.171	0.167	0.168	0.001	3
39	0.92	0.93	-7.517E-003	0.499	-0.416	-0.408	-0.407	0.006	33
40	0.70	0.72	-0.024	0.504	-1.354	-1.383	-1.394	0.067	39
41	0.99	0.98	6.207E-003	0.583	0.377	0.369	0.437	0.007	34
42	1.04	1.04	-6.308E-004	0.454	-0.033	-0.033	-0.030	0.000	8
43	1.49	1.47	0.022	0.495	1.198	1.211	1.201	0.050	13
44	0.60	0.62	-0.017	0.878	-1.963	-2.120	* -5.70	0.995	47
45	1.12	1.11	0.014	0.349	0.661	0.652	0.478	0.008	16
46	1.53	1.51	0.012	0.746	0.919	0.915	1.570	0.089	5
47	0.82	0.82	-4.619E-003	0.425	-0.239	-0.233	-0.201	0.002	32
48	1.14	1.16	-0.018	0.345	-0.857	-0.852	-0.619	0.014	17
49	1.20	1.19	3.392E-003	0.580	0.205	0.200	0.235	0.002	27

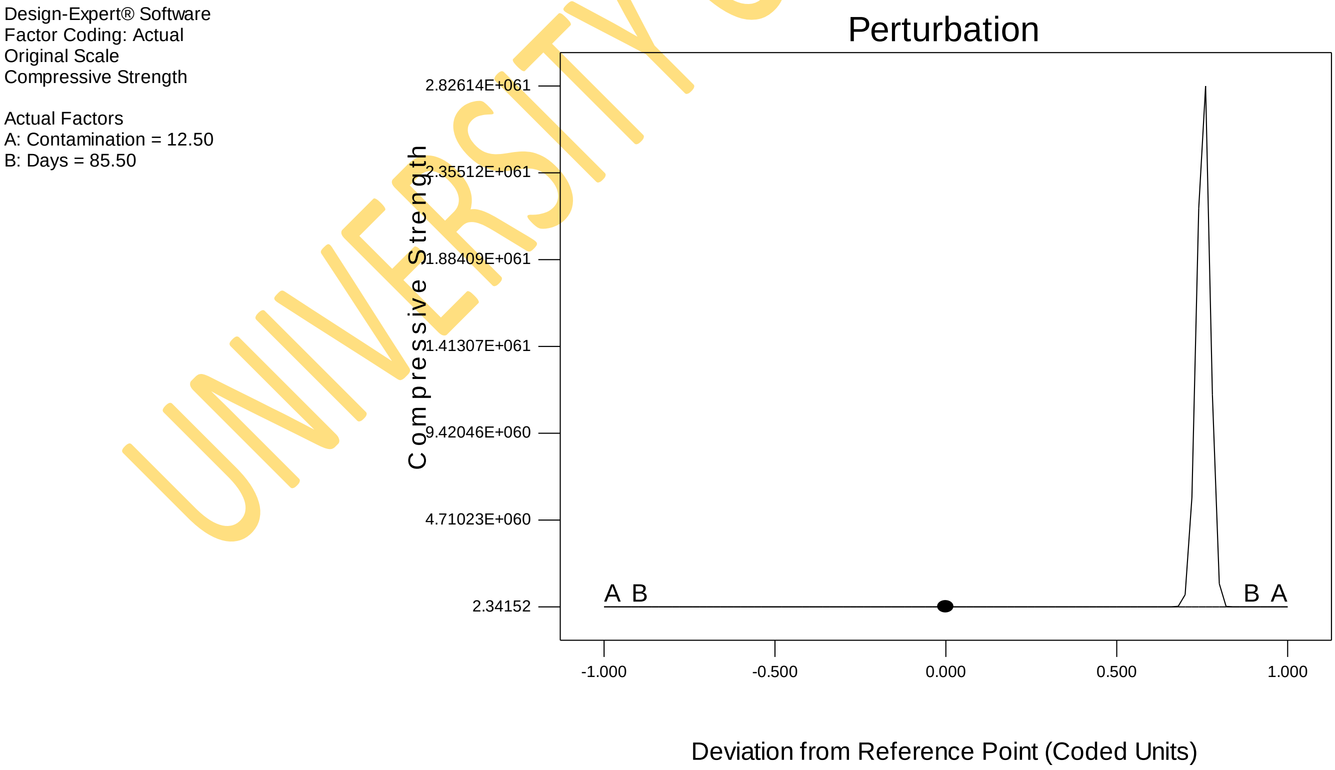
* Exceeds limits

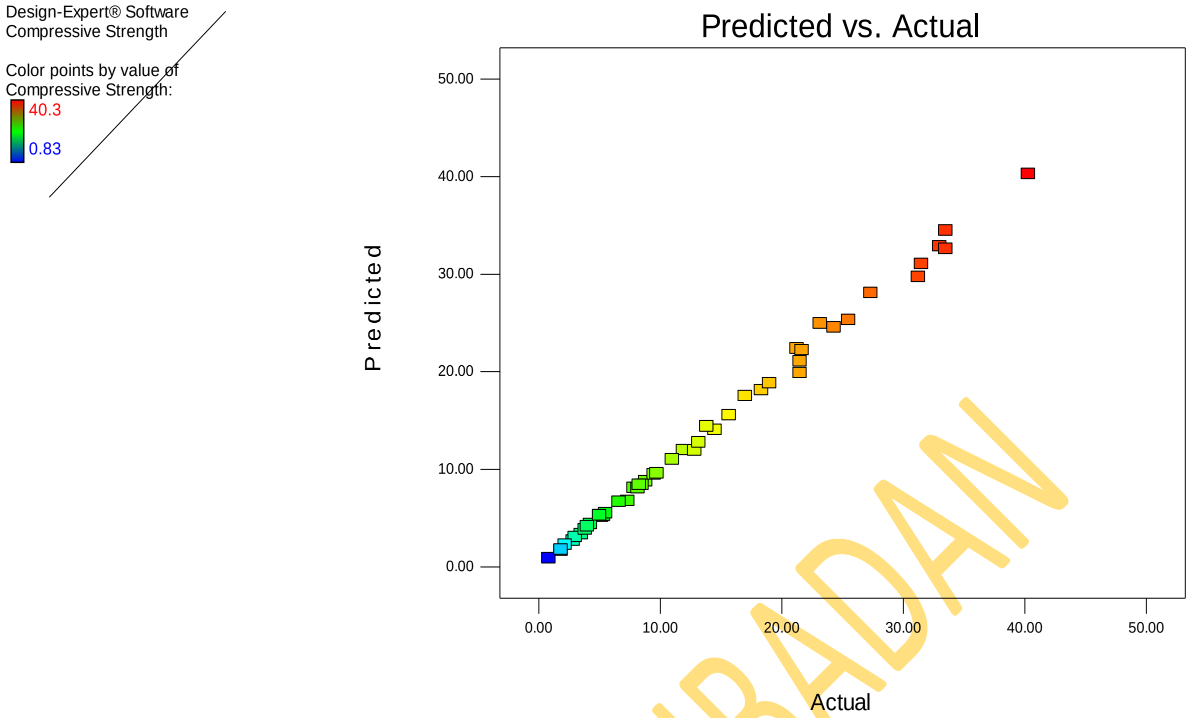
Current Transform:Base 10 LogConstant: 0.000

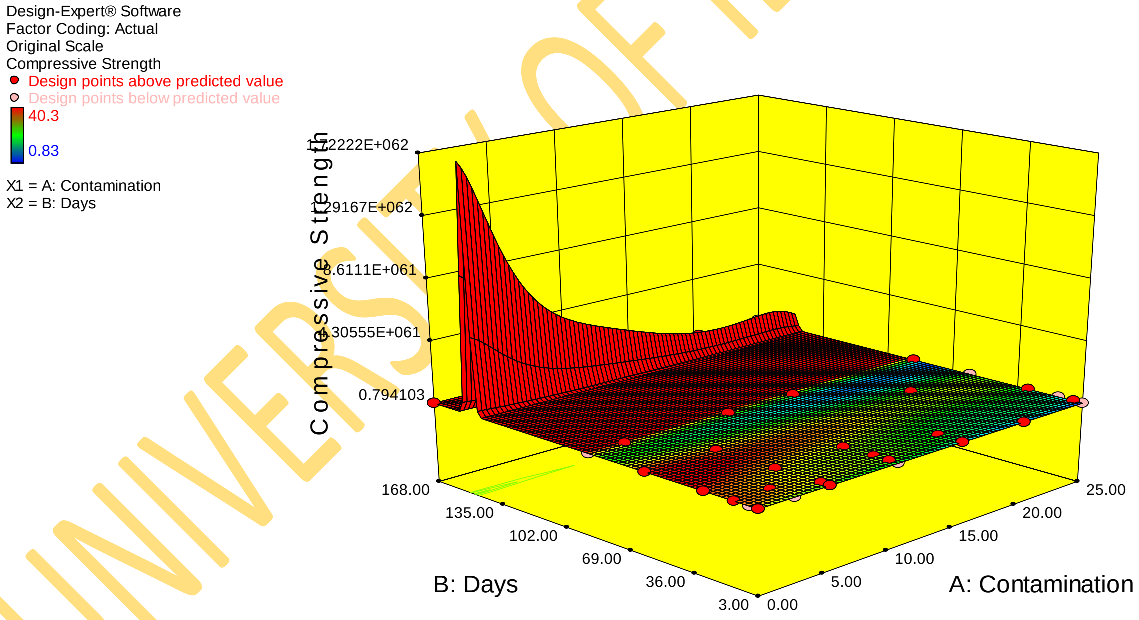
Box-Cox Power Transformation

Constant k	**95% CI Low**	**95% CI High**	**Best Lambda**	**Rec. Transform**
0.000	-1.000E-002	0.44	0.21	Log


Design-Expert® Software
Factor Coding: Actual
Original Scale
Compressive Strength
● Design Points
40.3
0.83
X1 = A: Contamination
X2 = B: Days
Compressive Strength
168.00
135.00
102.00
69.00
36.00
3.00
B: Days
1E+062
5E+061
0.00
5.00
10.00
15.00
20.00
A: Contamination


Design-Expert® Software
Factor Coding: Actual
Original Scale
Compressive Strength
Actual Factors
A: Contamination = 12.50
B: Days = 85.50
Perturbation
2.82614E+061
2.35512E+061
1.88409E+061
1.41307E+061
9.42046E+060
4.71023E+060
2.34152
Compressive Strength
A B
B A
-1.000
-0.500
0.000
0.500
1.000
Deviation from Reference Point (Coded Units)


Design-Expert® Software
Compressive Strength
Color points by value of
Compressive Strength:
40.3
0.83
Predicted vs. Actual
Predicted
50.00
40.00
30.00
20.00
10.00
0.00
0.00
10.00
20.00
30.00
40.00
50.00
Actual


Design-Expert® Software
Factor Coding: Actual
Original Scale
Compressive Strength
● Design points above predicted value
○ Design points below predicted value
40.3
0.83
X1 = A: Contamination
X2 = B: Days
Compressive Strength
1.72222E+062
1.29167E+062
8.6111E+061
4.30555E+061
0.794103
168.00
135.00
102.00
69.00
36.00
3.00
B: Days
0.00
5.00
10.00
15.00
20.00
25.00
A: Contamination

Model B (others)

Design Summary

File Version	8.0.5.2				
Study Type	Response Surface	**Runs**	7	**Analysis**	Polynomial
Design Type	One Factor	**Blocks**	No Blocks	**Trans**	None
Design Model	Quadratic	**Build Time (ms)**	6.16		

Factor	**Name**	**Units**	**Type**	**Sub-type**	**Actual Values**		**Coded Values**		**Mean**	**Std. Dev.**
					Min	**Max**	**Min**	**Max**		
A	Crude Oil	%	Numeric	Cont.	0.00	25.00	-1.00	1.00	10.11	9.52

Response	**Name**	**Units**	**Min.**	**Max.**	**Mean**	**Std. Dev.**	**Ratio**	**Model**
Y1	Slump	mm	30	200	106.429	61.3538	6.6667	Quadratic
Y2	C.F.	Ratio	0.45	0.85	0.6686	0.1536	1.8889	Linear
Y3	Flow	mm	230	370	284.286	58.4828	1.6087	Inverse Fifth
Y4	Flex St.	N/mm^2	0.113	5.865	3.298	2.2701	51.9027	Inverse Sqrt Quartic
Y5	Perm.	Kg	0	0.15	0.0557	0.05740	N/A	Sqrt Quadratic
Y6	L. S.	mm	0.02	0.09	0.0543	0.0263	4.5	Sqrt Fifth
Y7	Resist.		25.07	32.31	28.7857	2.5347	1.2888	Linear

SLUMP

Response **1** **Slump** **Transform:** **None**

Summary (detailed tables shown below)

Source	**Sequential p-value**	**Lack of Fit p-value**	**Adjusted R-Squared**	**Predicted R-Squared**	
Linear	0.0003		0.9282	0.8836	Suggested
Quadratic	0.3439		0.9302	0.8831	
Cubic	0.9737		0.9070	0.3285	
Quartic	0.2392		0.9413	-7.9099	
Fifth	0.0759		0.9983		
Sixth					

Sequential Model Sum of Squares [Type I]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Mean vs Total	79289.29	1	79289.29			
Linear vs Mean	21233.51	1	21233.51	78.51	0.0003	Suggested
Quadratic vs Linear	301.95	1	301.95	1.15	0.3439	
Cubic vs Quadratic	0.45	1	0.45	1.281E-003	0.9737	
Quartic vs Cubic	607.69	1	607.69	2.75	0.2392	
Fifth vs Quartic	435.87	1	435.87	69.77	0.0759	
Sixth vs Fifth	6.25	1	6.25			
Residual	0.000	0				
Total	1.019E+005	7	14553.57			

"Sequential Model Sum of Squares [Type I]": Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Model Summary Statistics

	Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**
Linear	16.45	0.9401	0.9282	0.8836	2627.93	Suggested
Quadratic	16.20	0.9535	0.9302	0.8831	2639.90	
Cubic	18.71	0.9535	0.9070	0.3285	15165.59	
Quartic	14.87	0.9804	0.9413	-7.9099	2.012E+005	
Fifth	2.50	0.9997	0.9983		+	
Sixth					+	

+ Case(s) with leverage of 1.0000: PRESS statistic not defined

Response 1 Slump
ANOVA for Response Surface Quadratic Model
Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	21535.46	2	10767.73	41.01	0.0022	significant
A-Crude Oil	*20362.70*	*1*	*20362.70*	*77.55*	*0.0009*	
A^2	*301.95*	*1*	*301.95*	*1.15*	*0.3439*	
Residual	1050.26	4	262.56			
Cor Total	22585.71	6				

The Model F-value of 41.01 implies the model is significant. There is only a 0.22% chance that a "Model F-Value" this large could occur due to noise.

Std. Dev.	16.20	R-Squared	0.9535
Mean	106.43	Adj R-Squared	0.9302
C.V. %	15.23	Pred R-Squared	0.8831
PRESS	2639.90	Adeq Precision	14.237

The "Pred R-Squared" of 0.8831 is in reasonable agreement with the "Adj R-Squared" of 0.9302.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 14.237 indicates an adequate signal. This model can be used to navigate the design space.

Coefficient Factor	**Standard Estimate**	**df**	**95% CI Error**	**95% CI Low**	**High**	**VIF**
Intercept	110.55	1	11.02	79.96	141.14	
A-Crude Oil	75.51	1	8.57	51.71	99.32	1.14
A^2	16.70	1	15.57	-26.53	59.92	1.14

Final Equation in Terms of Coded Factors:

Slump = $+110.55+75.51 * A+16.70 * A^2$

Response 1 Slump Transform: None

Diagnostics Case Statistics

Standard Order	**Actual Value**	**Predicted Value**	**Internally Studentized Residual**	**Leverage**	**Externally Studentized Residual**	**Influence on Fitted Residual**	**Value DFFITS**	**Cook's Distance**	**Run Order**
1	170.00	161.87	8.13	0.307	0.603	0.548	0.365	0.054	6

2	120.00	126.32	-6.32	0.413	-0.509	-0.456	-0.382	0.061	5
3	30.00	51.73	-21.73	0.353	-1.667	-2.612	-1.928	0.504	1
4	75.00	53.62	21.38	0.308	1.587	2.256	1.506	0.374	3
5	55.00	52.58	2.42	0.331	0.182	0.159	0.112	0.005	2
6	95.00	96.12	-1.12	0.451	-0.093	-0.081	-0.073	0.002	4
7	200.00	202.76	-2.76	0.837	-0.422	-0.374	-0.847	0.305	7

Current Transform: None

Box-Cox Power Transformation

Constant k	95% CI Low	95% CI High	Best Lambda	Rec. Transform
0.000	0.63	3.72	2.23	None

Response 1 Slump Transform: None

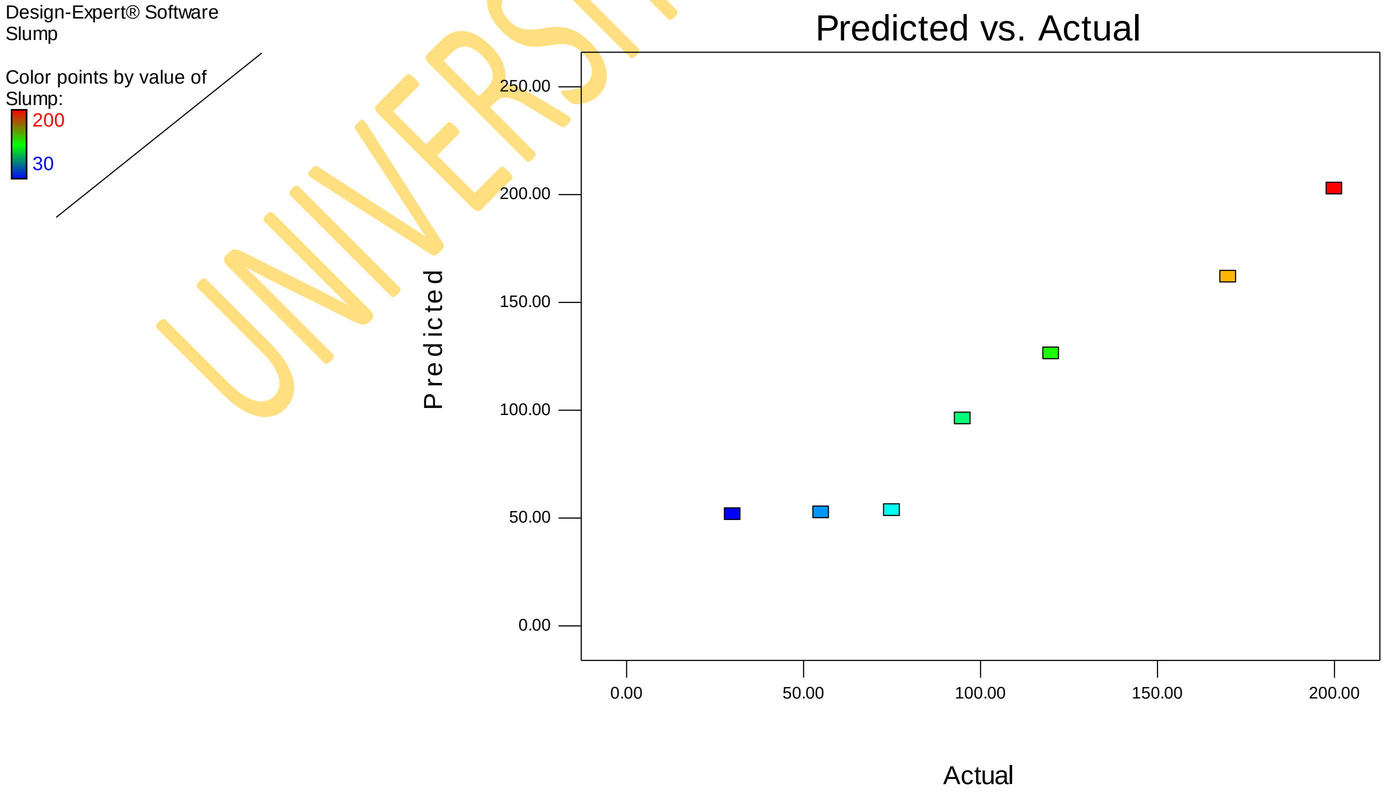
Diagnostics Case Statistics

Standard Order	Actual Value	Predicted Value	Internally Studentized Residual	Leverage	Externally Studentized Residual	Influence on Fitted Value Residual	Cook's DFFITS	Distance	Run Order
1	170.00	161.87	8.13	0.307	0.603	0.548	0.365	0.054	6
2	120.00	126.32	-6.32	0.413	-0.509	-0.456	-0.382	0.061	5
3	30.00	51.73	-21.73	0.353	-1.667	-2.612	-1.928	0.504	1
4	75.00	53.62	21.38	0.308	1.587	2.256	1.506	0.374	3
5	55.00	52.58	2.42	0.331	0.182	0.159	0.112	0.005	2
6	95.00	96.12	-1.12	0.451	-0.093	-0.081	-0.073	0.002	4
7	200.00	202.76	-2.76	0.837	-0.422	-0.374	-0.847	0.305	7

Current Transform: None

Box-Cox Power Transformation

Constant k	95% CI Low	95% CI High	Best Lambda	Rec. Transform
0.000	0.63	3.72	2.23	None



COMPACTING FACTOR

Response **2** **C.F.** **Transform:** **None**
Summary (detailed tables shown below)

Source	**Sequential p-value**	**Lack of Fit p-value**	**Adjusted R-Squared**	**Predicted R-Squared**	
Linear	0.0042		0.7988	0.6638	Suggested
Quadratic	0.5363		0.7743	0.6582	
Cubic	0.6997		0.7161	0.1927	
Quartic	0.4725		0.6927	-36.7777	
Fifth	0.3033		0.8707		
Sixth					

Sequential Model Sum of Squares [Type I]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Mean vs Total	3.13	1	3.13			
Linear vs Mean	0.12	1	0.12	24.82	0.0042	Suggested
Quadratic vs Linear	2.430E-003	1	2.430E-003	0.46	0.5363	
Cubic vs Quadratic	1.207E-003	1	1.207E-003	0.18	0.6997	
Quartic vs Cubic	5.589E-003	1	5.589E-003	0.77	0.4725	
Fifth vs Quartic	0.011	1	0.011	3.75	0.3033	
Sixth vs Fifth	3.049E-003	1	3.049E-003			
Residual	0.000	0				
Total	3.27	7	0.47			

"Sequential Model Sum of Squares [Type I]": Select the highest order polynomial where the additional terms are significant and the model is not aliased.

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.069	0.8323	0.7988	0.6638	0.048	Suggested
Quadratic	0.073	0.8495	0.7743	0.6582	0.048	
Cubic	0.082	0.8581	0.7161	0.1927	0.11	
Quartic	0.085	0.8976	0.6927	-36.7777	5.35	
Fifth	0.055	0.9785	0.8707		+	
Sixth					+	

+ Case(s) with leverage of 1.0000: PRESS statistic not defined

"Model Summary Statistics": Focus on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared".

Response 2 C.F.

ANOVA for Response Surface Linear Model

Analysis of variance table [Partial sum of squares - Type III]

	Sum of		Mean F	p-value		
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	0.12	1	0.12	24.82	0.0042	significant
A-Crude Oil	0.12	1	0.12	24.82	0.0042	
Residual	0.024	5	4.744E-003			
Cor Total	0.14	6				

The Model F-value of 24.82 implies the model is significant. There is only a 0.42% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

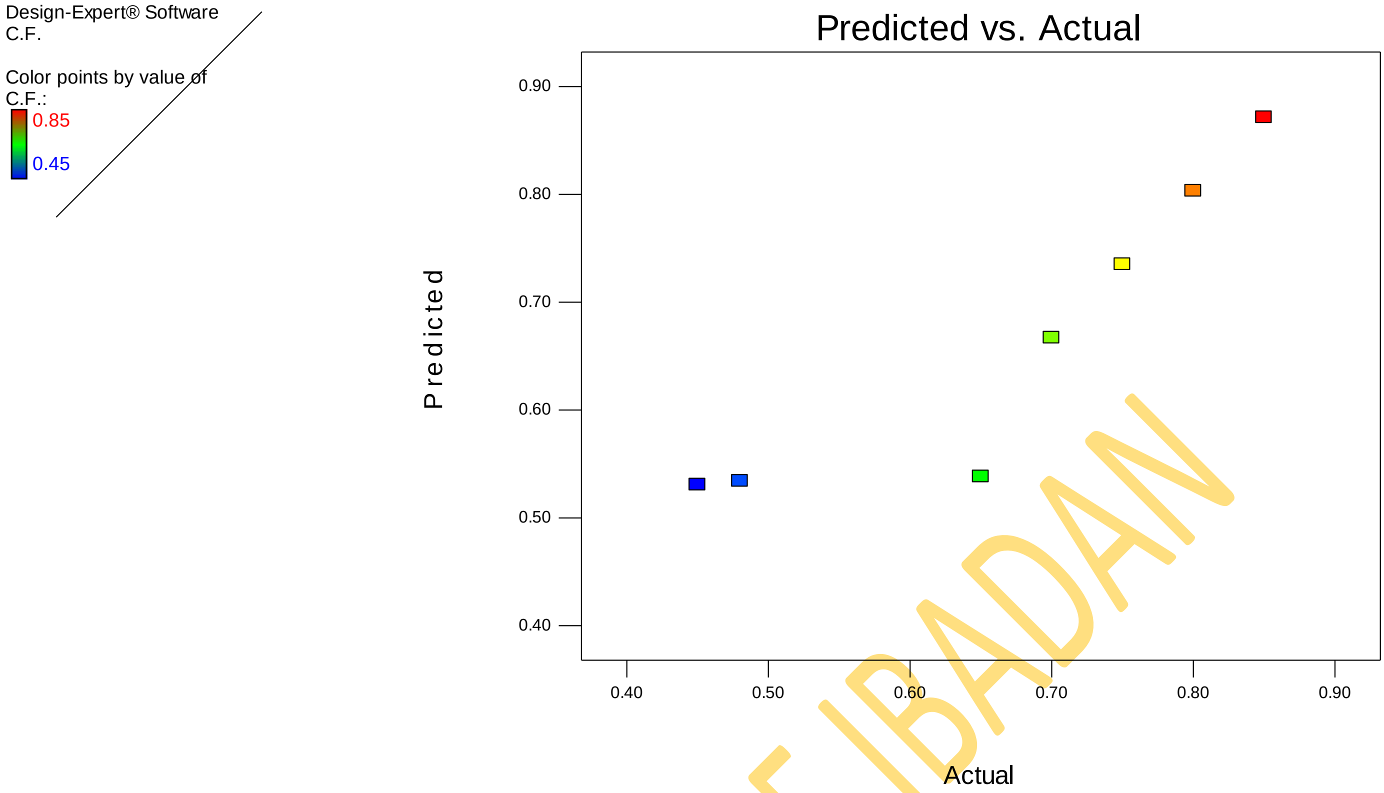
Std. Dev.	0.069	R-Squared	0.8323
Mean	0.67	Adj R-Squared	0.7988
C.V. %	10.30	Pred R-Squared	0.6638
PRESS	0.048	Adeq Precision	9.253

The "Pred R-Squared" of 0.6638 is in reasonable agreement with the "Adj R-Squared" of 0.7988.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 9.253 indicates an adequate signal. This model can be used to navigate the design space.

Final Equation in Terms of Coded Factors:

C.F. =+0.70+0.17 * A



FLOW TEST

Response **3** **Flow** **Transform:** **Inverse**

Summary (detailed tables shown below)

Source	**Sequential p-value**	**Lack of Fit p-value**	**Adjusted R-Squared**	**Predicted R-Squared**	
Linear	0.0005		0.9099	0.8900	Suggested
Quadratic	0.8620		0.8884	0.7210	
Cubic	0.2643		0.9084	-0.6891	
Quartic	0.4711		0.9011	-14.2503	
Fifth	0.0005		1.0000		Suggested
Sixth					

Sequential Model Sum of Squares [Type I]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Mean vs Total	9.280E-005	1	9.280E-005			
Linear vs Mean	2.743E-006	1	2.743E-006	61.63	0.0005	Suggested
Quadratic vs Linear	1.895E-009	1	1.895E-009	0.034	0.8620	
Cubic vs Quadratic	8.490E-008	1	8.490E-008	1.88	0.2643	
Quartic vs Cubic	3.798E-008	1	3.798E-008	0.78	0.4711	
Fifth vs Quartic	9.779E-008	1	9.779E-008	1.583E+006	0.0005	Suggested
Sixth vs Fifth	6.177E-014	1	6.177E-014			
Residual	0.000	0				
Total	9.577E-005	7	1.368E-005			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	2.110E-004	0.9250	0.9099	0.8900	3.263E-007	Suggested
Quadratic	2.349E-004	0.9256	0.8884	0.7210	8.275E-007	
Cubic	2.127E-004	0.9542	0.9084	-0.6891	5.009E-006	
Quartic	2.211E-004	0.9670	0.9011	-14.2503	4.523E-005	
Fifth	2.485E-007	1.0000	1.0000		+	Suggested
Sixth					+	

+ Case(s) with leverage of 1.0000: PRESS statistic not defined

Response **3** **Flow**
Transform: **Inverse**
ANOVA for Response Surface Fifth Model
Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2.966E-006	5	5.932E-007	9.602E+006	0.0002	significant
A-Crude Oil	4.453E-007	1	4.453E-007	7.209E+006	0.0002	
A^2	2.050E-009	1	2.050E-009	33188.87	0.0035	
A^3	1.432E-007	1	1.432E-007	2.318E+006	0.0004	
A^4	1.876E-009	1	1.876E-009	30372.82	0.0037	
A^5	9.779E-008	1	9.779E-008	1.583E+006	0.0005	
Residual	6.177E-014	1	6.177E-014			
Cor Total	2.966E-006	6				

The Model F-value of 9602036.92 implies the model is significant. There is only a 0.02% chance that a "Model F-Value" this large could occur due to noise.

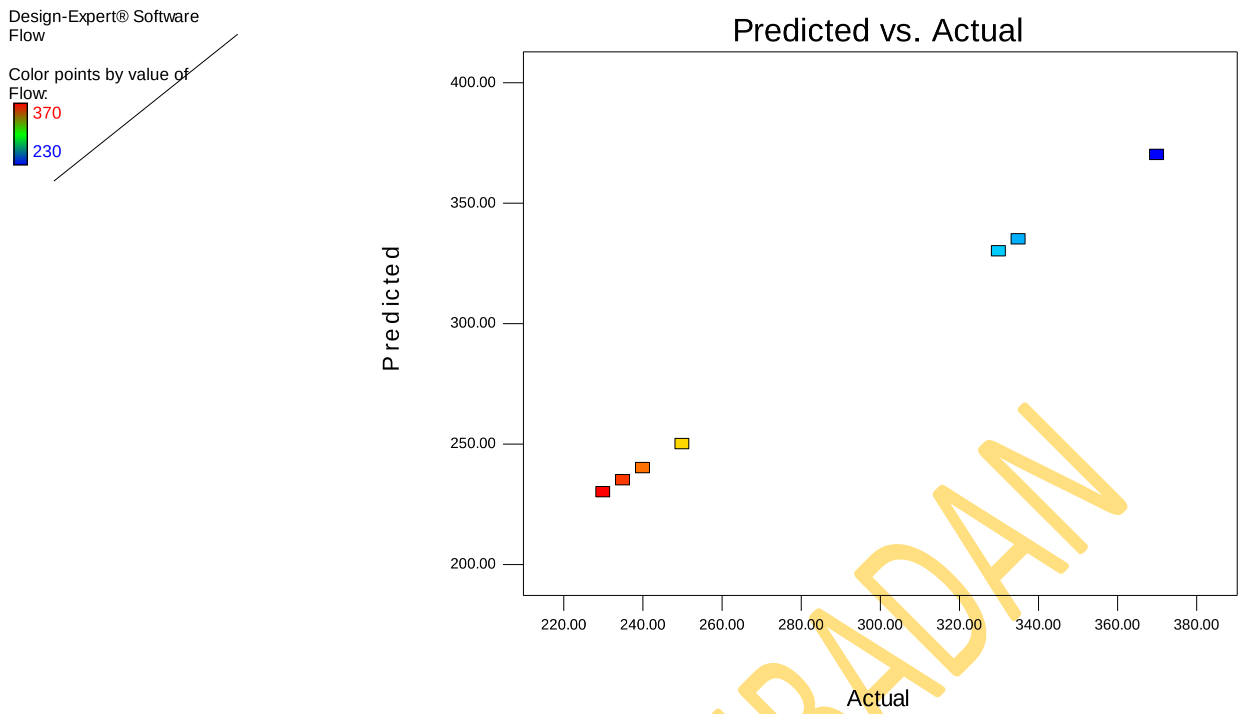
Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, A^2, A^3, A^4, A^5 are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Final Equation in Terms of Coded Factors:

$$1/(\text{Flow}) = +3.500E-003-2.663E-003 * A+3.848E-004 * A^2+6.129E-003 * A^3-3.599E-004 * A^4-4.289E-003 * A^5$$

Current Transform: **Inverse**
Box-Cox Power Transformation

Constant k	95% CI Low	95% CI High	Best Lambda	Rec. Transform
0.000	-1.01	-0.61	-0.81	Inverse



FLEXURAL STRENGTH

Response 4 Flex St Transform: Inverse Sqrt Constant: 0

Summary (detailed tables shown below)

Sequential Source	Lack of Fit p-value	p-value	Adjusted R-Squared	Predicted R-Squared	
Linear		0.0231	0.6116	0.1690	
Quadratic		0.0014	0.9702	0.8603	
Cubic		0.0016	0.9990	0.9779	Suggested
Quartic		0.0604	0.9998	0.9956	
Fifth		0.7415	0.9997		
Sixth					

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	6.64	1	6.64			
Linear vs Mean	3.67	1	3.67	10.45	0.0231	
Quadratic vs Linear	1.65	1	1.65	61.11	0.0014	
Cubic vs Quadratic	0.11	1	0.11	121.01	0.0016	Suggested
Quartic vs Cubic	2.304E-003	1	2.304E-003	15.06	0.0604	
Fifth vs Quartic	4.774E-005	1	4.774E-005	0.18	0.7415	
Sixth vs Fifth	2.582E-004	1	2.582E-004			
Residual	0.000	0				
Total	12.07	7	1.72			

Model Summary Statistics

Source	Std. Dev.		Adjusted R-Squared	Predicted R-Squared	R-Squared	PRESS
Linear	0.59	0.6764	0.6116	0.1690	4.51	
Quadratic	0.16	0.9801	0.9702	0.8603	0.76	
Cubic	0.029	0.9995	0.9990	0.9779	0.12	Suggested
Quartic	0.012	0.9999	0.9998	0.9956	0.024	
Fifth	0.016	1.0000	0.9997		+	
Sixth					+	

Response 4 Flex St
Transform: Inverse Sqrt Constant: 0
ANOVA for Response Surface Quartic Model
Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	5.43	4	1.36	8867.05	0.0001	significant
A-Crude Oil	*0.013*	*1*	*0.013*	*85.52*	*0.0115*	
A^2	*0.041*	*1*	*0.041*	*264.95*	*0.0038*	
A^3	*0.073*	*1*	*0.073*	*475.10*	*0.0021*	
A^4	*2.304E-003*	*1*	*2.304E-003*	*15.06*	*0.0604*	
Residual	3.060E-004	2	1.530E-004			
Cor Total	5.43	6				

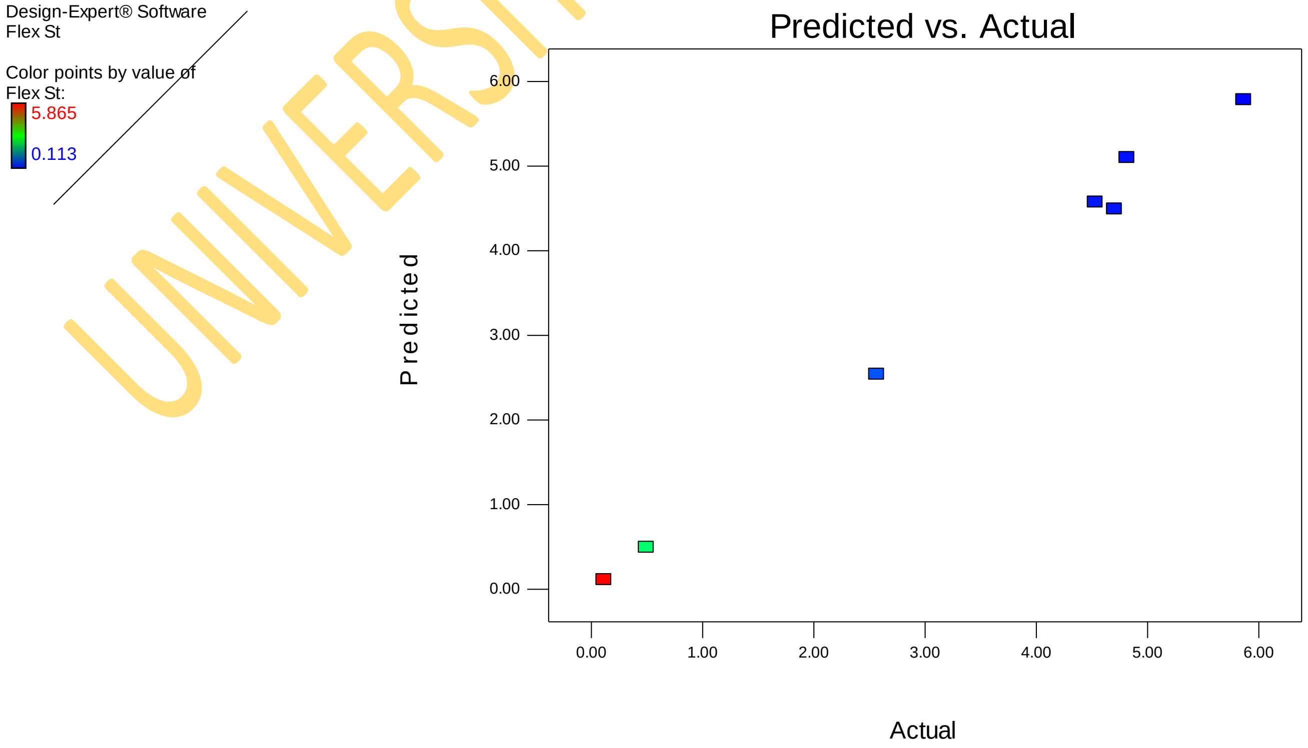
Std. Dev.	0.012	R-Squared	0.9999
Mean	0.97	Adj R-Squared	0.9998
C.V. %	1.27	Pred R-Squared	0.9956
PRESS	0.024	Adeq Precision	244.836

Final Equation in Terms of Coded Factors:

$$1/\mathrm{Sqrt}(\text{Flex St}) = +0.49+0.36 * A+1.57 * A^2+0.92 * A^3-0.36 * A^4$$

Current Transform: Inverse Sqrt Constant: 0.000
Box-Cox Power Transformation

Constant k	**95% CI Low**	**95% CI High**	**Best Lambda**	**Rec. Transform**
0.000	-0.91	0.16	-0.58	Inverse Sqrt



PERMEABILITY

Response 5 Perm Transform: Square Root Constant: 0
Summary (detailed tables shown below)

Sequential Source	**Lack of Fit p-value**	**p-value**	**Adjusted R-Squared**	**Predicted R-Squared**	
Linear		0.0021	0.8460	0.7388	Suggested
Quadratic		0.9089	0.8082	0.6731	
Cubic		0.5956	0.7710	0.5232	
Quartic		0.5677	0.7207	-37.9990	
Fifth		0.2044	0.9444		
Sixth					

Sequential Model Sum of Squares [Type I]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Mean vs Total	0.28	1	0.28			
Linear vs Mean	0.096	1	0.096	33.96	0.0021	Suggested
Quadratic vs Linear	5.243E-005	1	5.243E-005	0.015	0.9089	
Cubic vs Quadratic	1.477E-003	1	1.477E-003	0.35	0.5956	
Quartic vs Cubic	2.365E-003	1	2.365E-003	0.46	0.5677	
Fifth vs Quartic	9.264E-003	1	9.264E-003	9.05	0.2044	
Sixth vs Fifth	1.024E-003	1	1.024E-003			
Residual	0.000	0				
Total	0.39	7	0.056			

Model Summary Statistics

Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**		
Linear		0.053	0.8717	0.8460	0.7388	0.029	Suggested
Quadratic		0.059	0.8721	0.8082	0.6731	0.036	
Cubic		0.065	0.8855	0.7710	0.5232	0.053	
Quartic		0.072	0.9069	0.7207	-37.9990	4.31	
Fifth		0.032	0.9907	0.9444		+	
Sixth						+	

+ Case(s) with leverage of 1.0000: PRESS statistic not defined

Response 5 Perm
Transform: Square Root Constant: 0
ANOVA for Response Surface Quadratic Model
Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	*0.096*	*2*	*0.048*	*13.64*	*0.0164*	*significant*
A-Crude Oil	*0.086*	*1*	*0.086*	*24.40*	*0.0078*	
A^2	*5.243E-005*	*1*	*5.243E-005*	*0.015*	*0.9089*	
Residual	*0.014*	*4*	*3.533E-003*			
Cor Total	*0.11*	*6*				

The Model F-value of 13.64 implies the model is significant. There is only a 1.64% chance that a "Model F-Value" this large could occur due to noise.

Std. Dev.	0.059	R-Squared	0.8721
Mean	0.20	Adj R-Squared	0.8082
C.V. %	29.74	Pred R-Squared	0.6731

PRESS	0.036	Adeq Precision	7.986

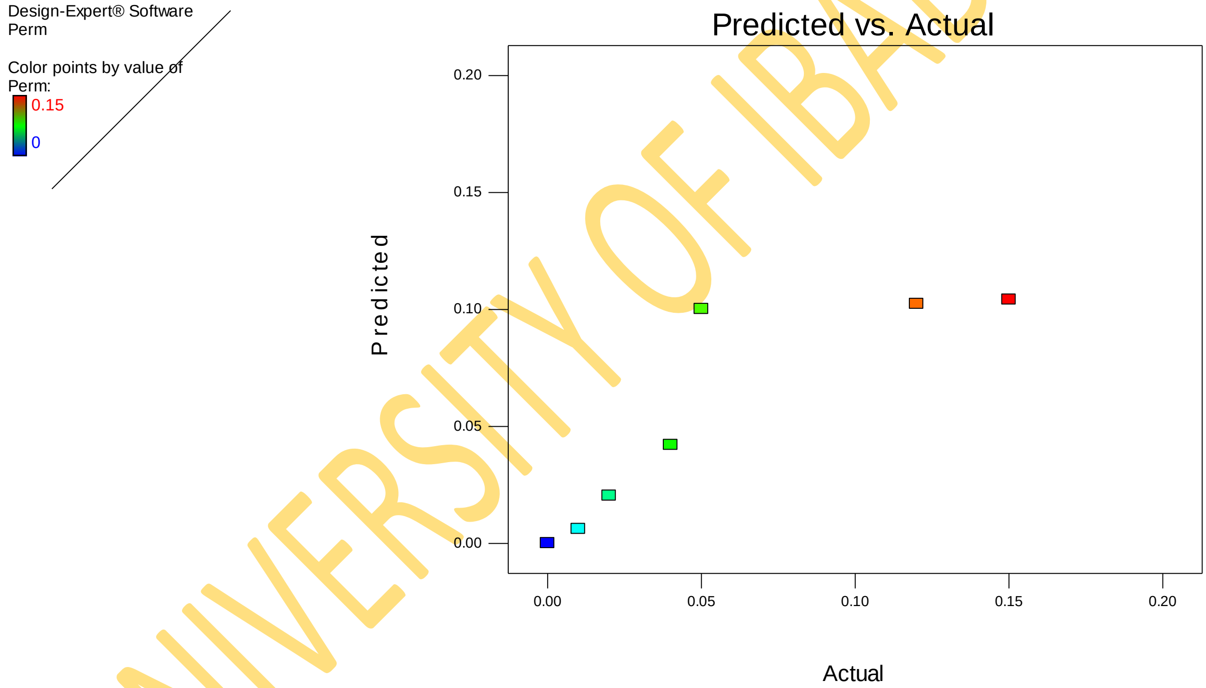
The "Pred R-Squared" of 0.6731 is in reasonable agreement with the "Adj R-Squared" of 0.8082.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 7.986 indicates an adequate signal. This model can be used to navigate the design space.

Coefficient		**Standard**	**95% CI**	**95% CI**		
Factor	**Estimate**	**df**	**Error**	**Low**	**High**	**VIF**
Intercept	0.17	1	0.040	0.062	0.29	
A-Crude Oil	-0.16	1	0.031	-0.24	-0.068	1.14
A^2	-6.957E-003	1	0.057	-0.17	0.15	1.14

Final Equation in Terms of Coded Factors:

$$\text{Sqrt(Perm)} = +0.17-0.16 * A \ \ -6.957\text{E-}003 * A^2$$



SHRINKAGE LINEAR

Response 6 S.L Transform: Square Root Constant: 0

Summary (detailed tables shown below)

Source	**Sequential p-value**	**Lack of Fit p-value**	**Adjusted R-Squared**	**Predicted R-Squared**	
Linear	< 0.0001		0.9686	0.9476	Suggested
Quadratic	0.8721		0.9611	0.9341	
Cubic	0.5650		0.9544	0.8532	
Quartic	0.4261		0.9542	-6.0660	
Fifth	0.0022		1.0000	Suggested	
Sixth					

Sequential Model Sum of Squares [Type I]

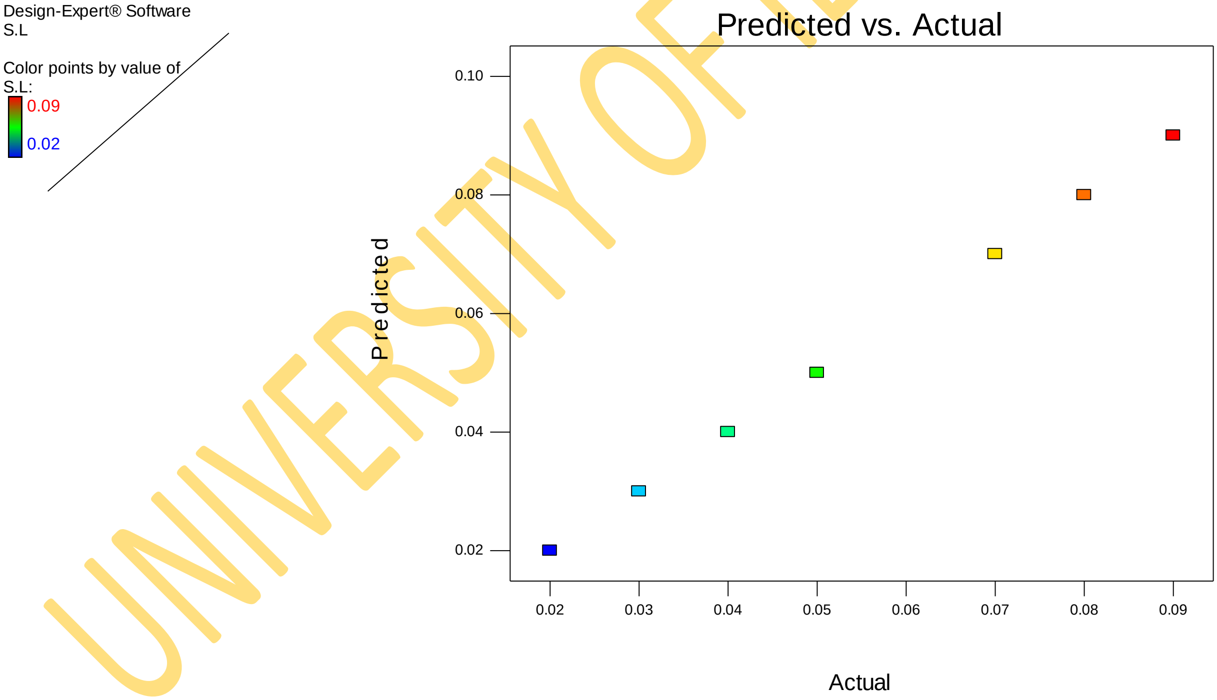
Sum of			**Mean**	**F**	**p-value**
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**

Mean vs Total	0.36	1		0.36	
Linear vs Mean	0.020	1	0.020	186.36	< 0.0001
Suggested					
Quadratic vs Linear	3.971E-006	1	3.971E-006	0.029	0.8721
Cubic vs Quadratic	6.572E-005	1	6.572E-005	0.42	0.5650
Quartic vs Cubic	1.562E-004	1	1.562E-004	0.98	0.4261
Fifth vs Quartic	3.180E-004	1	3.180E-004	82125.58	0.0022
Suggested					
Sixth vs Fifth	3.872E-009	1	3.872E-009		
Residual	0.000	0			
Total	0.38	7	0.054		

Model Summary Statistics

Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	0.010	0.9739	0.9686	0.9476	1.090E-003	Suggested
Quadratic	0.012	0.9741	0.9611	0.9341	1.373E-003	
Cubic	0.013	0.9772	0.9544	0.8532	3.055E-003	
Quartic	0.013	0.9847	0.9542	-6.0660	0.15	
Fifth	6.223E-005	1.0000	1.0000		+	Suggested
Sixth					+	

+ Case(s) with leverage of 1.0000: PRESS statistic not defined



RESISTIVITY

Response	**7**	**Resist**	**Transform:**	**None**

Summary (detailed tables shown below)

Sequential Source	**Lack of Fit p-value**	**Adjusted p-value**	**Predicted R-Squared**	**R-Squared**	
Linear	0.0048		0.7876	0.6638	Suggested
Quadratic	0.5373		0.7616	0.5523	
Cubic	0.9391		0.6829	-2.6999	

Quartic	0.1385		0.8774	-13.8967
Fifth	0.3007		0.9492	
Sixth				

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	5800.32	1	5800.32			
Linear vs Mean	31.73	1	31.73	23.25	0.0048	Suggested
Quadratic vs Linear	0.70	1	0.70	0.45	0.5373	
Cubic vs Quadratic	0.014	1	0.014	6.881E-003	0.9391	
Quartic vs Cubic	4.54	1	4.54	5.76	0.1385	
Fifth vs Quartic	1.25	1	1.25	3.83	0.3007	
Sixth vs Fifth	0.33	1	0.33			
Residual	0.000	0				
Total	5838.87	7	834.12			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	1.17	0.8230	0.7876	0.6638	12.96	Suggested
Quadratic	1.24	0.8411	0.7616	0.5523	17.26	
Cubic	1.43	0.8414	0.6829	-2.6999	142.62	
Quartic	0.89	0.9591	0.8774	-13.8967	574.22	
Fifth	0.57	0.9915	0.9492		+	
Sixth					+	

+ Case(s) with leverage of 1.0000: PRESS statistic not defined

Std. Dev.	1.17	R-Squared	0.8230
Mean	28.79	Adj R-Squared	0.7876
C.V. %	4.06	Pred R-Squared	0.6638
PRESS	12.96	Adeq Precision	8.956

The "Pred R-Squared" of 0.6638 is in reasonable agreement with the "Adj R-Squared" of 0.7876.

Final Equation in Terms of Coded Factors:

Resist =+29.32+2.80 * A

Response 7 Resist **Transform: None**

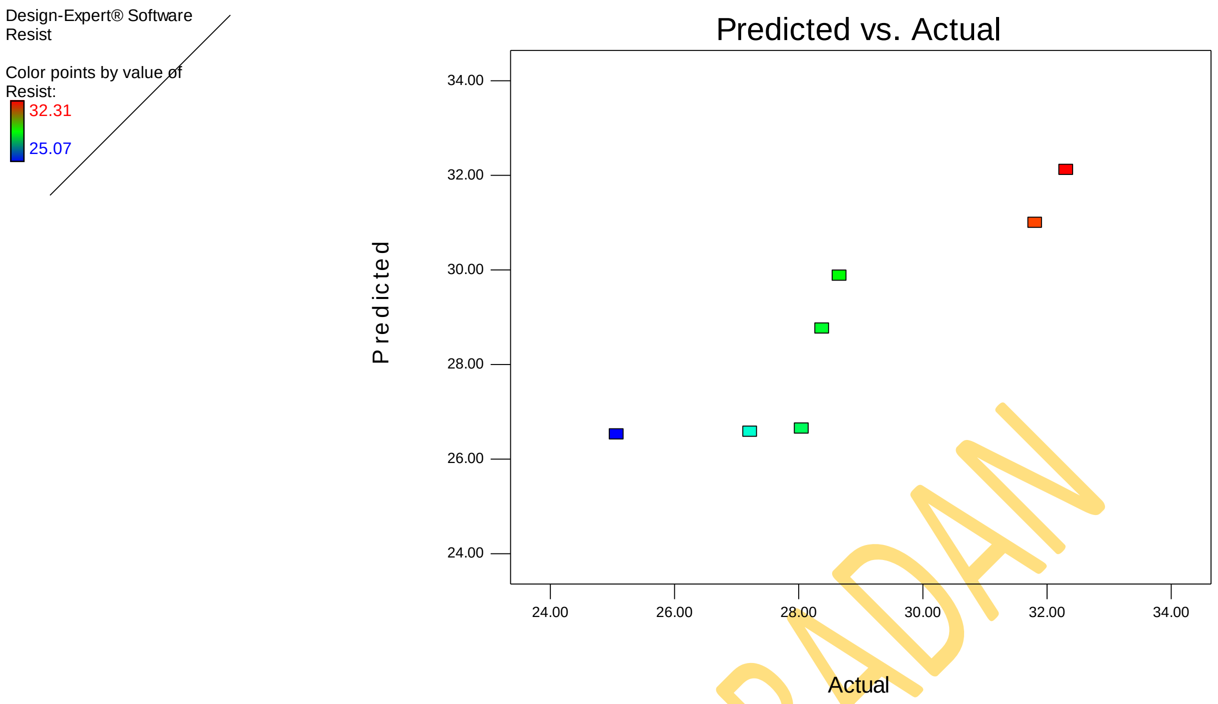
Diagnostics Case Statistics

Standard Order	Actual Value	Predicted Value	Studentized Residual	Studentized Leverage	Internally Fitted Value Residual	Externally Cook's Residual	Influence on DFFITS	Distance	Run Order
1	31.81	31.00	0.81	0.297	0.831	0.800	0.520	0.146	6
2	28.66	29.88	-1.22	0.180	-1.152	-1.203	-0.564	0.146	5
3	25.07	26.52	-1.45	0.304	-1.492	-1.792	-1.184	0.486	1
4	28.05	26.65	1.40	0.287	1.423	1.650	1.047	0.408	3
5	27.22	26.58	0.64	0.296	0.654	0.611	0.397	0.090	2
6	28.38	28.76	-0.38	0.143	-0.352	-0.318	-0.130	0.010	4
7	32.31	32.11	0.20	0.492	0.234	0.211	0.208	0.027	7

Current Transform: None

Box-Cox Power Transformation

Constant k	95% CI Low	95% CI High	Best Lambda	Rec. Transform
0.000	-4.87	9.57	2.35	None


Design-Expert® Software
Resist
Color points by value of
Resist:
32.31
25.07
Predicted vs. Actual
Predicted
Actual
34.00
32.00
30.00
28.00
26.00
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26.00
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34.00