CHARACTERIZATION OF THE SMART OILWELL CEMENT MODIFIED WITH METAKAOLIN

A Thesis

Presented to

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in Civil Engineering

by

Seyed Amirhossein Khodaean

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ABSTRACT

For a successful cementing operation, it is critical to determine the flow of cement slurry between the casing and formation, the setting of cement in place and performance of the cement after hardening. At present there is no technology available to monitor cementing operations in real time from the time of placement to the end of the borehole service life.

In this study well cement was modified using carbon fibers and other additives to give it better sensing properties, also known as smart cement, so that its behavior can be monitored during the cementing operation and its life time. The electrical resistivity was identified as the sensing property of the smart cement slurry and hardened cement. In this study up to 10% Metakaolin was used. Metakaolin increased the initial resistivity of cement by 25%, the piezoresistive behavior of the cement increased by about 60% and the cement compressive strength improved by about 20%. Contamination can be detected by means of the initial resistivity and its negative effect on the compressive strength and sensing properties was reduced by means of the addition of Metakaolin.

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Chapter 1

1- Introduction

1. 1- Overview

The Gulf of Mexico Oil Spill (also referred to as the BP Oil Spill) was the largest accidental marine oil spill in history. The oil rig was operated by British Petroleum (BP). It claimed 11 lives following the explosion of the oil rig. A sea-floor oil gusher flowed unabated for 87 days. The estimated total discharge was 4.9 million barrels. Investigations confirmed that the main cause of this accident was the defective cement in the oil well. Hence it is essential to ensure the quality of both casing joints and the outer oil well cement.

1. 2- Oil well cement

In oil and gas field cement slurries used for filling the area between the formation and the casing, Cement has to meet specific characteristics in order to ensure the integrity of the oil well both during its construction and its lifetime. These specific type of characteristics include low density, slump, certain amount of compressive strength, tensile strength and flexural strength, providing the zonal isolation in between the casing and formation in order to prevent slip, gas migration and blow out. Also it has to be modified in a way to make it applicable to be used in high temperature and high pressure conditions (De la Roij et al. 2012).

Cements such as class G and class H are used in oil well cementing applications. These cements are produced by pulverizing clinkers consisting essentially of calcium silicates with the addition of calcium sulphate (John 1992). Cementing is an important

operation at the time of oil well construction (Backe et al. 1997). When admixtures are added with cement, tensile and flexural properties will be modified. Also admixtures will have an effect on corrosion resistance, drying shrinkage, thermal conductivity, specific heat, electrical conductivity, and good radio-wave reflecting and absorbing properties of oil well cement (Han and Ou 2009). Oil well cement slurry will be used several thousand feet below ground level. Hence, determining cement setting time is always a challenge.

The quality of cement would directly impact various operations during drilling a well bore (Backe et al. 1997). Higher quality of cement would ensure the long-term durability of boreholes and prevent unnecessary costs to drilling operations (Pourafshary et al. 2009). Setting time of the oil well cement is very important to controlling the cementing operation (Zhang et al. 2010), pumping the cement would be difficult if the cement sets too early. Hence, it is important that this limit not be reached before the cement slurry fills the annulus (Smith 1990). Water-to-cement ratio (w/c), the composition and particle size distribution of cement, presence of additives (mineral and chemical), temperature, and pressure may affect the setting time of cement (Zhang et al. 2010). The cement slurry can become a rigid material from a workable plastic paste after setting.

As discussed, during cementing operation there would be a great need for a monitoring system to check the different quality indexes of oil well cement in order to ensure the high quality of cementing. Monitoring the oil well cement isn't limited to its construction phase—it has to be continually monitored to check for any sign of increase in pressure and temperature level, or crack and fracturing at the bottom of the oil well due to increase in the stress level.

As a result of the fact above, using structural sensors inside the cement would be unavoidable. However, use of sensors in cement would cause some limitation. The sensors suffer from (1) their sensing ability being limited to their immediate vicinities, (2) not being sufficiently durable, and (3) being too expensive for widespread use.

1. 3- Objective

The overall objectives were to evaluate some of the critical issues related to the behavior of modified cementitious materials. The specific objectives of this study are as follows:

1) Characterize the modified oil well cements based on the sensing properties during setting and after hardening.

2) Characterize the modified oil well cement based on the sensing properties during compressive loading.

3) Characterize the modified oil well cement due to the effect of contamination and interface failure based on the sensing properties

1. 4- Organization

This thesis is organized into six chapters. Chapter 1 is the introduction and includes the specific objectives for this study. Chapter 2 summarizes the background and literature review related to the characterization of oil well cement, Metakaolin, and its effect on the oil well cement, but it also describes the self-monitoring behavior of carbon fiber-reinforced cement. Chapter 3 discusses the different materials and methods of mixing, and types of devices and methodologies used. Chapter 4 studies the effect of Metakaolin on the electrical resistivity of oil well cement during hydration and on different curing conditions. It also discusses the effect of Metakaolin on the piezoresistivity of the oil well

cement, and the interface failure. Effect of contamination with heavy oil on the electrical properties of the oil well cement, both during hydration and under compressive load is discussed in Chapter 5. Finally, the conclusions and recommendations of this research have been summarized in Chapter 6.

Chapter 2

2- Background and Literature Review

2. 1- Introduction

The main purpose of this chapter is to provide a comprehensive literature review on the topics that are closely related to the proposed research. Such topics would include defining the oil well cement and its special characteristics as compared to the Portland cement; but also the in depth study of the hydration process and the effect of different additive, especifically Metakaolin. Also this Chapter discusses the characterization of structural and self-monitoring behavior of fiber-reinforced cement; summarizes the past and present research on oil well cement, and the current trends in fiber-reinforced cement. Self-monitoring behavior of structural material will also be reviewed, se well as theoretical work carried out to-date on predicting the self-monitoring behavior of multiphase conductive-insulative solids for better understanding the piezoresistive behavior of materials.

2. 2- Oil Well Cement

2. 2. 1- Overview

Cementing is one of the critical steps in well completion (Nelson 1990). Rarely is the time and commitment taken to get a good job. A considerable amount of time has to be spent in order to correct the bad cement job. Cement fills and seals the annulus between the casing string and the drilled hole. Cementing the well is done for three reasons: (1) zone isolation and segregation, (2) corrosion control, and (3) formation stability and pipe strength improvement (Nelson 1990). Cement can form strong, good bonding and nearly

impermeable seal from thin slurry around. The properties of the cement slurry and its behavior depend on the components and the additives in the cement slurry. Most cement used in the oil industry is a modified Portland cement. The name Portland was taken from an English Channel island with a limestone quarry that was used as a source of stone for the development of Portland cement. Portland cement is produced from limestone and either clay or shale by roasting it at 2600 to 3000°F (Smith 1990). The high temperature fuses the mixture into a material called clinker cement. After the roasting step, the rough clinker product is ground to a size specified by the grade of the cement. The size of the cement particles has a direct relationship with how much water is required to make slurry without producing an excess of water at the top of the cement or in pockets as the cement hardens. The crystals seen in set cement include: C_3S - tricalcium silicate, C_2S - dicalcium silicate, C_4AF - tetracalcium aluminoferrite, C_3A - tricalcium aluminate, MgO - periclase or magnesium oxide, and CaO - free lime. Not all cements, even those made from the same components, will react in the same manner when mixed with water. Basically, the differences are in the fineness of the cement, quality of the water, and some minor additives added during the cement manufacturing process (Smith 1990).

Table 2.1 Composition of different types of cements (John 1992)

Type	C3S	C2S	C3A	C4AF	Gypsum	Surface area (m^2/kg)
Class H	63.94	15.84	0.57	11.33	1.8	220-300
Class G	56.5	18.06	1.17	14.29	--	270-350
Portland cement	50	25	12	8	3.5	----

Oil well cement is hydraulic cement modified for oil and gas field application under API Standard; it has a slow setting rate and is used to support the casing by filling the

space between the formation and casing. Compared to the Portland cement there are some differences in the composition as summarized in Table 2.1

Table 2.2 Temperature and pressure profile of oil well (Smith 1990)

Depth (ft)	Circulating Temperature (F)	Static Temperature, (F)	Pressure, (psi)
1000	80	92	700
6500	120	158	3850
9800	150	198	6160
14300	200	252	9655
18300	250	300	13285
21750	300	341	16650

Every oil well around the world has unique characteristics in terms of temperature and depth. Table 2.2 lists different temperatures and pressures based on the depth of the oil well.

Due to the condition in the oil well in terms of temperature and pressure with depth gradient, API has defined different cement classes of cement were in response to deeper and hotter downhole conditions. Note that the useful depths given in the data are derived from average pumping times of neat (no additives) cement for average temperatures involved at these depths (John 1992). The actual well environment controls the limits of the cement. Also, additives such as accelerators and retarders can be used to modify the behavior of the cement. In this manner, two of the most common types of cement are class H and G.

Class G cement is produced using a raw material containing an argillaceous component (clay or shale), a calcareous component (such as chalk or limestone), and a source or iron oxide (such as haematite or pyrites residues) (John 1992). A small addition

of quartz sand is enough to allow sufficient silica to be present in totol in the raw material, if necessary. The raw meal composition is designed to produce a clinker of suitable reactivity for oil well cement usage (John 1992).

Gypsum addition is normally kept low, giving total cement SO_3 content within the range 1.7-2.3% (to minimize the acceleration of the hydration reaction of tricalcium silicate (alite) with sulphate (John 1992). Higher SO_3 levels may be tolerated if the total alkali content is low (John 1992). Class H cement is produced by a similar process, except that the clinker and gypsum are ground relatively coarser than for a Class G cement, to give cement a surface area generally in the range of 220-300 m^2/kg (John 1992).

2. 2. 2- Chemical Reaction

When water is added to the cement, each of the compounds inside contributes to the final product and from the strength point of view. The compounds that contribute to the strength are tri and di calcium silicates. Tricalcium silicate is responsible for the first 7 days of strength, while dicalcium silicate contributes only to the strength at a later time. The equation for the hydration of tricalcium silicate is expressed as followes (De la Roij et al. 2012):

Tricalcium Silicate + water ---> Calcium Silicate Hydrate +Calcium Hydroxide + Heat

$$2\ Ca_3SiO_5 + 7\ H_2O \text{ ---> } 3\ CaO.2SiO_2.4H_2O + 3\ Ca(OH)_2 + 173.6\ Kj. \qquad (2\text{-}1)$$

when adding water, tricalcium silicate reacts rapidly to release calcium ions, hydroxide ions, and heat. After a while, this reaction is slowed down with the decrease in heat of hydration. The chemical reactions continue to produce more calcium hydroxide until the system gets saturated and crystallization of calcium hydroxide occurs. At the

same time calcium silicate hydrate begins to form. Ions conditions accelerating the reaction of tricalcium silicate to calcium hydroxide, a process also known as Le Chatlier's principle (De la Roij et al. 2012). The evolution of heat is then dramatically increased again. The formation of calcium hydroxide and calcium silicate hydrate crystals provide seed, which then allows more calcium silicate hydrate to form. Those crystals grow thicker which makes it almost impossible for the water to get into unhydrate tricalcium silicate. The reaction pace is controlled by the rate at which water diffuses through the calcium silicate hydrate on. This coating thickness over time causes slower production of calcium silicate hydrate. Dicalcium silicate also affects the strength of concrete through its hydration. Dicalcium silicate reacts with water similar to tricalcium silicate does, but at a much slower rate expressed as (De la Roij et al. 2012):

Dicalcium silicate + water ---> Calcium Silicate Hydrate + Calcium Hydroxide + Heat

$$2\ Ca_2SiO_4 + 5\ H_2O \text{ ---> } 3\ CaO.2SiO_2.4H_2O + Ca(OH)_2 + 58.6\ kJ. \quad (2\text{-}2)$$

The other major components of Portland cement, tricalcium aluminate and tetracalcium aluminoferrite also react with water; however, the chemistry is different than tricalcium silicate and dicalcium silicate since tricalcium aluminate and tetracalcium aluminoferrite involve reaction with gypsum as well as water. The final product does no contribute to the strength of final material (De la Roij et al. 2012).

2. 2. 3- Additives

The cement must meet a wide range of short term criteria such as free water, thickening time, filtration loss, gelling, strength development, shrinkage, and certain long-term requirements such resistance to chemical attack, thermal stability, and mechanical integrity of cement sheath. Many studies have concluded that failure in the oil

well cementing operation does not necessarily occur from lack of ultimate compression strength, but rather low tensile strength. Hence, new materials are being developed and evaluated in an attempt to enhance the elastic and tensile properties of specialized cementing systems, which would allow for better, long-term zonal isolation at the anticipated induced stresses throughout the life of a well. In many instances these new systems are of a medium or low density in order to try to reduce the hydrated cement's Young's modulus and hence reduce induced stress. There are different types of additives used by the oil and gas industry some are briefly described below:

Polyvinyl Alcohol (PVA) ($CH_2CH(OH)_n$): This synthetic polymer, manufactured by the hydrolysis of ploy vinylacetate. This additive, dependent on its hydrolysis, is typically used at temperatures up to 300^oF, with concentrations ranging from 0.2 to 2% by weight of cement (Davidson 1980). The film forming properties of this material can contribute to a reduction in permeability by limiting the inner particle flow within the cement matrix (Davidson 1980). Because of its adhesive properties, it also enhances bounding between cement and casing/wellbore (Davidson 1980).

Silica Fume (SF) (SiO_2): by-product of silicon metal, or ferrosilicon alloy production and consists primarily of amorphous silicon dioxide. When added to Portland cement, the silicon dioxide in the SF reacts with the calcium hydroxide to form calcium silicate hydrate (CSH) gel. This reaction will contribute to compressive strength improvement, as well as reduction in the permeability of the cement matrix. The additive is typically used in temperatures up to 400^oF, and used in the range of 1.5 to 15 % by weight of cement. When used in conjunction with suitable fluid loss control additive, it can also improve antigas migration properties (Nelson 1990). It is also used to enhance compressive

strength, and improve free fluid control as well as CO_2 resistance of oil and gas well cement systems (Nelson 1990).

Metakaolin (MK) (Al_2O_3 $2SiO_2$): It is an amorphous, alumino-silicate produced through dehydration of kaolin clay mineral. Metakaolin is a highly reactive pozzolan with a high specific area (Heinold et al. 2002). When added to Portland cement, it reacts aggressively with calcium hydroxide, a normal cement hydration by-product, which makes it very suitable as a cementing material. This additive is typically used over a temperature range from 32^{o}F to 180^{o}F, with concentrations ranging from 1.0 to 25% by weight of cement. It contributes to the improvement of various properties of oil and gas well cement, such as permeability, compressive strength development, flexure and tensile strength, gas control and sulfate resistance (Heinold et al. 2002).

Wollastonite (**$CaSiO_3$**): It is a white calcium-silicate powder and sometimes referred to as a naturally-occurring mineral fiber. It is less reactive than metakaolin but produces a wide range of benefits when added to Portland cement. This additive can typically be used over a wide temperature range of 32^{o}F to 400^{o}F with concentrations ranging usually from 10 to 50 % by weight of cement. Similar to metakaolin, it can contribute to improve the various properties of oil and gas well cements, such as permeability, compressive strength development, flexural and tensile strength, gas control and sulfate resistance (Heinold et al. 2002).

Styrene Butadiene Latex (SBL): milky suspension of small spherical particles, normally stabilized with a surfactant package to improve freeze/thaw resistance and prevent coagulation when added to Portland cement (Heinold et al. 2002). This additive has been used in temperatures up to 400^{o}F, with concentrations ranging from 0.5 to 4

gal/sk. The film forming properties of latex modified cement system can lead to a reduction in permeability, increased tensile strength, better fluid loss control, enhancement bonding between cement and casing/wellbore and improved acid resistance (Nelson 1990).

Hydroxyethyl cellulose (HEC) (CH_2CH_2OH): This white powder which is water soluble, manufactured with different grades that differ, in terms of molecular weight. This additive can be used in temperatures above 300^oF, with concentrations ranging from 0.1 to 1.0% by weight of the cement. This additive can improve the fluid loss properties and be used over a wide range of oil well cement (Davidson 1980).

Sodium Metasilicate (Na_2SiO_2) (SMS): This is a water soluble powder produced by fusion of silica with sodium carbonate at 1400^oC (Heinold et al. 2002). Once added to Portland cement, silicates react with lime to form calcium silicate gel. It can ensure the usage of a large quantity of mix water without affecting the slurry stability that might be caused by the separation of excessive free water. This additive is used in temperature up to 200^oF, with concentration ranging from 0.1 to 4% by weight of cement. This additive is used to produce a low density slurry system with good free water control properties and enhances the compressive strength development (Heinold et al. 2002).

2. 3- Metakaolin

The cement industry accounts for 5 to 8% of the worldwide CO_2 emission (Scrivener and Kirkpatrick 2008); with the manufacture of just one ton of cement, 0.8 tons of CO_2 launches into the atmosphere (Rashad and Zeedan 2011). Not only does CO_2 release from cement manufacture but also SO_3 and NO_X are released which can cause the greenhouse effect and acid rain (Park and Kang 2008). These cause serious environmental impacts, in

addition to consuming considerable amount of virgin materials (limestone and sand) and energy (energy demands about 1700-1800 MJ/ton clinker), producing each ton of Portland cement (PC) of which about 1.5 tons of raw material is needed (Rashad and Zeedan 2011). To reduce the environmental impact of cement industries, MK (metakaolin) and other cementitious materials are used to replace part of cement or act as a source of new cement-less materials. MK (metakaolin) reacts chemically with hydrated cement to form a modified paste microstructure. In addition to its positive environmental impact, Mk improves concrete workability, mechanical properties and durability. The term MK pozzolan refers to a silecious material which, in finely divided form and in the presence of water, reacts chemically with calcium hydroxide to form cementitious compounds. Also in an effort to reduce the environmental impact resulting from cement industries, alkali-activated MK (future cement) or MK geopolymers are used (Rashad 2013). The name kaolin is derived from the Chinese word ‘kao-ling’meaning high ridge and the name of a hill near Jauchau Fu, where this material was mined centuries ago for ceramics (Rashad 2013). The main constituent, kaolinite is a hydrous aluminum silicate of approximate composition $Al_2O_32SiO_22H_2O$. Kaolinite is the clay mineral that provides the plasticity of the raw material and change during firing to produce a permanent material. Structurally, kaolinite consists of alumina octahedral sheets and silica tetrahedral sheets stacked alternately with the theoretical composition of 46.54% SiO_2, 39.5% Al_2O_3 and 13.96% H_2O. The kaolinite crystals are pseudo-hexagonal along with plates, some larger books, and vermicular stacks (Rashad 2013). The physical and chemical properties of kaolin determines its use as an industrial mineral. The applications are governed by several factors, including the geological conditions under which kaolin

was formed, the total mineralogical composition of the kaolin deposit, and the physical and chemical properties (Prasad et al. 1991). Kaolin has a particle size ranging from 0.2 to 15 µm with a specific area of 10,000–29,000 m^2/kg (Rashad 2013). The coarser kaolin is usually used as filler clays and the finer materials as coating products. The shape and distribution of kaolin are important factors in controlling many other properties such as equivalent diameter, determined by a sedimentation method from a flocculated suspension of clay in water Kaolin is one of the most widely used industrial minerals; the world's total output exceeds 25 million tones (Nkoumbou et al. 2009). Kaolin is an extremely useful mineral raw material. Its properties of white color, softness, small particle size and chemical inertness make it suitable for a number of different industrial applications. However, MK ($Al_2O_32SiO_2$) is a natural pozzolan produced by heating kaolin-containing clays over a temperature range of about 600–900 ^{0}C which it recrystallizes, rendering it to mullite ($Al6Si_2O_{13}$) or spinel ($MgAl_2O_4$) and amorphous silica (Rashad 2013). The first documented use of approximately 250,000 metric tons (227,300 tones) of MK was in 1962, when it was incorporated into the concrete used in the Jupia Dam in Brazil (Rashad 2013). It has been commercially available since the mid-1990s. MK typically contains 50–55% SiO2 and 40–45% Al2O3 (Poon et al. 2001). Other oxides present in small amounts include CaO and MgO. MK particles are generally one-half to five microns in diameter, – an order of magnitude smaller than cement grains and larger than silica fume particles. MK is white in color whereas silica fume is typically dark gray or black, making it particularly attractive in color matching and other architectural applications. Due to the controlled nature of processing MK powders are

very consistent in appearance and performance (Rashad 2013). Metakaolin's unique properties have been always been taken to account by many scholars.

Table 2.3 Summary of the past studies on Metakaolin

Reference	Material	Metakaolin percentage	Tests	Variable	Remark
(Nadeem et al. 2013)	Metakaolin (MK), Fly ash (FA), Ordinary Portland cement (OPC)	10%, 20%	Standard damage test (SDT), plastic strain (PS), damage index (DI)	Temperature	Metakaolin (MK) showed higher plastic starin (PS) and damage index (DI) compared to the Flyash (FA) at elevated temperature and both lowered than ordinary portland cement (OPC)
(Dhinakaran et al. 2012)	Metakaolin (MK), Ordinary Portland cement (OPC)	5%, 10%, 15%	Compressive strength, Chloride resistance	Curing age, electrical charge passing, penetration depth, w/c ratio	Increased strength effectively at early age and especially higher w/c ratio with the optimum amount considered at 10%. Minimum depth of chloride penetration reduced by 78%, 38%, 25% and 25% for w/cm ratios 0.32, 0.35, 0.40 and 0.50 respectively.
(Brooks and Megat Johari 2001)	Metakaolin (MK), Ordinary Portland cement (OPC)	5%, 10%, 15%	Autogenous shrinkage, Creep	Short term and long term curing	Metakaolin (Mk) reduced the early age autogenous shrinkage with higher rate at higher replacement, however it increase the long term shrinkage with reducing trend at higher replacement, comparing to control sample MK shrinkage is mainly constituted by autogenous shrinkage and the small part of it is because of drying shrinkage. Total creep, basic creep and drying creep greatly reduced.

2. 4- Self-Monitoring Structural Material

2. 4. 1- Introduction

Self-monitoring structural material refers to that type of material that can sense itself without using any type of sensors within. Using this type of sensor has many advantages over the conventional sensors that were used for monitoring structures among which are a very low cost, large sensing volume, and no need for any future maintenance. This type of smart material can be used for different purposes that can be categorized in two different stages. First it can be used during the construction in order to monitor hydration development, study temperature change, as well as sense contamination. In the next stage, during the life-time of structure, these sensors can be used to monitor the crack, increase in stress level as well as measure the deformation and change in the strain.

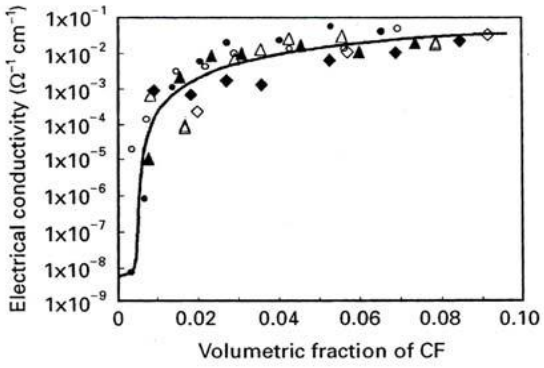
2. 4. 2- Carbon Fiber-Reinforced Material

One of the most common types of self-monitoring structural materials is carbon fiber, which has been widely used in the literature. Fibers tend to improve the flexural, tensile and fracture strength (Balaguru 1992). Fibers change the mode of failure by means of improving the post-cracking mechanism and the ductility of concrete(Banthia and Sheng 1996). Different types of fiber are used with hydraulic cement such as steel and glass, and new fibers like carbon or Kevlar. Concrete made with either steel or carbon fibers have been used for a variety of structural and non-structural applications. For example, electromagnetic interface shielding, electro static discharge, self-regulated heaters, and catholic protection (Chung 2003). Carbon fiber exhibits exceptional characteristics compared to other types of fibers. first of all, carbon fiber is electrically conductive in contrast to glass fibers that are not, steel fibers are conductive but have a typical diameter

of around 60 μm, which is larger than a carbon fiber at around 10 μm. The two main processes used for making carbon fibers are based on different starting materials—either PAN (polyacrylonitrite) carbon fibers or petroleum and coal tar pitch (pitch-based carbon fibers).

2. 4. 3- Percolation Theory

At the macrostructure level, the conductivity of the carbon fiber reinforced cement can be best described by means of Percolation theory (Xie et al. 1996). The theory determines how the set of conductive phases which is randomly placed in some space, is interconnected. At some critical probability point, a connected network of conductive phases causes the system to percolate, at which point fibers touch one another and form a continues conductive path. Wen and Chung (2003) and Xie et al. (1996) used the DC current on the dry mix and calculated the electrical conductivity as shown in Figure 2.1.



*** Water-cement ratio (*w*/*c*): (◇) 0.25, (◆) 0.30, (△) 0.35, (▲) 0.40, (○) 0.45, (●) 0.50. Carbon fibre length = 3 mm. 1 day hydration

Figure 2.1 Conductivity versus carbon fiber content (Xie et al. 1996)

From the graph, it can be seen that conductivity increased several orders when the fiber volume reached a critical value. Also different water to cement ratio don't affect the electrical conductivity, and is independent of sand to cement ratio (Xie et al. 1996). There are four different fiber positions defined based on fiber conductivity. At 4 fibers

are in contact with each other within a single cluster, and the parameter of characteristic length is defined as (Xie et al. 1996):

$$l = \max\{|r_i - r_j|\}_{i,j \ \ in\ cluster}, \tag{2-3}$$

where r_i and r_j are the position coordinates of two sites I and j in the cluster. The average spanning length for all clusters, l_{av}, obeys a power-law once the fiber concentration approaches the percolation threshold (Xie et al. 1996):

$$(\phi_c - \phi) \to 0 \quad \text{and}$$
$$l_{av} \propto \frac{1}{(\phi_c - \phi)^v}, \tag{2-4}$$

where the exponent v is a positive value, ϕ is the volume fraction of carbon fiber, and ϕ_c is the threshold value. Experiments showed that as ϕ approaches the ϕ_c then l_{av} reaches infinity, which means that the cluster is in contact with one another, and a network has been formed. It can be conclude that the conductivity, σ, of the composite can be defined as (Xie et al. 1996):

$$\sigma \propto (\phi_c - \phi)^t, \tag{2-5}$$

where t is factor dependent on the fiber properties and is found from the experiment.

2. 4. 4- Piezoresistivity

Change in the electrical resistivity of material due to the applied stress is known as piezoresistivity. Many researchers have investigated the piezoresistivity of CFRC (carbon fiber-reinforced cement) under different loading conditions and for different specimen configurations with different amounts of carbon fibers.

Chen and Chung (1995) studied the piezoresistivity of the cubic specimen under the compression cyclic loading after 7 days with the four-probe method and DC

measurement. Chen and Chung (1995) test that specimen with 0.5% of added carbon fiber during compressive load. change in relative reistivity of specimen deacreased during loading and increased during unloading of specimen ranging from 0% to 15%.

Fu and Chung (1997) studied the effect of curing age on the piezoresistive behavior of cement mortar. Cubic specimen were used. Carbon fiber was added by 0.5% by total weight of cement and silica fume was added by 15% of weight of cement, and resistivity was measured by means of DC device and the four-probe method. At 7 days of curing, due to better bonding between the carbon fiber and cement matrix under compressive load, change in relative resistivity increased up to failure of 250%; however, 28 days specimens showed decrease in change in relative resistivity during the initial stress to 50% because of fiber pull in effect and at a higher stress level due to the damage propagation change in relative resistivity increased up 250%.

Wen and Chung (2001) studied the piezoresistivity of carbon fiber-reinforced cement under two different additives including latex and silica fume. DC device and the four-probe method were used. Authors investigated the piezoresistivity of CFRC both for cubic and beam shape specimen. Cubic specimens were used in order to study the Longitudinal Piezoresistivity and beam specimen was tested for transverse piezoresistivity. Uniaxial compression of carbon fiber-reinforced cement paste in the elastic regime caused reversible decreases in both longitudinal and transverse electrical resistivity. In contrast, uniaxial tension caused reversible increases in both longitudinal and transverse resistivity. The gage factor, defined as change in relative resistivity per unit strain, essentially equal to the change in relative resistance per unit strain, gage

factor magnitude was higher for carbon fiber silica fume cement paste than carbon fiber latex cement paste, whether under uniaxial compression or uniaxial tension.

Wen and Chung (2001) studied the electrical resistivity of carbon fiber-reinforced cement paste and the electric polarization effect. By increasing the conductivity of the cement paste through the use of carbon fibers that were more crystalline, the polarization effect diminished. It was concluded that when the four-probe method was used, voltage polarity switching effects were dominated by the polarization of the sample itself, but when the two-probe method was used, voltage polarity switching effects were dominated by the polarization at the contact sample interface.

2. 5- Contamination

Over the past two decades, the amount of hydrocarbon contamination of soil and the environment has continually increased, and presently it constitutes a significant fraction of waste materials in the environment. Some major sources of hydrocarbon contamination are oil spill, leaking of petroleum from underground storage tanks, oil pipe vandalization, drilling, and treatment activities for exploration and production of hydrocarbons, and hydrocarbon waste disposed from industries. One form of contamination in the concrete could be the aggregate used inside. 18–90% compressive strength was lost due to 2.5–25% crude oil contamination, respectively (Ajagbe et al. 2012).

Based on the review of literature related to oil well cement characterization and methods of monitoring the cementitous materials, the following can be summarized:

1. Oil Well cement has to be modified in order to tolerate the extreme conditions of oil wells and has to meet various criteria.
2. Various additives were used to alter the setting time of the cement slurry and also to improve early compressive strength and flexural strength of the cement mortar.
3. Metakaolin is a natural pozzolan produced by heating kaolin-containing clays over a wide range of temperatures.
4. Metakaolin is one of the additives that has been used with the cmenet. Up to 15% has been used based on the literature.
5. Using metakaolin reduce minimum depth of chloride penetration reduced by 78%, 38%, and 25% also it reduced the early age autogenous shrinkage with higher rate at higher replacement, total creep, basic creep and drying creep were greatly reduced.
6. There have been no reports on the literature about characterization of oil well cement by electrical resistivity.
7. Accurate measurement of electrical resistivity is a challenge due to high interfacial factors.
8. Many researches have suggested the use of AC resistivity measurements to minimize the effect of polarization.
9. Modifying the cement with carbon fibers will turn it into a self-sensing materials that can be used in health monitoring of the structures.
10. Contamination of cement with oil will reduce the compressive strength of cement with higher effect at early age.

Chapter 3

3- Materials and Test Method

3. 1- Introduction

In this chapter, different types of materials and their concentrations and methods of mixing are discussed. Sample preparation, different mix design, and method of measuring resistance at different curing conditions and different loading test device and procedure were explained. Metakaolin up to 10% was used in mix and materials were mixed using a high speed mixer. During the slurry phase resistance and resistivity of the specimens were measured and K parameter is defined in order to calculate the resistivity at any time after the hardening. Compression test and anchor tests were done on the specimens and change in relative reistivity versus the stress were measured.

3. 2- Specimen Preparation

Plastic mold with the 2 in diameter and 4 in of height were used, 4 holes were punched on the side of the mold with 2in distance side to side and 1in of distance from top and bottom of mould edge. Two shredded wires were installed, each of them uncoated for 0.75 in. a rod has been placed at the middle of the specimen for use in slip friction test.

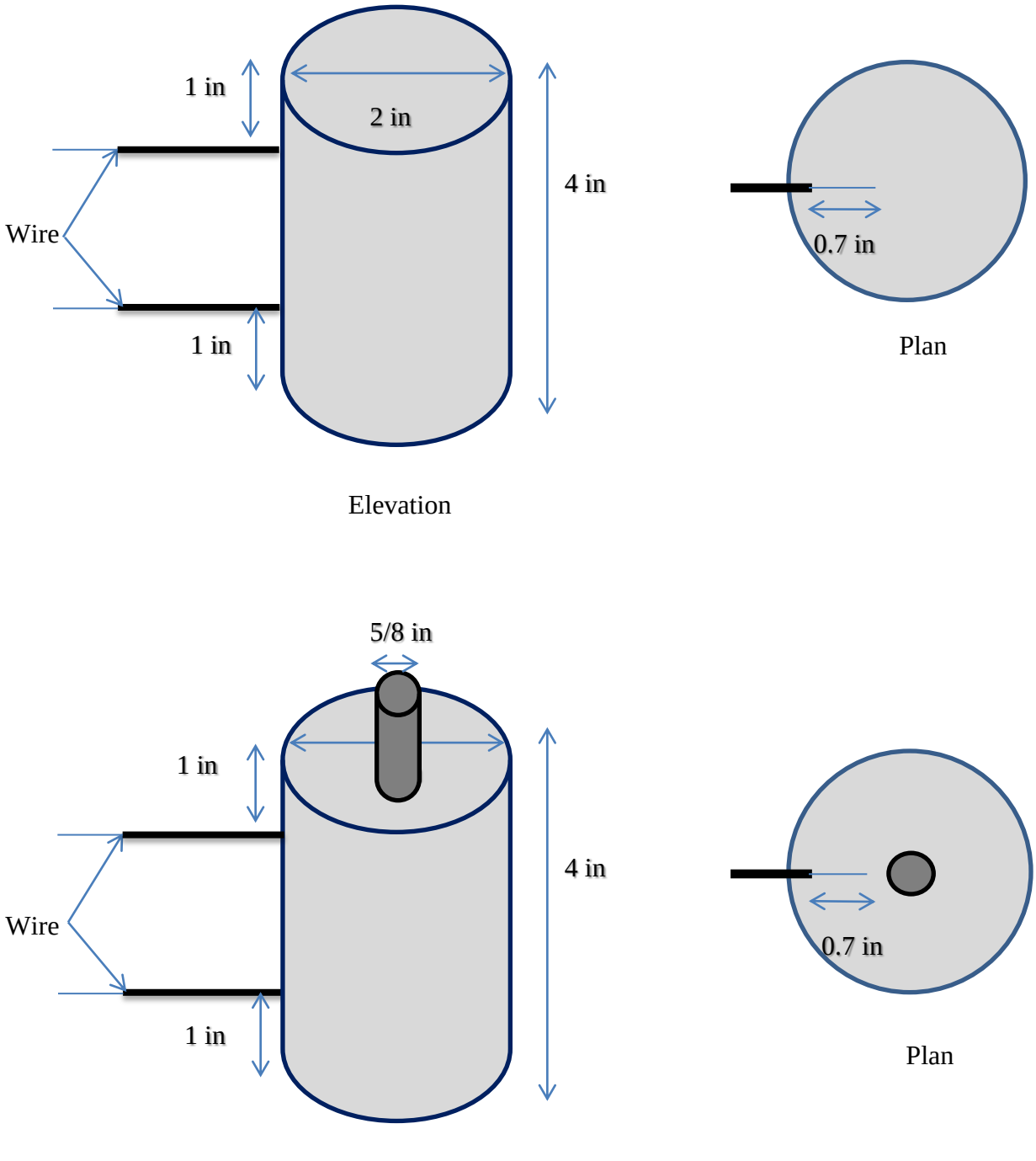


Figure 3.1 Mould configuaration a) compression tets b) anchor test

3. 3- Materials

Oil well cement class H was used along with Metakaolin for comparison purposes. Since the metakaolin has a high specific area its particle absorbs more water which is reduced the slump of the cement slurry. In order to improve the workability of the cement paste made with the metakaolin, glenium a type of admixture was added to mix. Carbon fiber was used in order to improve the piezoresistivity of the material.

Table 3.1 table of different mix design

	Control sample	Metakaolin sample	Oil contaminated sample
Cement	55%	49.5%-52.25%	55%
Water	45%	45%	45%
Metakaolin	0	5.5%-2.75%	0
Carbon fiber	0.1% btw	0.1%btw	0.1%btw
Admixture	0	0.2% bwoc	0
Heavy oil	0	0	6%btw

3. 4- Sample Preparation

Samples were prepared according to the API standard. High speed mixer was used to mix the materials. Carbon fiber was used at a concentration of 0.1% by total weight. Additive was added to the water before mixing with cement, then it was stirred for about a minute at the speed of 4000 rpm, followed by addition of carbon fiber, which was mixed in for another minute. After that, cement with or without metakaolin was added and then mixed for 3 minutes at the speed of 4000 rpm, then at the speed of 1200 rpm for 30 seconds, in order to study the effect of contamination, 6% of heavy oil was also added at this stage and mixing continued for another minute. Water to cement ratio was kept in the range of 0.45 for most of the samples. After that, the slurry was poured into the mould.

3. 5- Electrical Resistivity

Electrical resistivity of the sample can be calculated from the measurement of the electrical resistance, having a known uniform cross section and uniform length according to the following equation:

$$R = \rho \frac{L}{A}, \tag{3-1}$$

where ρ is the resistivity of the sample, R is the measured resistance, A is the cross-sectional area, and l is the distance between two probes.

3. 6- Mold Calibration

In order to measure the resistivity of samples after their setting time every mold was calibrated with the standard salt solution. Resistance and resistivity of the sample were measured using the LCR meter and conductivity meter device. A/L is defined as a K parameter of the specimen which is defined as

$$K = \frac{\mathrm{R}}{\rho} \qquad \text{and} \qquad K = \frac{\mathrm{l}}{A}, \tag{3-2}$$

in a different time interval for the specimen up to 3 hours. An average K is reported for every sample that is assumed to be constant.

3. 7- Conductivity Measurement

Conductivity of the samples was measured using the Orion conductivity meter model 125. Before measurement conductivity meter was calibrated using the standard solution. Standard solutions vary based on different applications. In this case, since the samples conductivity is around 10 mS/cm, the standard solution with the standard conductivity of 12.9 mS/cm in 25^{o}C was prepared. In order to prepare this solution, 7.23 gr of NaCl was

stirred inside 1 liter of deionized water and then calibration of the conductivity meter was performed based on the equation:

$$calibration\ factor = \frac{standard\ condcutivity}{measured\ conductivity}. \tag{3-3}$$

With this equation, a calibrated coefficient is given to the conductivity meter and with that the device is then calibrated. Sample conductivity was then measured using the calibrated conductivity meter device and based on the equation:

$$\rho\ (\Omega.m) = \frac{1}{measured\ conductivity(\frac{mS}{cm})} \times 10\ ' \tag{3-4}$$

resistivity calculated. Conductivity and resistance of the specimens were measured up to 3 hours after preparation of the sample, upon which the K parameter was calculated.

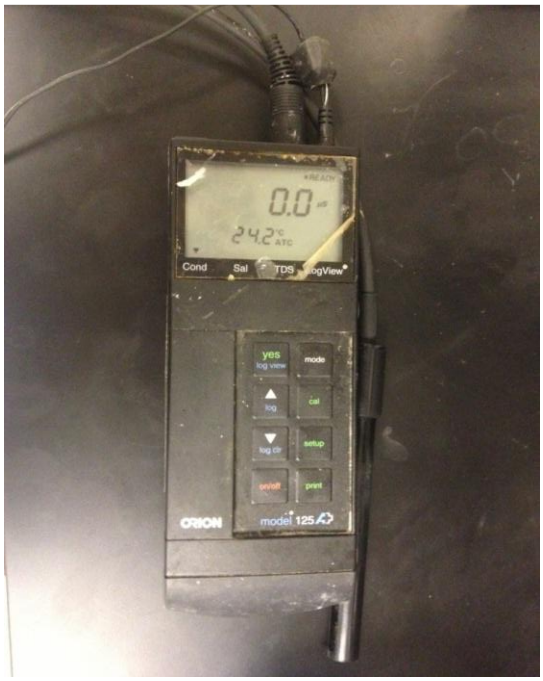


Figure 3.2 Conductivity meter device

3. 8- Resistance Measurement Devices

Resistance was measured by the two-wire method using different types of devices ranging from AC to DC measurement. Agilent E4980A LCR meter was used for AC measurement with a frequency range between 20 Hz to 300 kHz.

Figure 3.3 AC measurement device

Resistance was also measured by means of the DC device, Agilent 34970A. The data was monitored both manually and also remotely by the device memory.

Figure 3.4 DC measurement device

3. 9- Curing

After 24 hours samples were demoulded and cured under different condition, ranging from air and saturated sand cured both under temperature range from 23ºC to 80ºC.

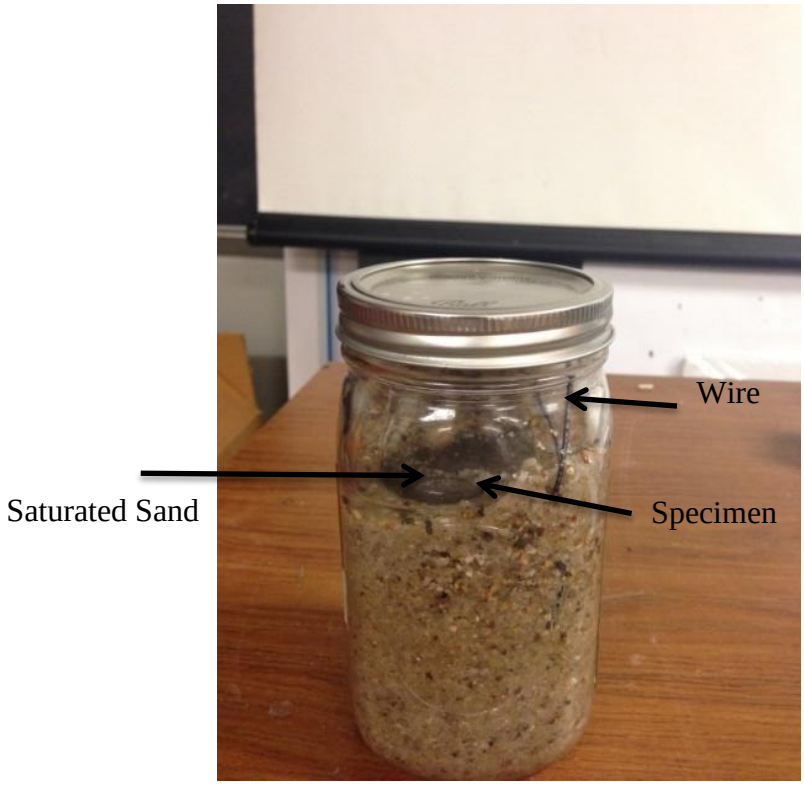


Figure 3.5 Curing under saturated soil

3. 10- Compressive Strength Test

Uniaxial compression test set up is shown in Fig. 3-3. The cylindrical specimen was placed at the center of the circular loading plate, and uniaxial compression load was applied on the specimen at a predetermined loading rate. Ultimate compression load of the specimen could be determined from the test.

The dimension of the specimen was measured using Vernier calipers and entered into the computer attached to the machine. The loading graph was digitally saved using a computer attached to the compression machine.

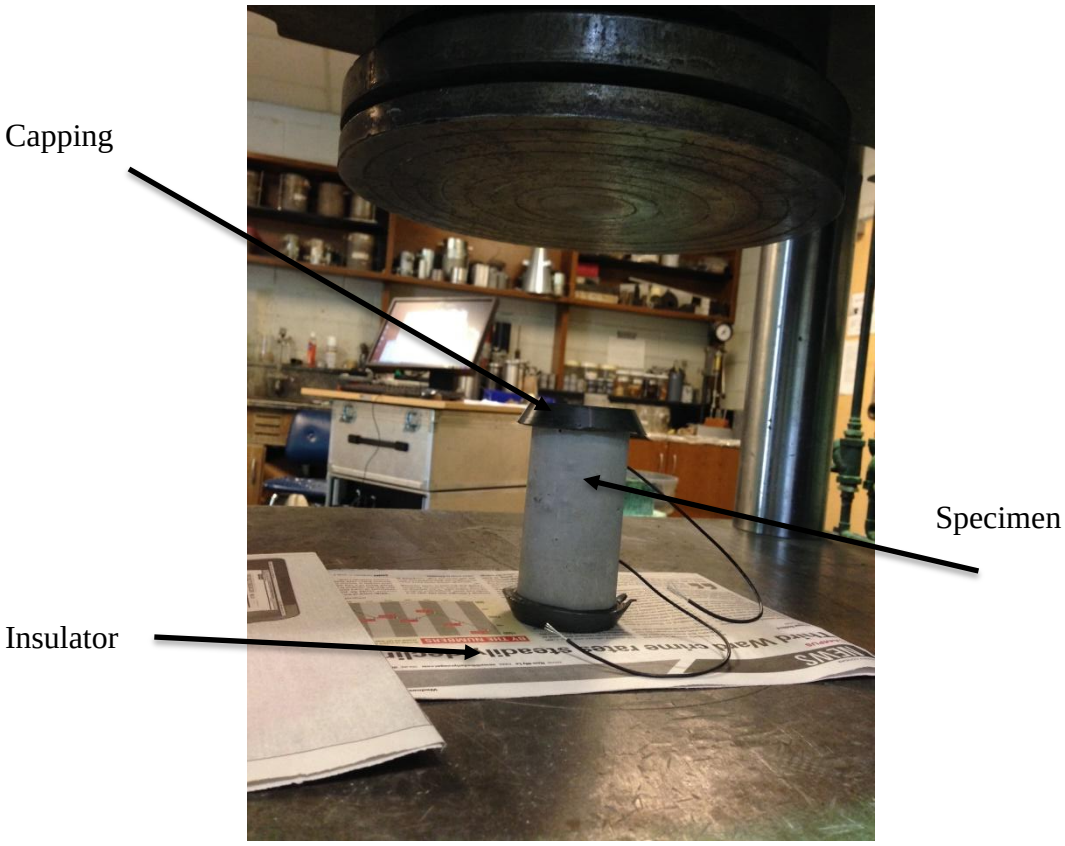


Figure 3.6 Compression device

3. 11- Summary

Based on the review of literature related to oil well cement characterization and methods of monitoring cementitous materials, the following can be summarized:

1. Various additives were used to alter the setting time of the cement slurry and also to improve early compressive strength and flexural strength of the cement mortar.
2. Metakaolin is a common oil well cement additive that improves the compressive strength and permeability of cement, and prevents the cement strength retrogression.
3. The importance of using carbon fiber in cement is to enhance the pressure-sensing ability of carbon fiber/cement composites.

4. Accurate measurement of electrical resistivity is a challenge due to high interfacial factors.
5. Researches has suggested the use of AC resistivity measurements to minimize the effect of polarization.
6. Modifying the cement with carbon fibers will turn it into a self-sensing material that can be used in health monitoring of the structures.
7. Acuracy of the compression test device was at 10 pounds.
8. AC device ferequcy range is between 20 Hz to 300 kHz.

Chapter 4

4- Metakaolin Modified the Smart Oil Well Cement

4. 1- Introduction

This chapter mainly discusses the effect of the addition of metakaolin on the different properties of oil well cement, specially on the resistance of the oil well cement during hydration and curing time, and also on the piezoresistivity under compressive loading.

4. 2- Impedance Characterization of Oil Well Cement

In order to understand the self-sensing ability of cement, the material properties were characterized under AC measurement using the two-wire method. The two wire method was selected because of its simplicity and practicality specially in the field. However, measuring the resistance using this method was associated with contact resistance at the interface of the wires and cement (Wen and Chung 2006). Hence, quantifying contact and bulk resistance was important to obtaining the sensing properties.

4. 2. 1- Theory

Identification of the most appropriate equivalent circuit to represent the electrical properties of a material is essential in order for the material's properties to be further understood (West et al. 1997). In this study, an equivalent circuit to represent the smart cement was required for better characterization through analysis of the Impedence specroscopy (IS) data. There were many difficulties associated with choosing a correct equivalent circuit. It was necessary to somehow make a link between the different elements in the circuit and the different regions in the impedance data of the corresponding specimen (West et al. 1997). Given the difficulties and uncertainties,

researchers tended to use a pragmatic approach and adopted a circuit that they believe was most appropriate based on their knowledge of the expected behavior of the material under study, and then demonstrated that the results were consistent with the circuit used. In this study, based on past researches (Vipulanandan and Prashanth 2013), two possible equivalent circuits were analyzed in order to find an appropriate equivalent circuit to represent the smart cement measured responses.

Case 1: General Bulk Material (Resistance and Capacitor)

In the equivalent circuit for Case 1, the contacts were connected in series, and both the contacts and the bulk material were represented using a capacitor and a resistor connected in parallel, see Figure 4.1. In the equivalent circuit for Case 1, R_b and C_b are the resistance and capacitance of the bulk material, respectively, and R_c and C_c are the resistance and capacitance of the contacts, respectively.

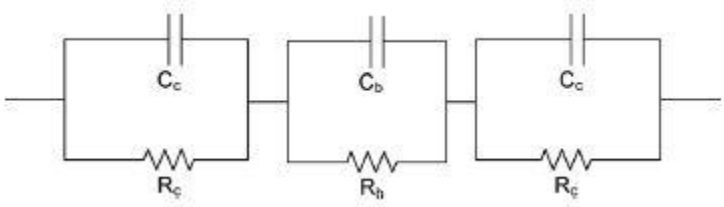


Figure 4.1 Equivalent circuit for Case 1 (Vipulanandan and Prashanth 2013)

The total impedance of the equivalent circuit for Case 1 (Z1) can be represented as follows (Vipulanandan and Prashanth 2013):

$$Z_1 = \frac{R_b}{1+\omega^2 R_c^2 C_c^2} + 2\frac{Rc}{1+\omega^2 R_c^2 C_c^2} - j\left\{\frac{2\omega R_c^2 C_c}{1+\omega^2 R_c^2 C_c^2} + \frac{\omega R_b^2 C_b}{1+\omega^2 R_b^2 C_b^2}\right\} \quad (4\text{-}1)$$

In Eq (4-1) ω is the angular frequency of the applied signal. When the frequency of the applied signal is very low, $\omega \to 0$ and $Z_1=R_b+2R_c$, and when it is very high, $\omega \to \infty$ and $Z_1 = 0$.

Case 2: Special Bulk Material (Resistance Only)

In Case 2, as a special case of Case 1, the capacitance of the bulk material (C_b) was assumed to be negligible (Figure 4.2).

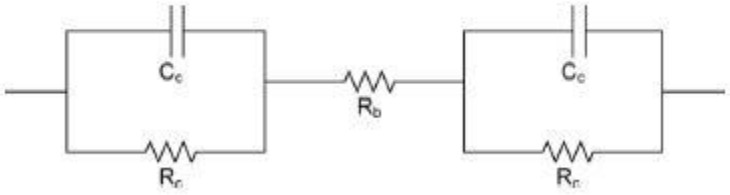


Figure 4.2 Equivalent circuit for Case 2 (Vipulanandan and Prashanth 2013)

The total impedance of the equivalent circuit for this case (Z_2) is as follows: (Vipulanandan and Prashanth 2013):

$$Z_2 = R_b + 2\frac{Rc}{1+\omega^2 R_c^2 C_c^2} - j\left\{\frac{2\omega R_c^2 C_c}{1+\omega^2 R_c^2 C_c^2}\right\} \quad (4\text{-}2)$$

When the frequency of the applied signal is very low, $\omega \to 0$ and $Z_2=R_b+2R_c$ and when it is very high $\omega \to \infty$ and $Z_2= R_b$. A comparison of the typical responses of equivalent circuits for Case 1 (Figure 4.1) and Case 2 (Figure 4.2) is shown in Figure 4.3.

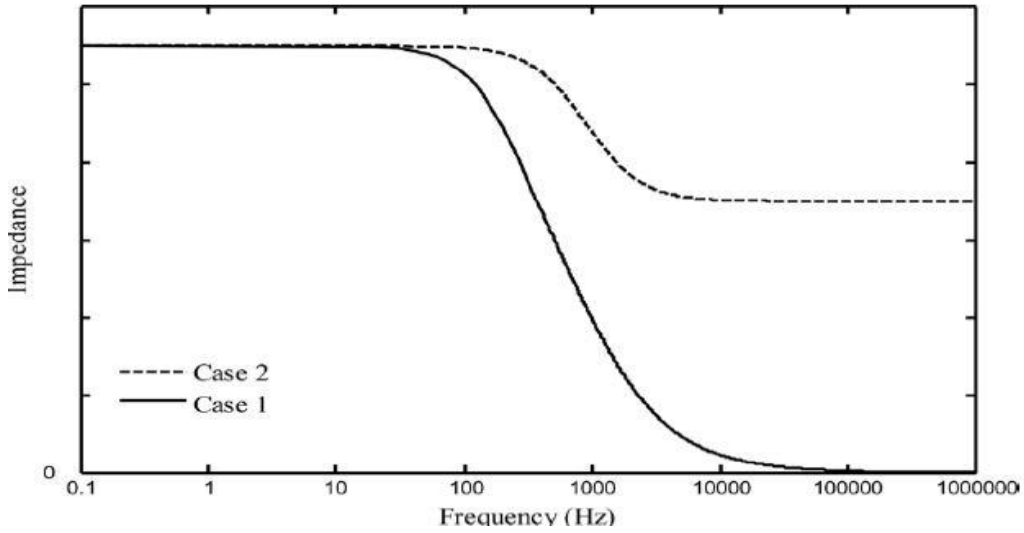


Figure 4.3 Comparison of typical responses of equivalent circuits for Case 1 and Case 2

In this study, the impedance spectroscopy (IS) test was performed on the cement samples to quantify the bulk and contact resistance at various curing ages. During the test, the frequency of the constant amplitude AC signal varied from 20 Hz to 300 kHz, and the corresponding impedances of the smart cement were measured using an LCR meter. The IS test results for the cement slurry right after mixing and 14 days of curing are shown in Figure 4.4 and Figure 4.5. The IS experimental results trend was identical to the equivalent circuit for Case 2 (Figure 4.4, Figure 4.5, Figure 4.6 and Figure 4.7). As a result, Case 2 (resistance-only material) was selected as the most appropriate one to represent the smart cement.

The model predictions of the IS using Eq (4-2) are plotted with the experimental observations in Figure 4.4, Figure 4.5, Figure 4.6 and Figure 4.7. From the Eq (4-2) the bulk resistance of the fresh cement slurry immediately after mixing was obtained as 42 Ω, whereas the bulk resistance of the hardened cement after 28 days of curing was increased to 334 Ω. The contact resistance for the fresh slurry and hardened cement were 24979 Ω and 799833 Ω, respectively. The contact capacitance (C_c) of the fresh cement slurry was estimated as 1.26 µF. For the hardened cement, the contact capacitance was 0.5 µF. Bulk resistance of the 10% Metakaolin slurry immediately after mixing was obtained as 68 Ω, whereas the bulk resistance of the hardened cement after 28 days of curing was increased to 1294 Ω. The contact resistance for the fresh slurry and hardened cement were 36676 Ω and 1056081 Ω, respectively. The contact capacitance (C_c) of the fresh cement slurry was estimated as 1.96 µF. For the hardened cement the contact capacitance was 0.24 µF.

The tests indicated that the measured resistance at high frequency converged to the bulk resistance obtained from the Eq. 4-7. The variation of the bulk resistance obtained

from the model was almost zero at 300 kHz frequency for both fresh cement slurry and the hardened cement. Therefore, the bulk resistance of the cementitious materials can be determined by measuring the resistance at 300 kHz frequency.

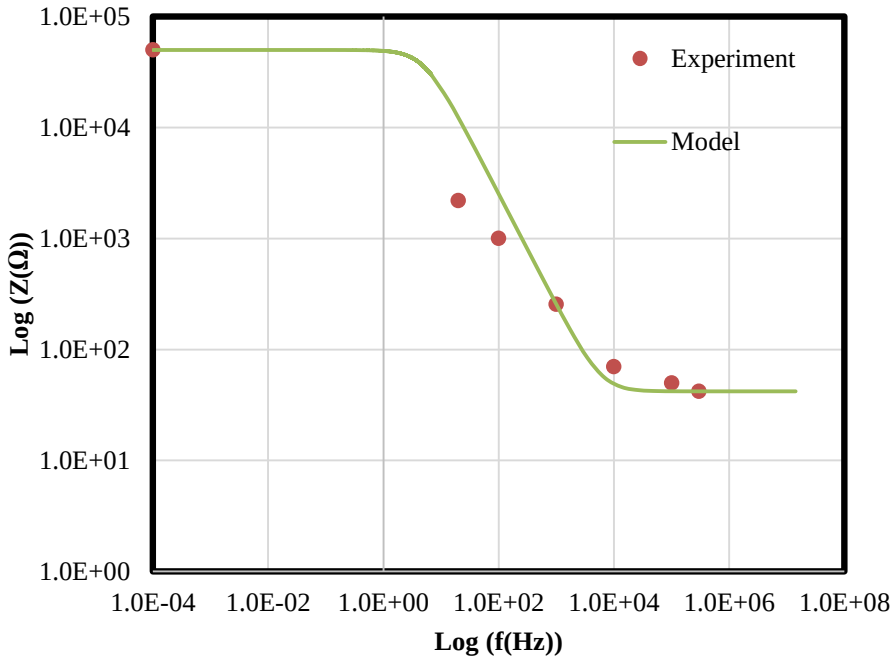


Figure 4.4 Impedance versus frequency for control slurry after mixing

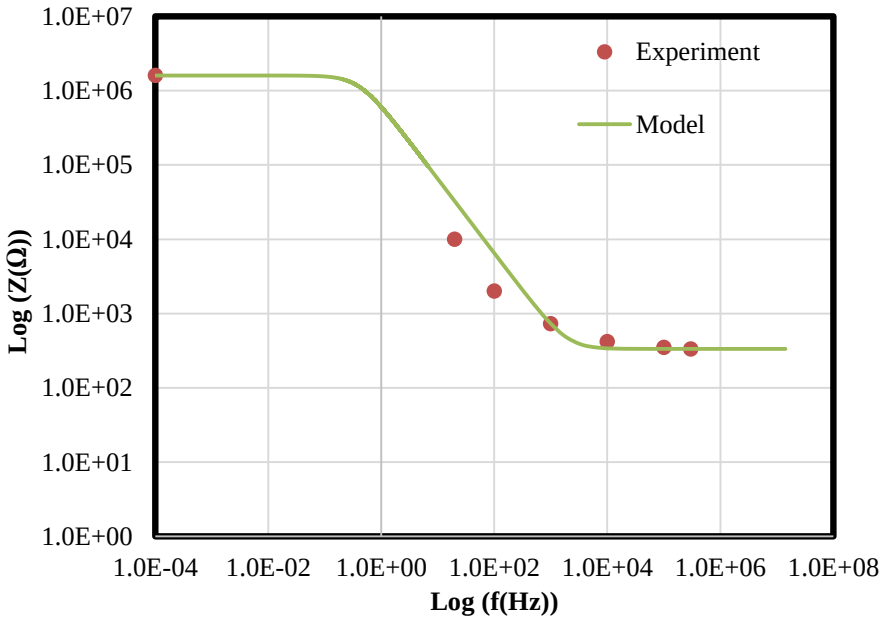


Figure 4.5 Impedance versus frequency for control specimen cured for 14 days in saturated sand

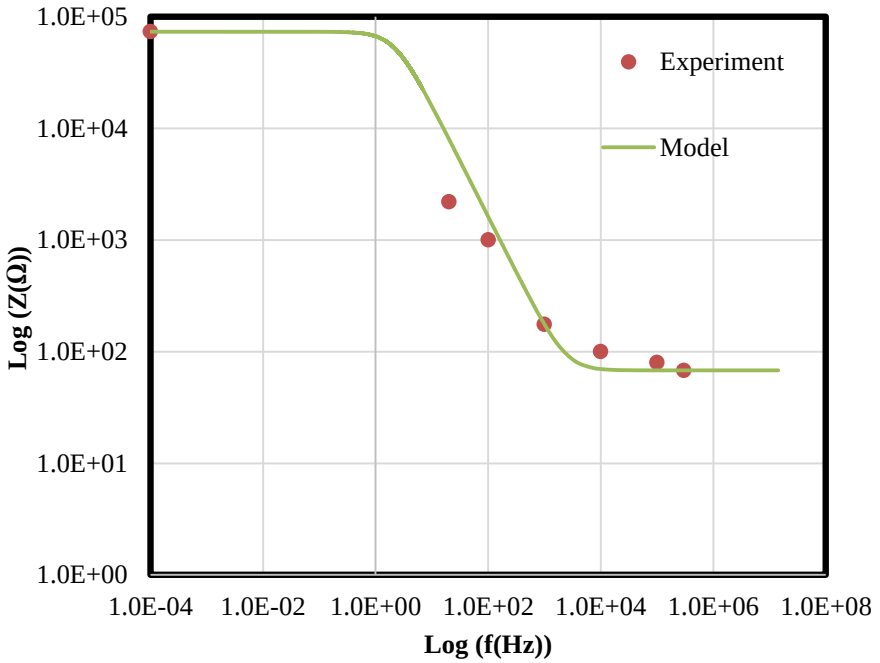


Figure 4.6 Impedance versus frequency for 10% Metakaolin slurry after mixing

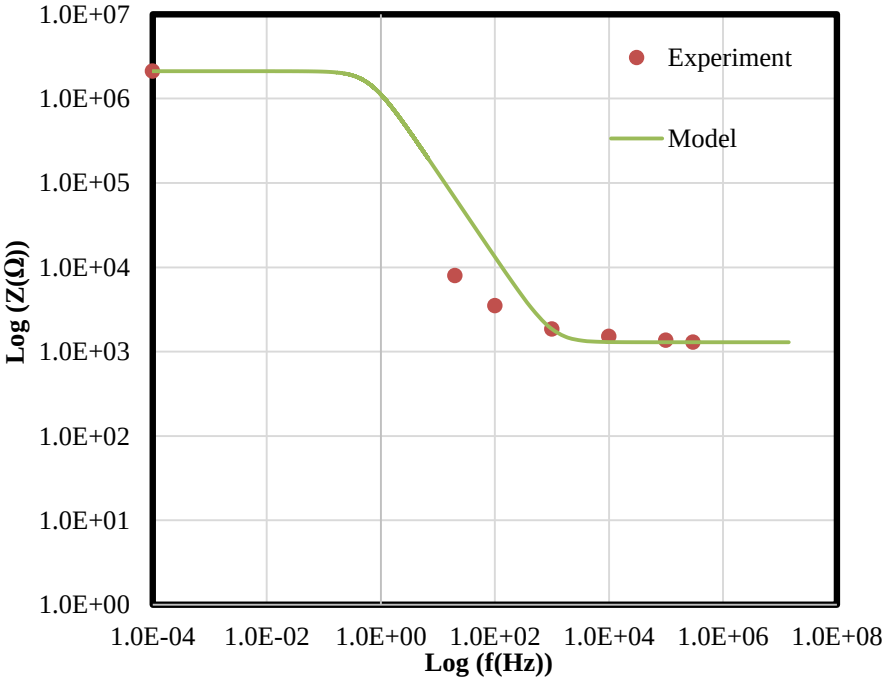


Figure 4.7 Impedance versus frequency for 10% Metakaolin specimen cure for 14 days in sand

Table 4.1 Summary of impedance spectroscopy for control specimen

Control specimen	R_b (Ω)	R_C (Ω)	C_C (Ω)
Fresh Slurry	42	24979	1.26
14 days specimen	334	399833	0.49

Table 4.2 Summary of impedance spectroscopy for 10% Metakaolin specimen

10% Metakaolin	R_b (Ω)	R_C (Ω)	C_C (Ω)
Fresh specimen	68	36676	1.96
14 days specimen	1294	1056081	0.24

Table 4.1 and Table 4.2 summarized the impedence characterization of different mix design under different curing age.

4. 3- Initial Curing

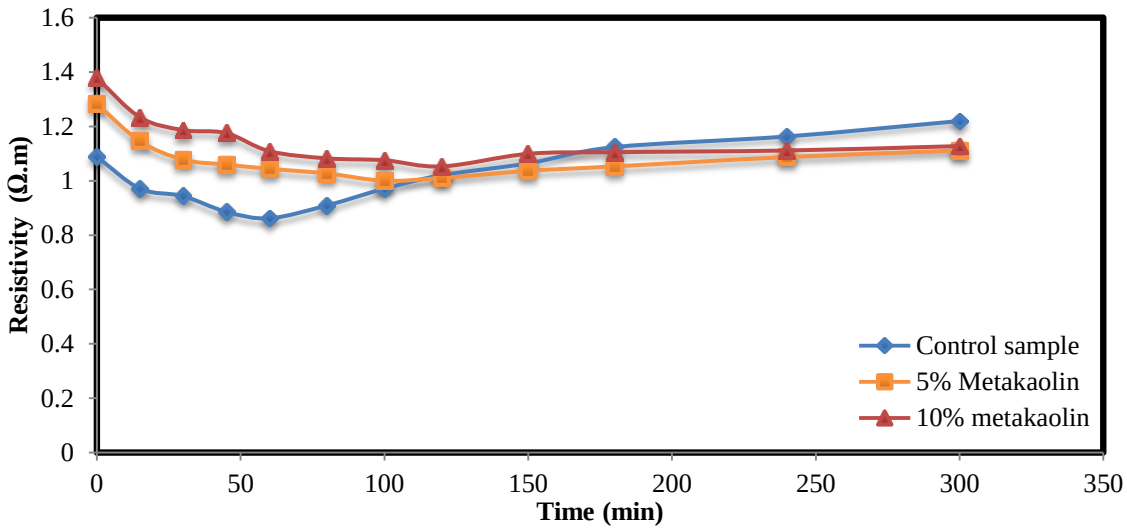


Figure 4.8. Resistivity of control specimen versus 5% and 10% metakaolin specimen

The effect of the addition of 10% and 5% metakaolin to cement slurry was studied during the initial setting and the electrical resistivity was measured up to 5 hours using

the conductivity meter probe. The initial resistivity of the control sample was around 1.1 Ω.m while the initial resistivity of the sample contain 10% and 5% metakaolin was increased by 25% and 16% and reached 1.38 and 1.28 Ω.m. The reason for the increase could be due to the high specific surface of the metakaolin particle, which absorbs more water compared to the cement particle. As a result, there is lower amount of water available for cement particles to react with and as a result less free Ion produced. Absorption of water by the metakaolin particle would control and slow down the hydration of the cement particle and as a result less free Ion exists in the mix, which reduces the conductivity of the cement slurry (Figure 4.8). There is a minimum resistivity observed for all type of mix. Minimum resistivity occurred as a result of highest rate of the hydration for all specimen, however the occurrence time of this minimum resistivity did not coincide for different type of mix. Time to reach the minimum resistivity for control specimen occurred at 60 minutes, while for 5% and 10% metakaolin specimen occurred after 100 and 120 minutes respectively.

4. 4- K Parameter

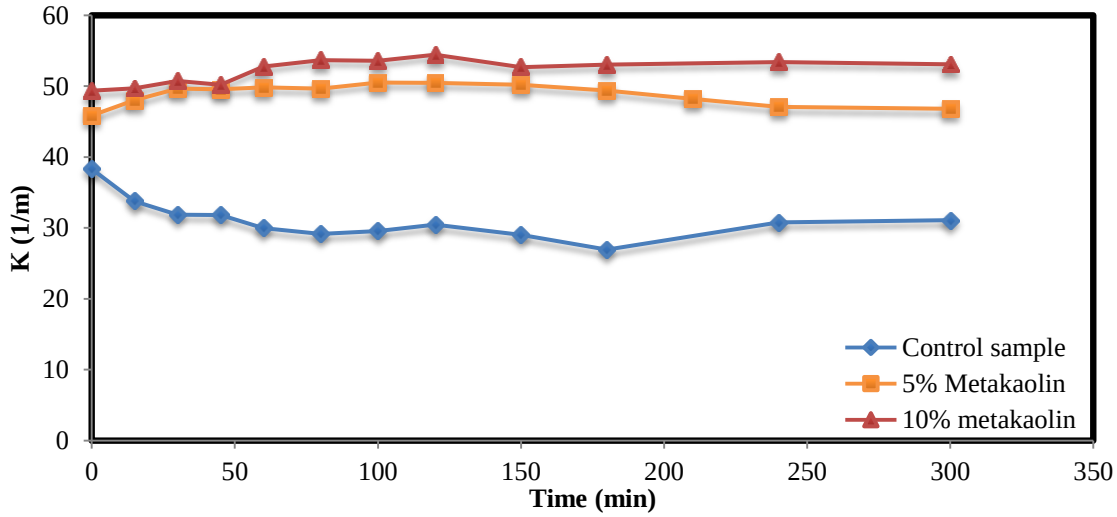


Figure 4.9. Calculation of K for control, 5% and 10% metakaolin specimen form mixing to 3 hours

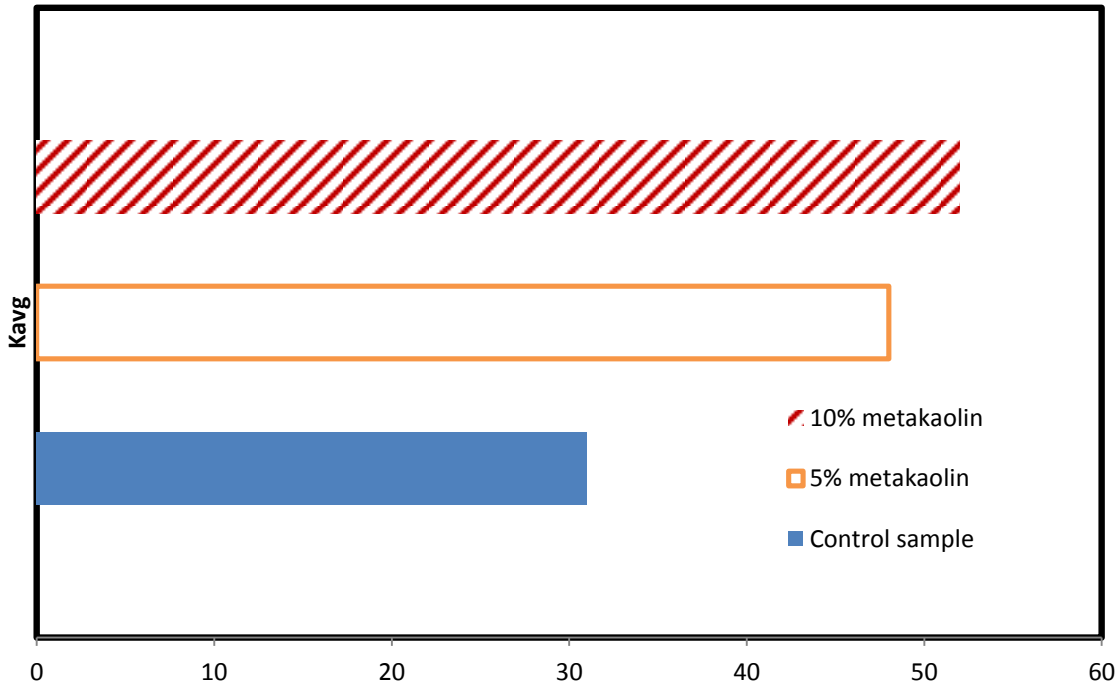


Figure 4.10. K_{avg} for the first 3 hours after mixing

Resistance and resistivity of the samples were measured up to 3 hours. K parameter was calculated during the first 3 hours after mixing the cement. K_{avg} was calculated and used later to calculation resistivity beyond the first 3 hours. Correlation between the minimum reistivity and metakaolin percentage is shown on **Error! Reference source not found.**.

Figure 4.11. Correlation between the minimum resistivity and time correspond to that

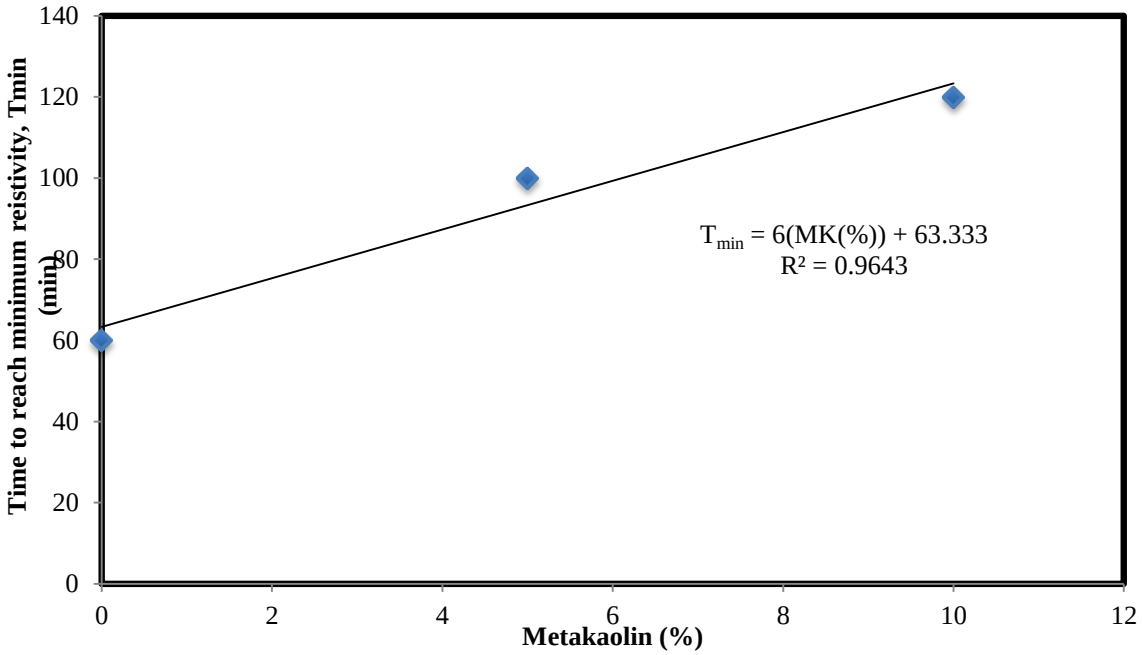


Figure 4.12. Correlation between the metakaolin percentage and Tmin

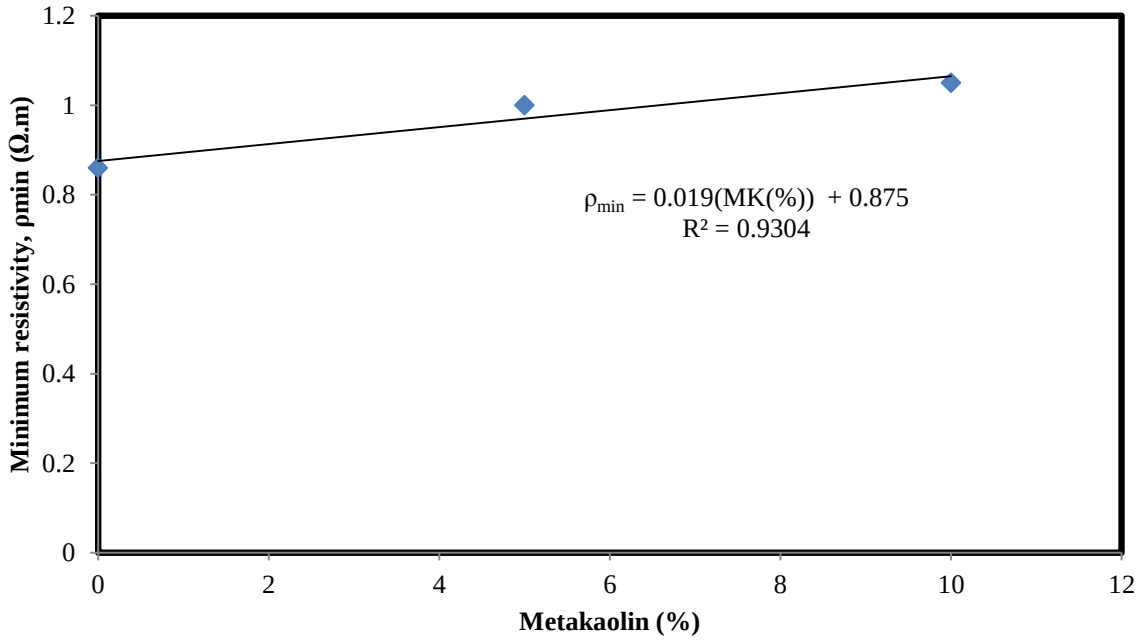


Figure 4.13 Correlation between the minim um resistivity and metakaolin percentage

4. 5- Electrical Resistivity During Curing

Electrical resistances of the samples were measured after pouring the slurries into the mould up to 24hours. Then samples were demoulded and measuring the resistance continued during curing time of specimens under different curing condition.

4. 5. 1- Curing Under 100% Relative Humidity and Room Temperature

Electrical resistances for the samples were measured and K parameters were calculated up to 3 hours, K_{avg} then calculated during 3 hours and then based on the K_{avg}, resistivity of the specimens was calculated by means of the K parameter at any time after the first 3hours.

From Figure 4.14, it can be seen that electrical resistance of the all the samples started to increase during the curing time, which was due to formation of solid phase and decreasing amount of free ion inside the sample. Resistivity of the control sample reached 9.14 Ω.m after 14 days, while resistivity of the samples containing 5 and 10% metakaolin reached 14.68 Ω.m and 21.66 Ω.m, which showed 61% and 136% increase in the amount of resistivity. The bulk conductivity of the samples depended upon two different factors including electrolyte and electronic, since the amount of carbon fiber was the same for all of the mixtures, so the effect of the electronic conduction was the same and the difference was due to the electrolyte. The reason for different electrolyte conduction between the control sample and the samples containing metakaolin was the fact that metakaolin particles absorb water and react with the cement free ion inside the mix, which decreases the amount of conductivity, or in other word increase the amount of resistivity of the samples.

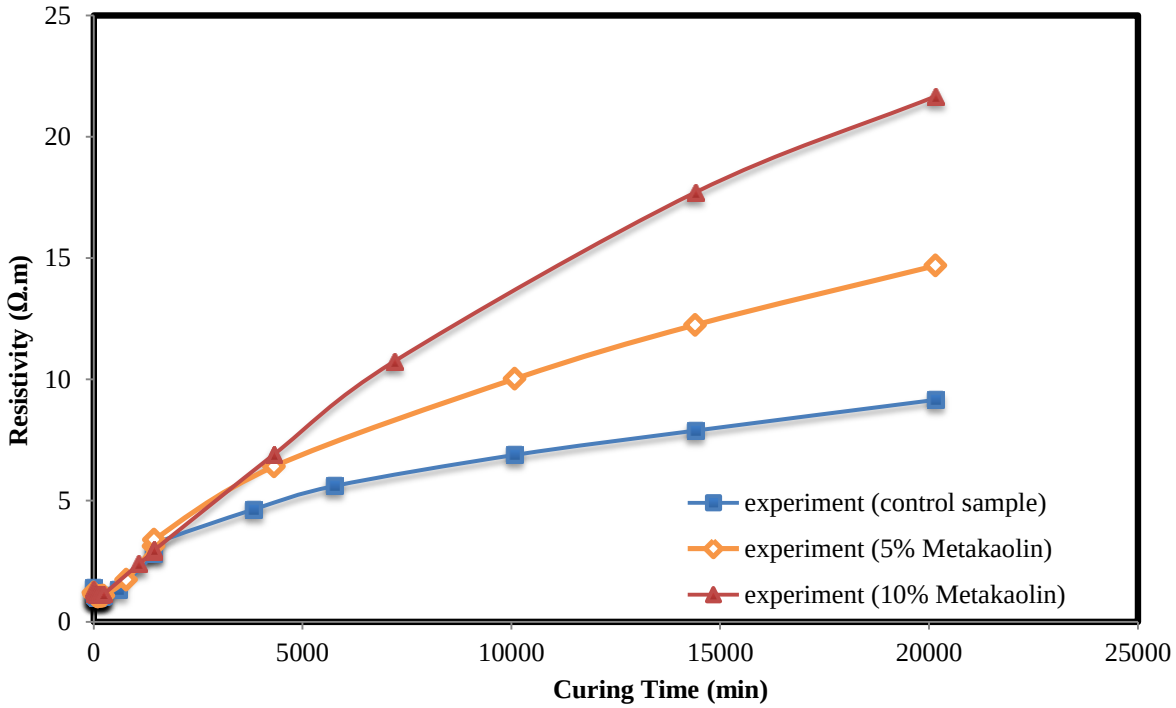


Figure 4.14 Electrical resistivity versus time for samples cured in saturated sand room temperature conditions

From Figure 4.15, it can be understand that even though there was a small amount of weight loss before demoulding the samples could take place, moisture loss was prevented by the saturated sand curing condition. The weight of samples increased in the range of 0.5-2.3% during the 14 days of curing. From the graph it can be seen that samples containing metakaolin absorbed more water in the saturated sand as compared to the control sample.

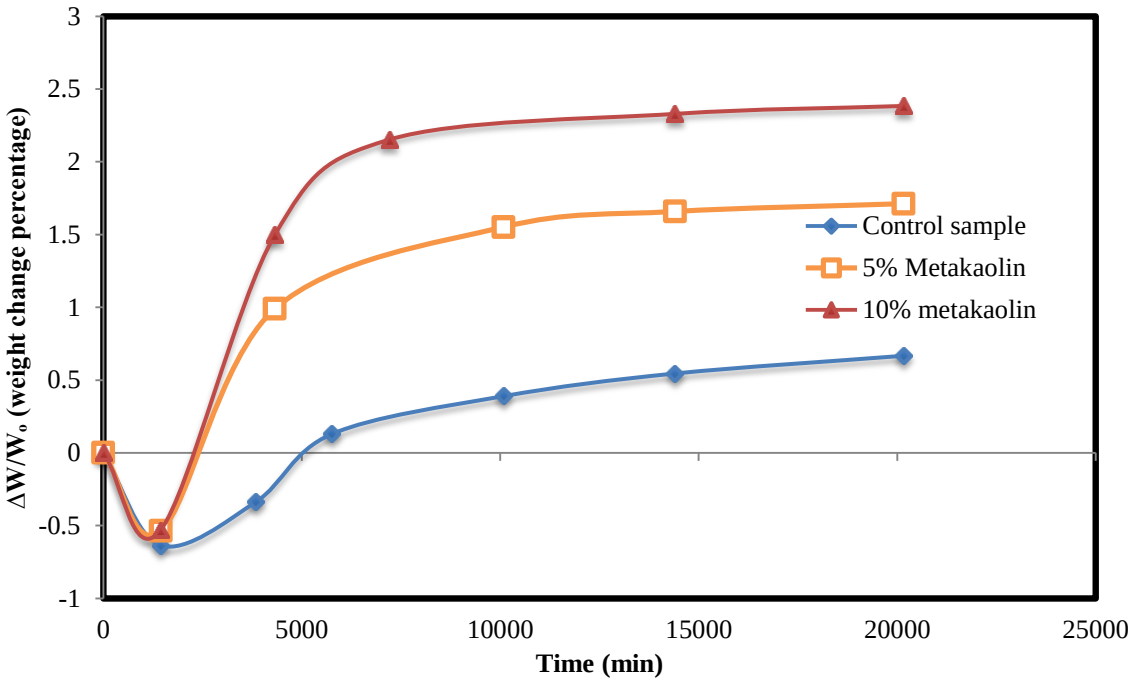


Figure 4.15 Weight change of control, 5 and 10% metakaolin specimen cured in saturated sand

4. 5. 2- Modeling the Electrical Resistivity under 100% Relative Humidity Room Temperature Curing Conditions

Electrical resistivity of the control and metakaolin sample, which were cured in 100% relative humidity condition are modeled with a hyperbolic equation as:

$$\rho = \frac{(t - t_{min})}{(A + B \times (t - t_{min}))} + \rho_{min}\ , \qquad (4\text{-}3)$$

where :

ρ_{min} : minimum resistivity during curing time

T_{min} : time in which the sample reach minimum resistivity

A, B : parameters.

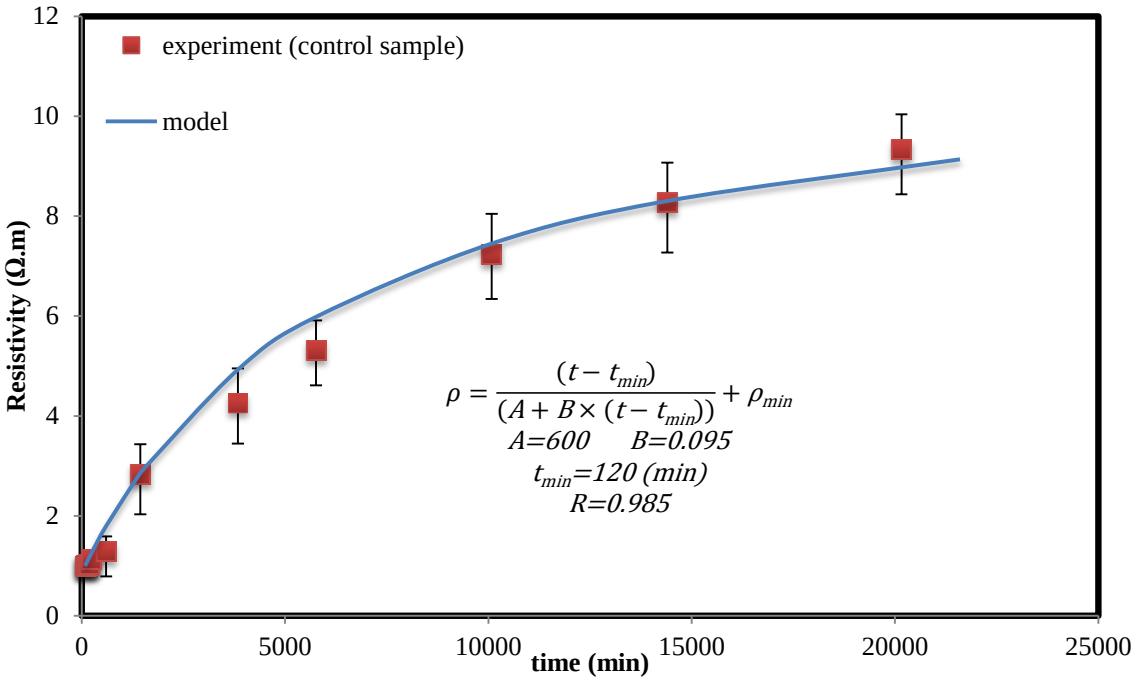


Figure 4.16 experimental versus modeled graph of control specimen during 14 days of curing in saturated sand

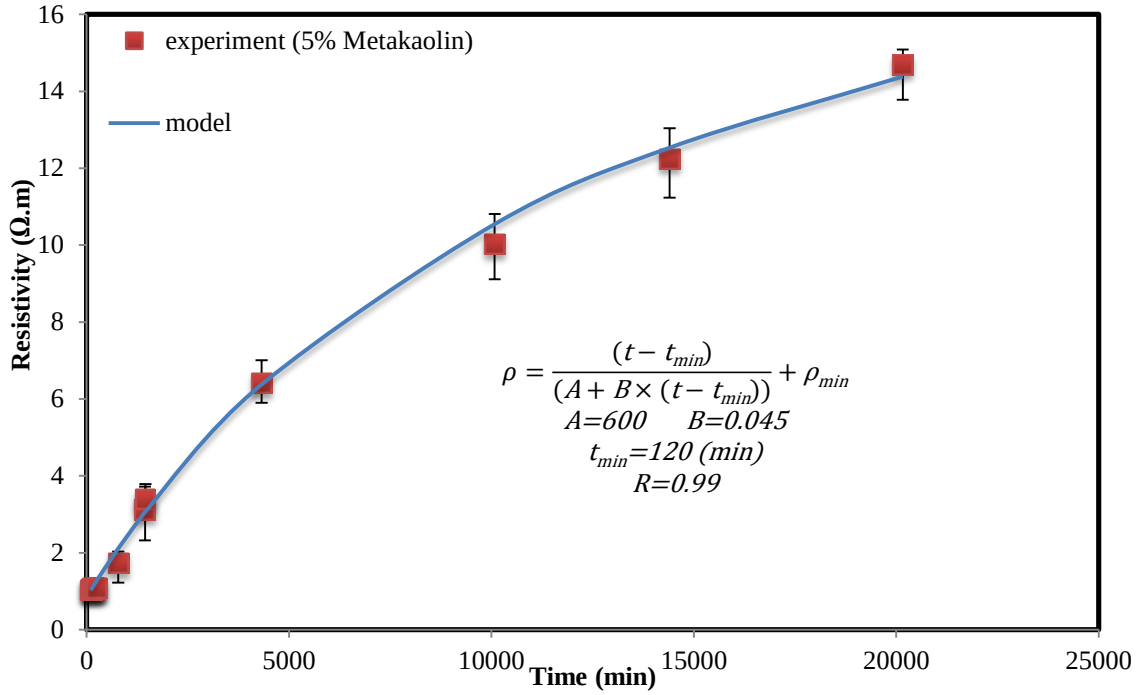


Figure 4.17 experimental versus modeled graph of 5% metakaolin specimen during 14 days of curing in saturated sand

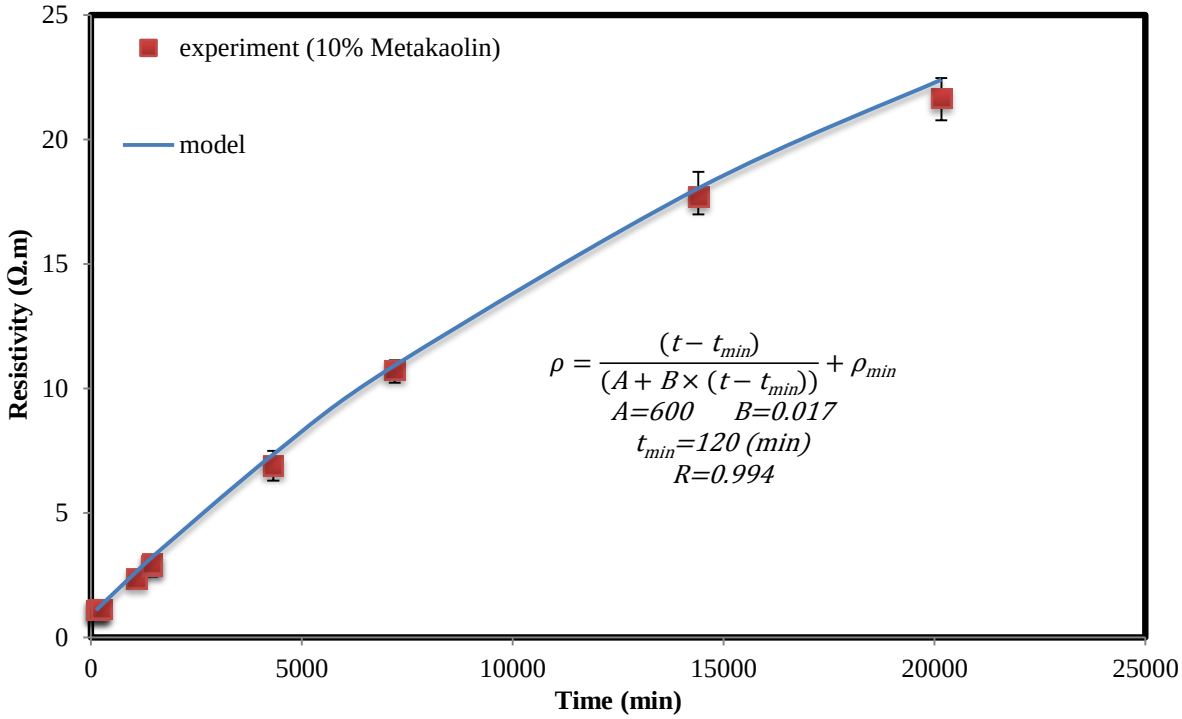


Figure 4.18 Experimental versus modeled graph of 10% metakaolin specimen during 14 days of curing in saturated sand

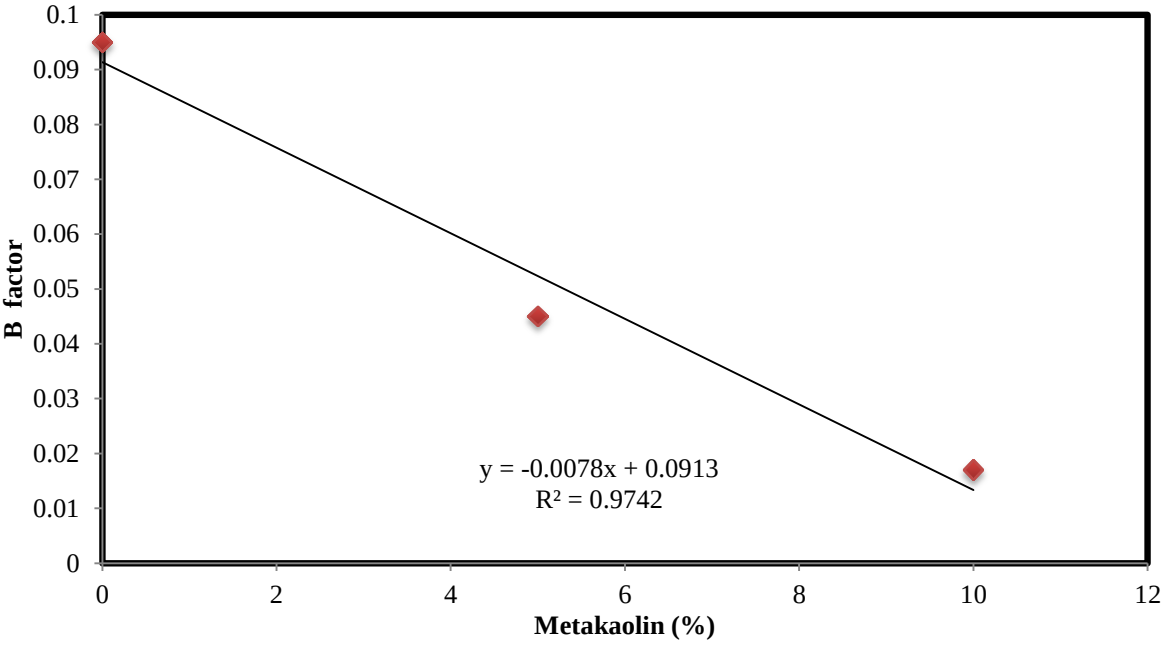


Figure 4.19 Correlation between metakaolin and B factor

For each of the experiment minum of five specimen were tested. From the modeled equations on the graph of control, 5% and 10% Metakaolin it can be understand that the

A parameter is independent of the metakaolin. However, the B parameter was changed by changing the percentage of the metakaolin. In the following graph, B parameter has been correlated and modeled by the liner equation to the percentage of metakaolin (Figure 4.19) as:

$$B = -0.008M + 0.0917\,, \tag{4-4}$$

where :

B: none dimensional factor in the curing model presented before in Eq (4-3)

M: metakaolin percentage.

4. 5. 3- Curing under 100% Relative Humidity and 80 °C

Electrical resistance for the samples were measured and K parameters were calculated up to 3 hours and after based on the K_{avg}, resistivity of the specimens, was then calculated by means of the K parameter.

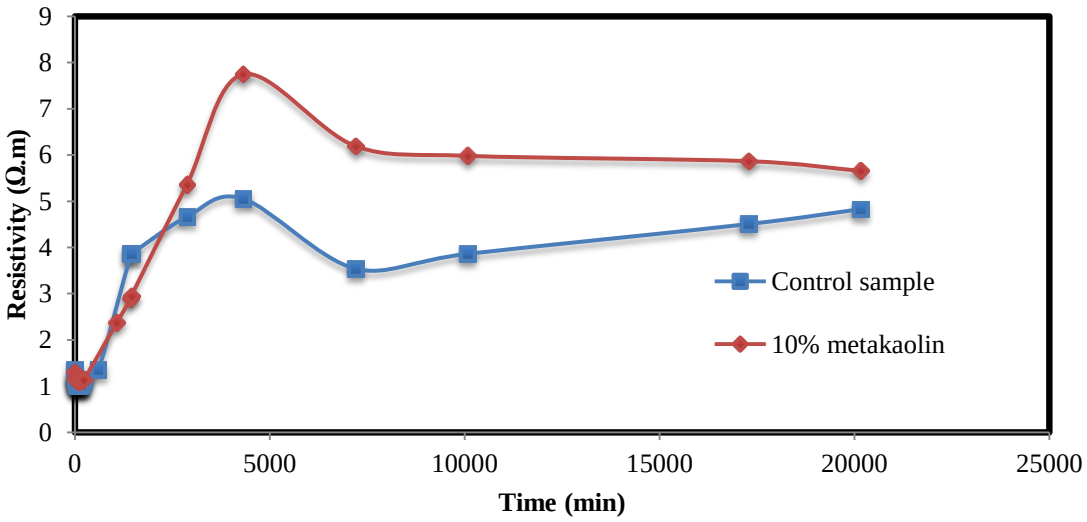


Figure 4.20. Electrical resistivity versus time of specimen cured in sand and under 80 °C

From Figure 4.20 it can be understand that high curing temperature affect the resistivity during curing time by decreasing the resistivity strated after 3 days and

continued up to 5 days of curing, after 5 days resistivity then started to going up until 14 days.

4. 6- Effect of Metakaolin on the Electrical Resistivity under Air Curing Condition

Electrical resistance of the samples was measured after pouring the slurries into the mould up to 24 hours. Samples were then demoulded and measurements continued up to 14 days of curing in air.

4. 6. 1- Curing under the Air

Electrical resistances of the samples were measured and K parameters was calculated until 3 hours. Resistivity of the samples was calculated by means of the K parameter.

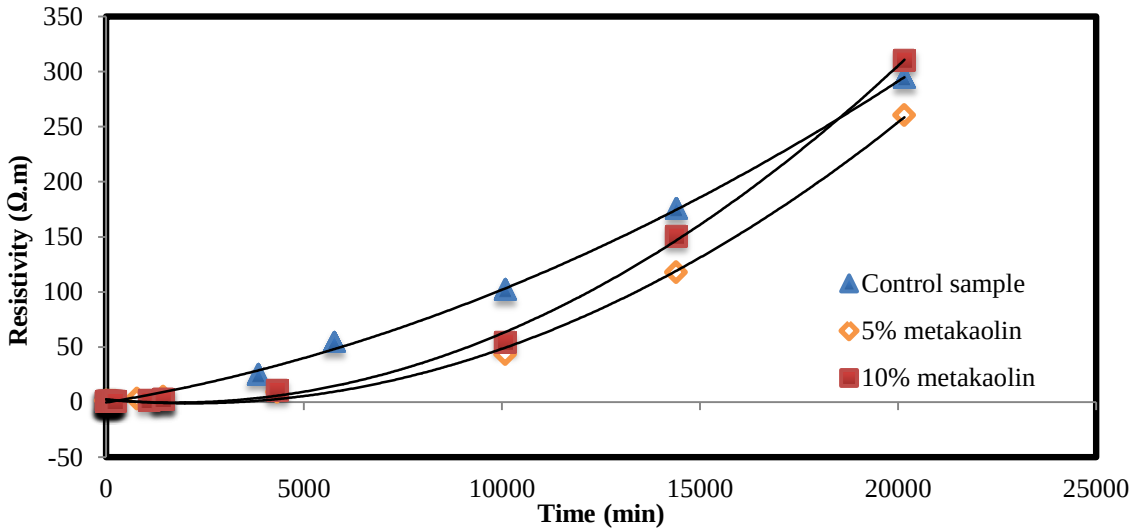


Figure 4.21. Curing of control sample and 5 and 10% of metakaolin in air

Figure 4.21 shows the resistivity change under air curing condition. As it can be seen from the graph, the final resistivity after 14 days of curing was higher than it was under saturated sand curing conidtion. After 14 days of curing in the air, resistivity of the control samples reached the value of 294 Ω.m, as compared to the 9 Ω.m of the control

samples was cured in saturated sand, showed around 30 times higher resistivity. The same happened for the 5 and 10 % metakaolin samples, in which resistivity reached 260 and 310 Ω.m for 5 and 10% metakaolin cured in air, as compared to the same samples that were cured in the saturated sand with resistivity of 14 and 21 Ω.m also showed respectively around 18 and 13 time increase in resistivity. The rate of developing the resistivity for the samples cured in air was changed by using metakaolin, as it can be seen from the Figure 4.21. At any time during curing time and after demoulding, resistivity of control samples were higher as compared to the metakaolin samples, while after 14 days of curing resistivity of sample containing 10% metakaolin exceeded the control sample. Reason for this phenomenon could be due to the weight loss during curing time of the samples. As it can be seen from Figure 4.22, weight loss after 3 days was around 8% and 12.5% for control and 10% for metakaolin samples respectively, while after 14 days, weight loss was around 14% and 17% for control and 10% metakaolin samples respectively. The difference in the weight loss changed from 4.5% to 3%, which was due to the metakaolin particles having a high capacity of keeping moisture inside them, and also considering that the resistivity was so sensitive to the moisture that losing more water for the control samples caused a higher rate of resistivity development at the beginning of the curing time, while later metakaolin samples also lost more water and the final resistivity of metakaolin samples placed higher than the control sample.

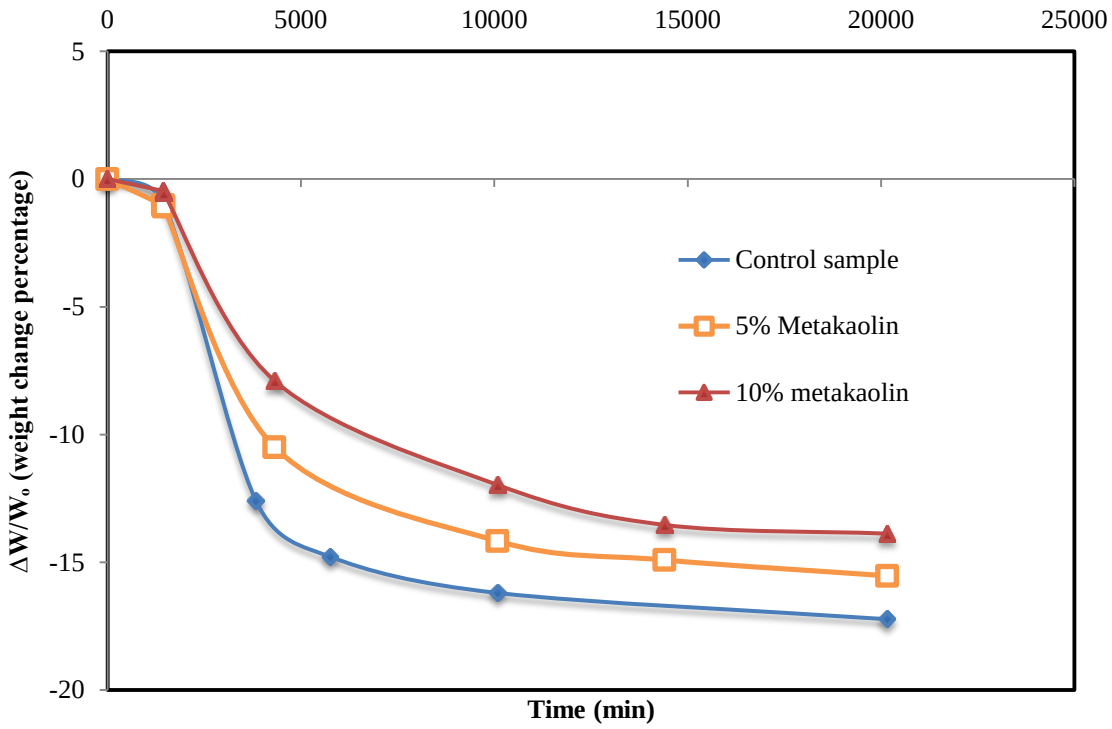


Figure 4.22. Weight change of control and 5 and 10% metakaolin samples in air curing condition

4. 7- Study the Piezoresistivity Characteristic of Oil Well Cement with Addition of Metakaolin

4. 7. 1- Introduction

Electrical sensing properties of the cement with 0.1% added carbon fiber was studied under the compressive strength which is referred to as piezoresistivity. The effect of the addition of metakaolin under different curing conditions and ages has been investigated. Specimens were tested under different curing conditions includes saturated sand condition under room temperature at age of 14 days and 4 months and air cured specimens at the age of 14 days.

4. 7. 2- Study of the Piezoresistivity Resistivity of Samples Cured in Saturated Sand Conditions.

As can be seen from Figure 4.23, Figure 4.25 and Figure 4.27 change in the electrical resistivity versus the compressive strength was plotted for 14 days specimens cured in saturated sand. the figures showed that change in the electrical resistivity started decreasing at first and then increasing up to the failure of specimens. The reason for decreasing in the electrical resistivity of the samples could be due to the fact that applying compression whitin elastic region of specimen, cause elastic volumetric compression which led the conduction length reduced by fiber pushed into closer proximity and as a matter of fact, resistivity to decrease. As the compressive load increased, micro cracks started initiating and the specimen micros structure started evolving. Damage started to propagate in the specimen, and the cement and carbon fiber matrix started to break and cause increase in the specimen resistivity until failure occured. 14 days compression test on the specimens cured in saturated sand showed that the addition of metakaolin increased the piezoresistivity of the specimen at the peak. The control specimen showed the change in relative resistivity of 105% at the peak, while addition of 5% and 10 % metakaolin increased the piezoresistivity of the specimen to 143% and 158%, respectively. From the Figure 4.23, Figure 4.25 and Figure 4.27, it can be concluded that the addition of 5% and 10% metakaolin increased the 14 days compressive strength by 16% and 20% respectively. cracks also captured either visually or by sound. From Figure 4.24, Figure 4.26 and Figure 4.28 it can be conclude that cracks were correspond to the peack point of the slope of farctional change in reistivity versus stress.

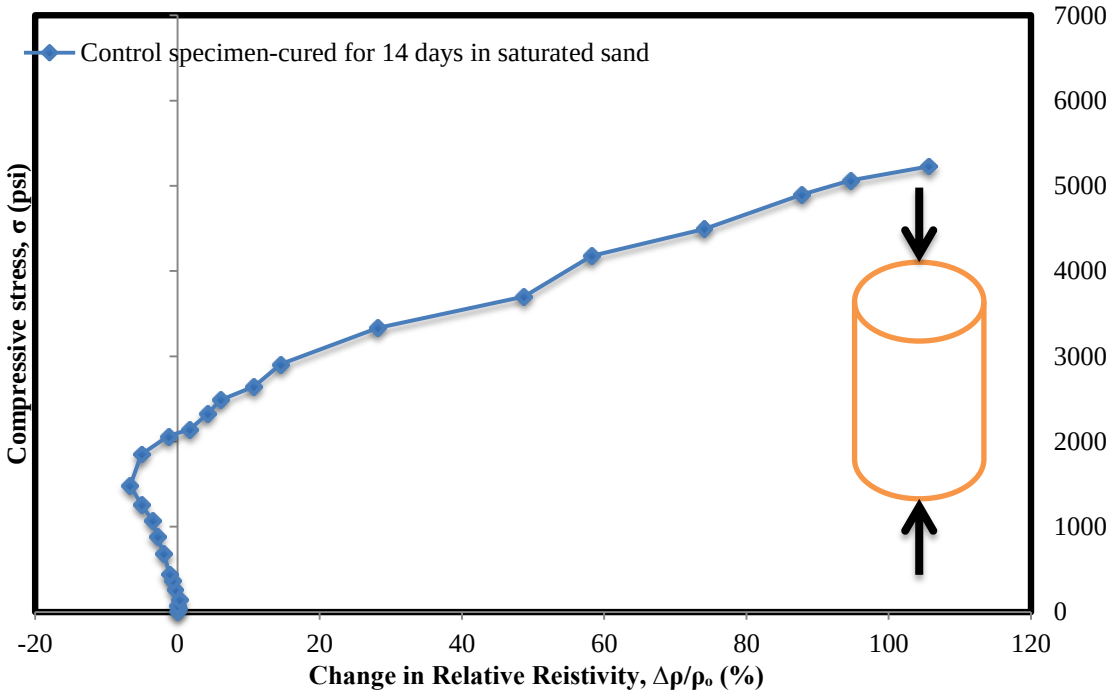


Figure 4.23 Control specimen-cured for 14 days in saturated sand

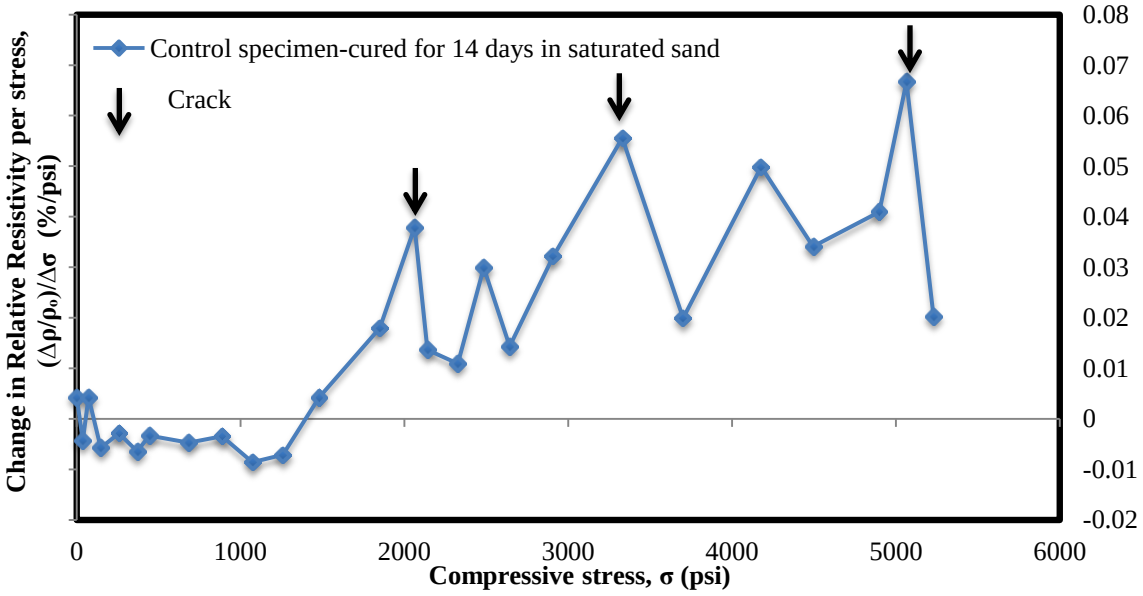


Figure 4.24 Slope of change in relative reistivity per unit of stress versus compressive stress

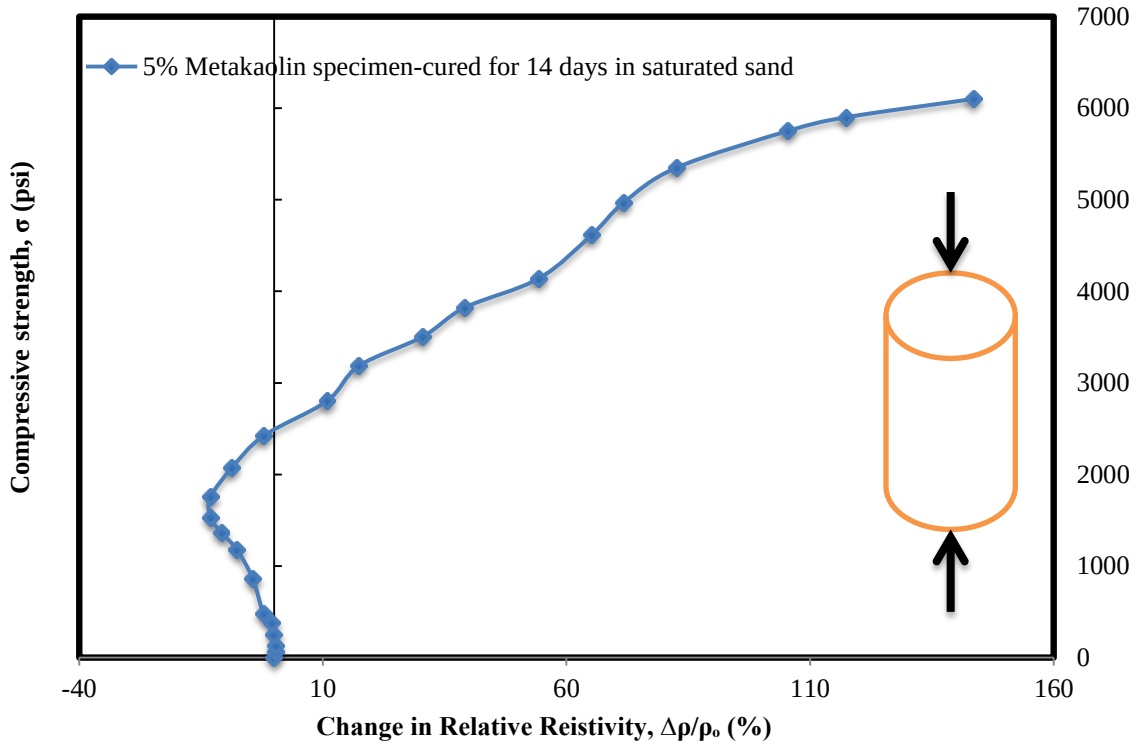


Figure 4.25 5% Metakaolin specimen-cured for 14 days in saturated sand

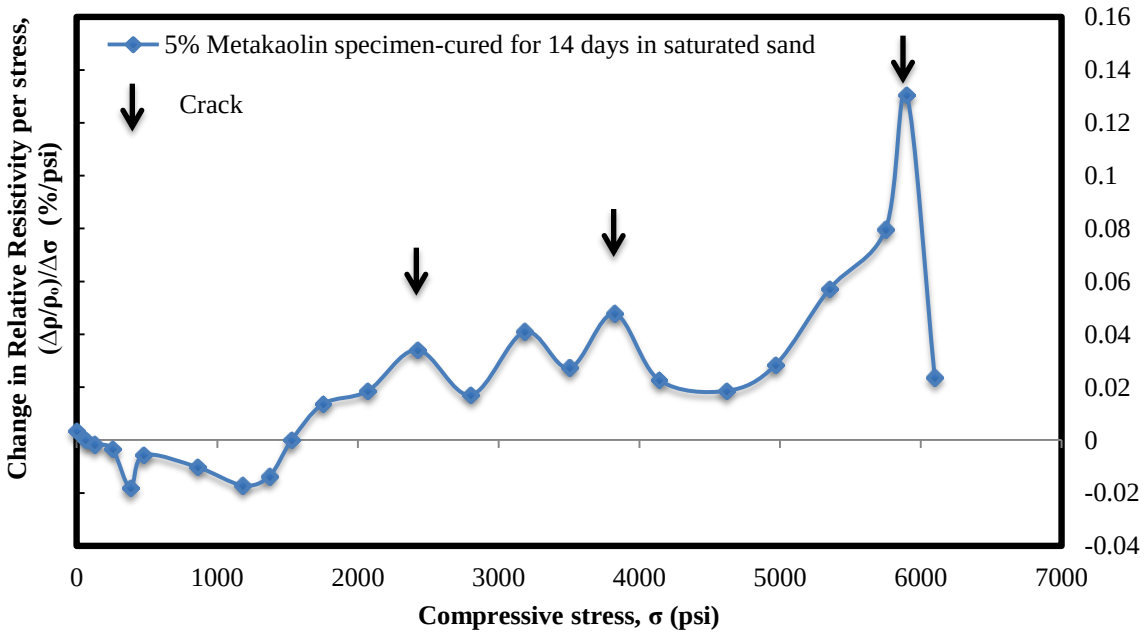


Figure 4.26 Slope of change in relative reistivity per unit of stress versus compressive stress

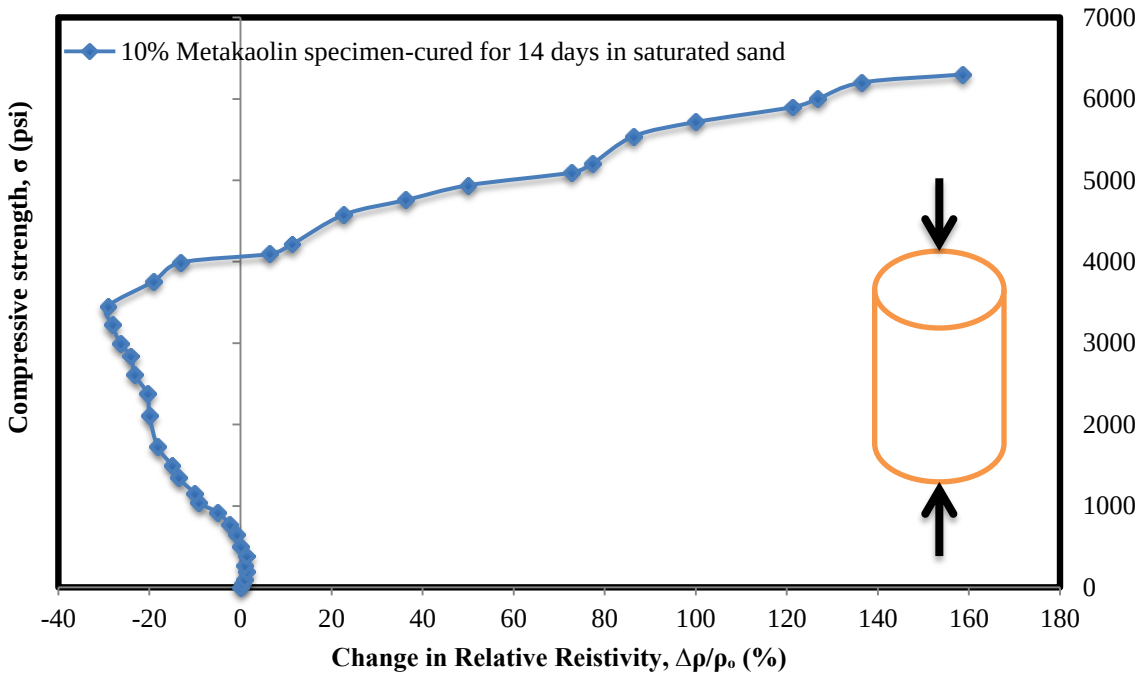


Figure 4.27 10% Metakaolin specimen-cured for 14 days in saturated sand

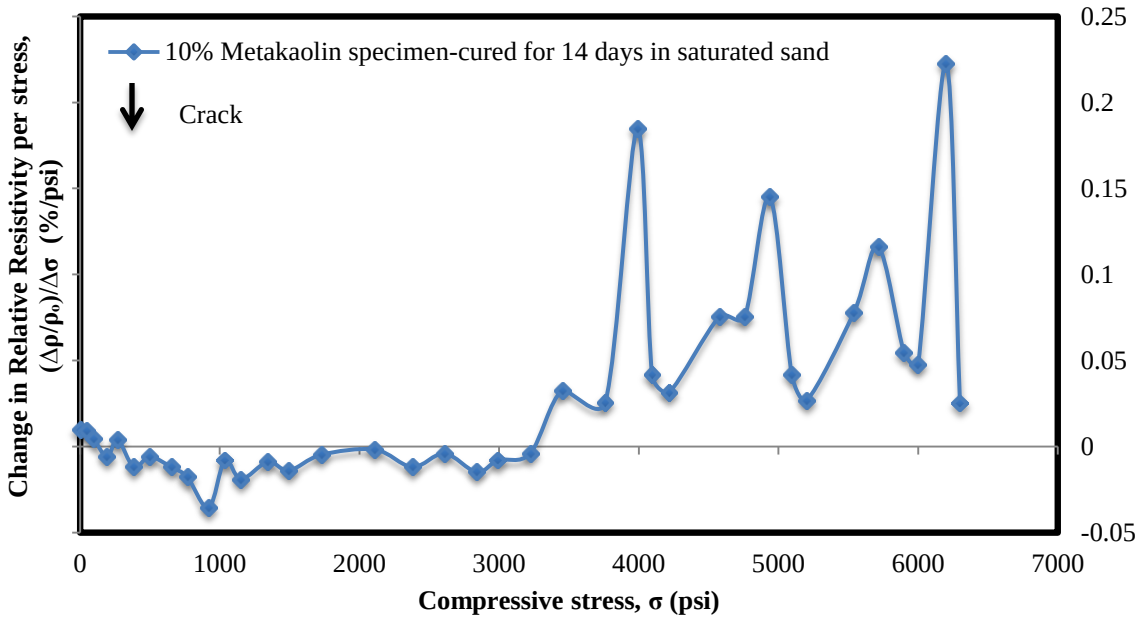


Figure 4.28 Slope of change in relative reistivity per unit of stress versus compressive stress

Figure 4.29, Figure 4.30 and Figure 4.31 showe the change in electrical resistivity under the compressive loading for specimens cured for 4 months on saturated sand. Change in the electrical resistivity under the compressive load showed the same trend as the 14 days sample, with resistivity decreasing during the initial stage of loading and then increasing up to failure. As discussed before, the reason for such a trend is the elastic volumetric compression for decreasing the change in relative resistivity and initiation of micro crack followed by the major crack could be the reason for increasing in the change in relative resistivity up to failure of the specimen. After 4 months of Curing under saturated sand it can be seen that the addition of metakaolin increased the piezoresistivity of the specimen. As it can be seen, the control specimen showed the change in relative resistivity of 131% while the addition of 5% and 10% metakaolin increased the change in relative resistivity at peak load to 190% and 222%, respectively. Also, the addition of 5% and 10% metakaolin increased the compressive strength of the specimen cured for 4 months in saturated sand by 6% and 10% respectively. compaing the different curing age conition, it can be concluded that higher curing age increase the sensing properties of the specimens at the peak load. compaing the grapsh of 14 days and 4 months cured specimen showed that piezoresistivity increased by 25%, 33% and 40% for control specmen, 5% metakaolin and 10% metakaolin specmen respectively. it can be also conclude that curing age has more significant effect on the piezoresistivity on metakaolin specimen.

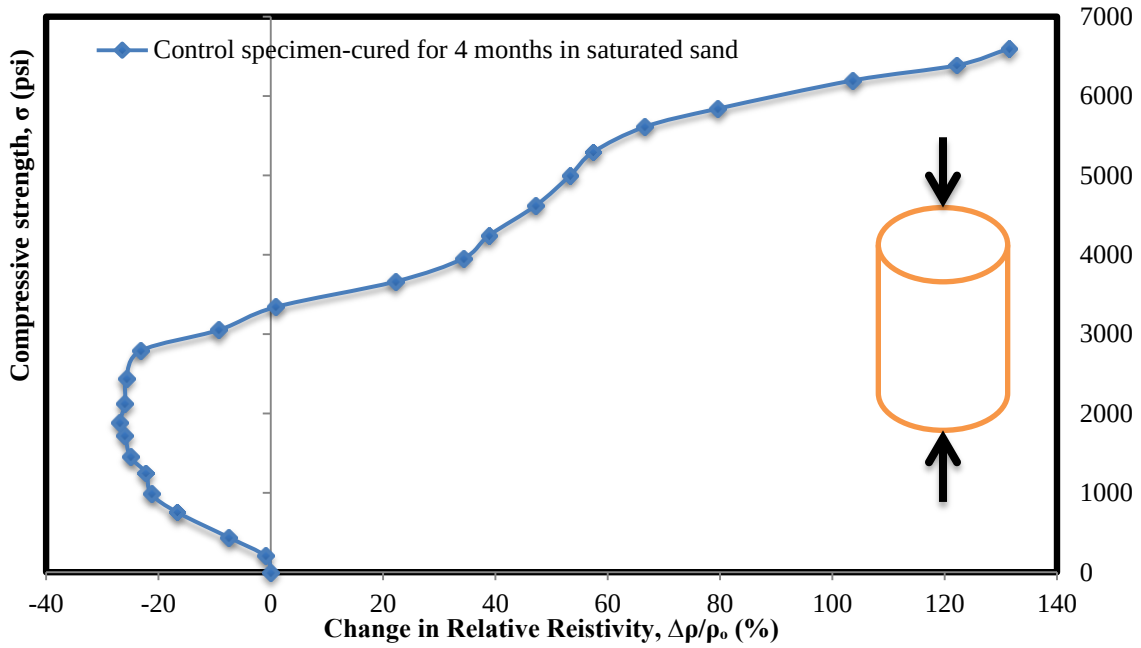


Figure 4.29 Control specimen-cured for 4 months in saturated sand

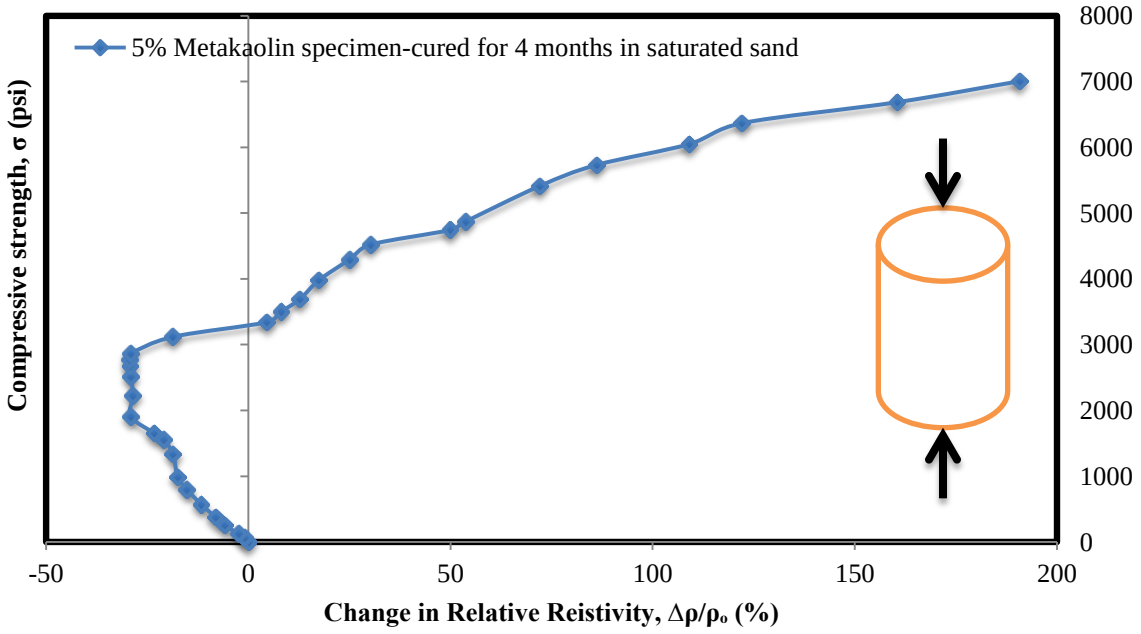


Figure 4.30 5% Metakaolin specimen-cured for 4 months in saturated sand

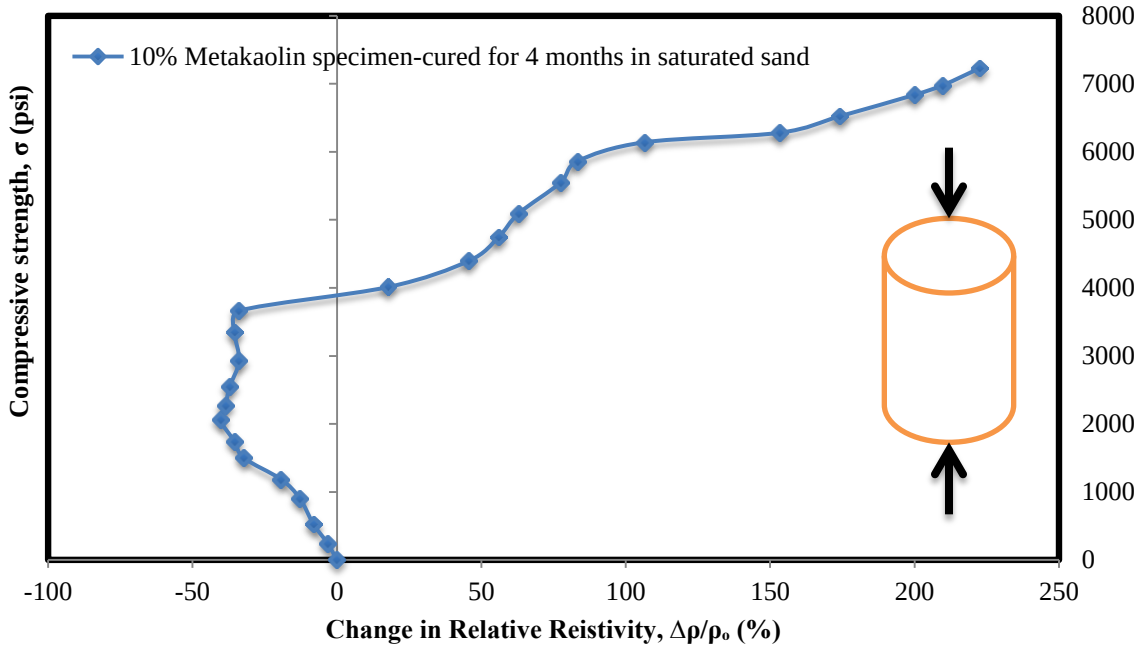


Figure 4.31 10% Metakaolin specimen-cured for 4 months in saturated sand

Figure 4.32, Figure 4.33 and Figure 4.34 showed change in the electrical resistivity specimen cured in air for 14 days under compression load. From the figures it can be understood that, unlike specimens cured in saturated sand, electrical resistivity didn't decrease during the initial stage of loading and start increasing from the start of loading up to failure. The reason could be due to the fact that the specimen cured in air lost weight and the weight loss was because of water evaporation from the surface of the specimen, which left pores inside the specimen. During compressive loading of the specimen, micro cracks started to occur at the very beginning of loading the specimen, the initiation of micro cracks caused the resistivity to increase, simultaneously volumetric compression which cause the fiber reach to the closer proximity and is the reason for reduction in the reistivity is also exist, however the effect of damage propagation because of the micro crack have been more intense. The addition of metakaolin did not change the piezoresistivity of the specimen cured in air as can be seen from the figures, the change in

relative resistivity of control, 5% and 10% metakaolin specimen was around 50 to 60% and compressive strength of all the specimens were almost at the same level. The summary of the test result was also represented in the Table 4.3.

RI_{24} has been defined as an index to correlate with the compressive strength of the specimen at different curing conditions and ages. RI_{24} defined as:

$$RI_{24} = \frac{\rho_{24} - \rho_{min}}{\rho_{min}}. \quad (4\text{-}5)$$

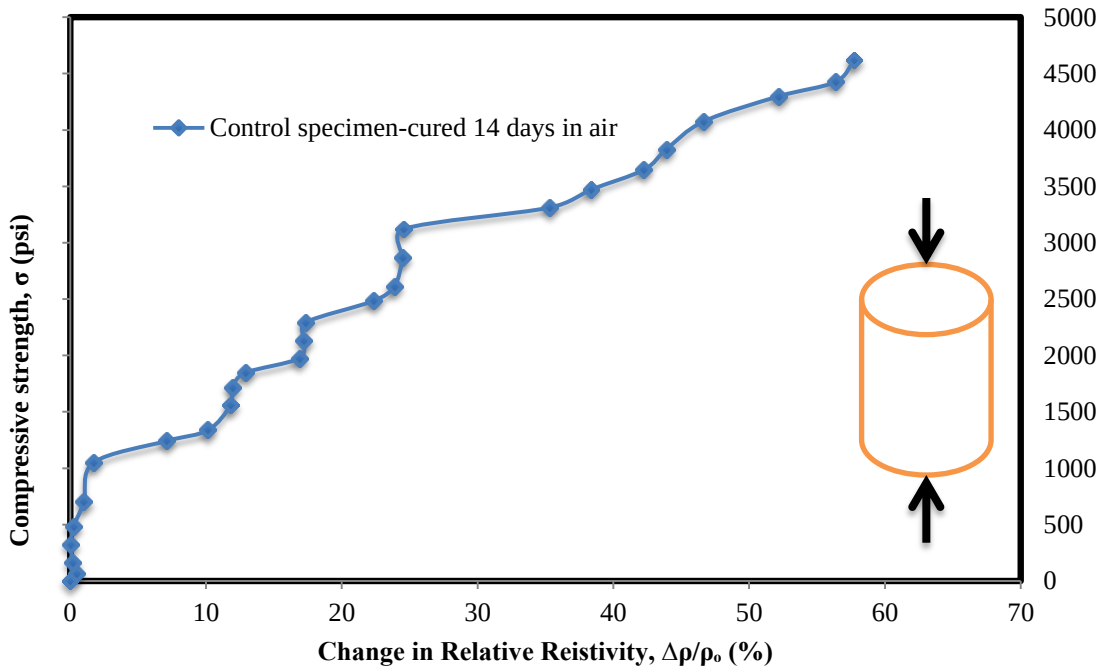


Figure 4.32 Control specimen-cured for 14 days in air

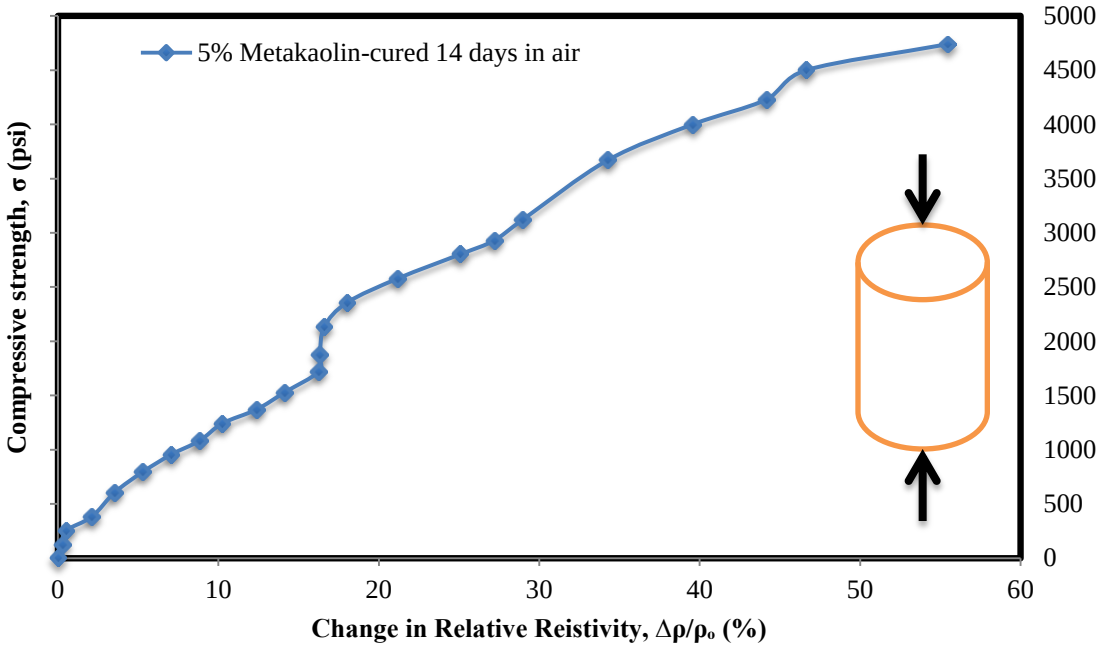


Figure 4.33 5% Metakaolin-cured for 14 days in air

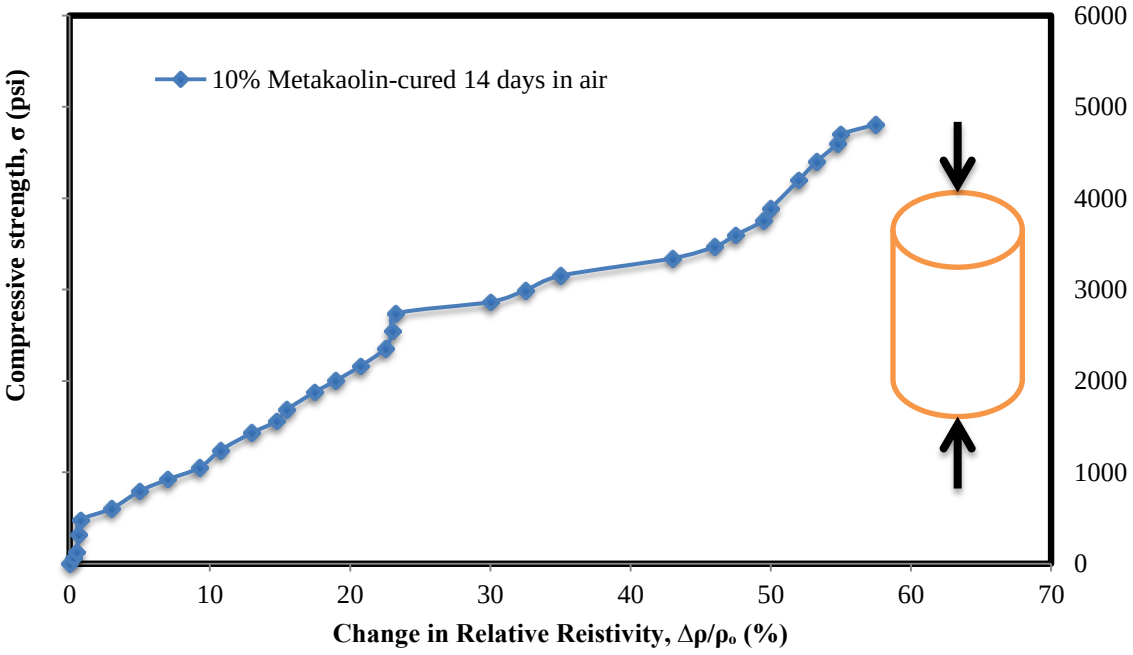


Figure 4.34 10% Metakaolin-cured for 14 days in air

Table 4.3 Summary of RI_{24} calculation and compressive strength for different curing condition

	ρ_{min}	ρ_{24}	$\frac{(\rho_{24}-\rho_{min})}{\rho_{min}}$	14 days sand cured (psi)	4 months sand cured (psi)	Air cured (psi)
Control sample	0.86	2.31	2.31	5230	6600	4617
5% Metakaolin	1	3.19	3.19	6100	7000	4740
10% Metakaolin	1.05	3.6	3.50	6300	7230	4810

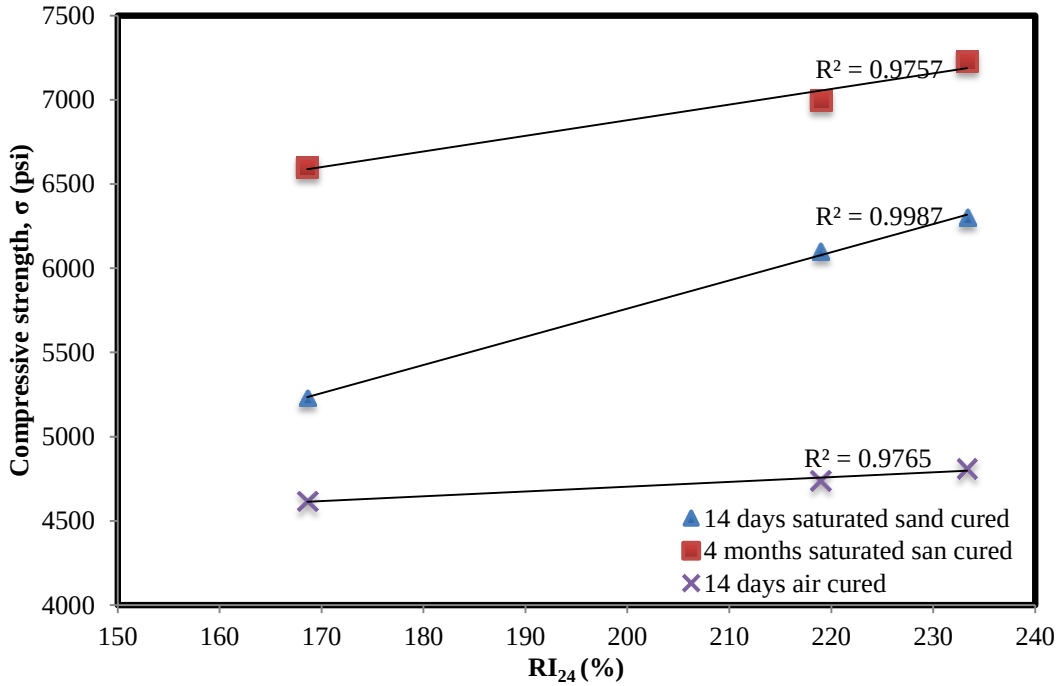


Figure 4.35 Correlation between RI_{24} and compressive strength

For specimens under different curing ages and conditions RI_{24} was calculated. Figure 4.35 showed that RI_{24} had direct correlation to the compressive strength of the specimens. Compressive strength and electrical resistivity development depends on the hydration process and resistivity change used as a parameter to monitor the resistivity since it related to the amount of free ions and change by free ion consumption during

hydration process, the more the hydration of cement progressed it would less path for electrons to pass throw the slurry. Table 4.3 showed the summary of RI_{24} for control specimens and 5% Metakaolin and 10% metakaolin specimens under different curing conditions. From Figure 4.35, it can be understand that, except 14 days air cured specimen, the rest of the specimens showed liner correlation with the RI_{24} index. The 14 days Air cured specimen underwent different curing condition which affect its strength properties.

4. 8- Summary

The following conclusions are taken from the above discussions:

1. Impedance spectroscopy test has proven that 300kHz of frequency would almost eliminate the effect of contact resistance
2. Hydration has been characterized by electrical resistivity for OWC and Metakaolin added mix.
3. Resistivity of the specimens cured under saturated sand increased up to 20 times, while resistivity of the specimens cured in air increased up to 300 time as compared to the their initial respectively.
4. Addition of 10% metakaolin increased the initial resistivity of the specimen by 25%.
5. Addition of 5% and 10% metakaolin increased the piezoresistivity effect under the compressive loading respectively by 35% and 50% at 14 days, and 45% and 68% after 4 months of curing.
6. Curing age increases the piezoresistivity of the specimen in the range of 25 to 40% with higher effect on the metakolin specimens.

7. RI_{24} was used as an index to predict the compressive strength and improvement of compressive strength for control and the metakaolin specimen.

Chapter 5

5- Oil well Contamination

5. 1- Introduction

In reality the oil well cement failure occured not because of cement compressive failure. Many other failure mechanisms in the oil well cement happened as a result of secondary effect phenomenon. Oil wells usually constructed in the soils have a high amount of hydrocarbon. An amount of high hydrocarbon increases the possibility of cement contamination from the surrounding formation. Likelihood of this incident increases the need of study of the oil well contamination. Oil wells undergo different loading patterns during their life-times that might not necessarily be in the form of compression. Cement/casing interface is one of the weak points of the oil wells, and failure due to interface could have a detrimental impact on the society and environment. The main purpose of this chapter is to study the effect of contamination on the oil well cement, characterize the interface behavior between the casing and cement by means of electrical resistivity.

5. 2- Effect of Oil Contamination on the Electrical Resistivity During Hydration

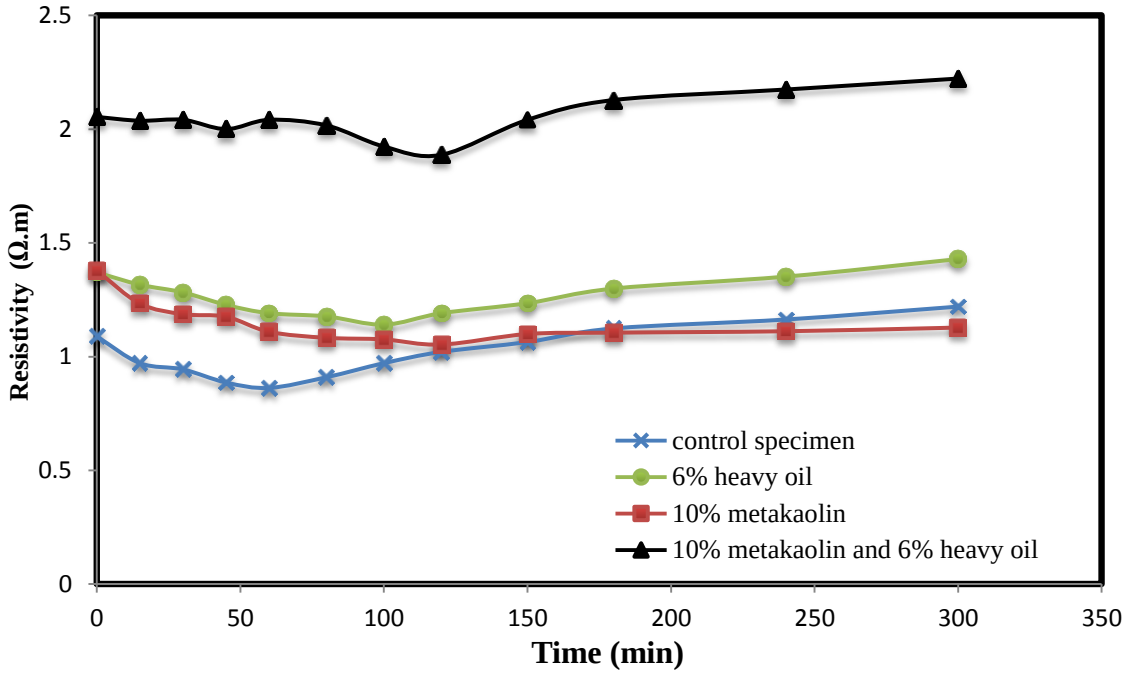


Figure 5.1 Monitoring the resistivity of control specimen versus 4% heavy oil and 10% Metakaolin and 4% heavy oil with 10% metakaolin specimens from the mixing to 3 hours

The main type of contamination that can happen for the oil well cement would be hydrocarbon. Effect of contamination on the initial resistivity and the piezoresistive properties of oil well cement have been investigated.

Conductivity of specimens containing 6% heavy oil, 10% metkaolin and 6% heavy oil and 10% metakaolin along with the control specimen, were measured from the initial mix up to 5 hours, with water to cement ratio fixed for all the mix at 0.45. From the Figure 5.1, it can be inferred that contamination of 6% heavy oil increased the initial resistivity by 26% from 1.09 Ω.m to 1.37 Ω.m. The addition of 10% metakaolin to the control specimen increased the initial resistivity by 25%. Addition of 10% metakaolin to the contaminated specimen increased the initial resistivity by 50% and adiition of 10%

metakaolin and 6% heavy oil increased the initial resistivity by 88%. Minimum time corresponding to the minimum resistivity for the control specimen occured at 60 minutes after mixing, for the 6% heavy oil contaminated specimen it occurred around 80 minutes after mixing, and for 10% metakaolin and 10% metakaolin with 6% heavy oil specimen it occurred around 120 minutes after mixing Figure 5.2.

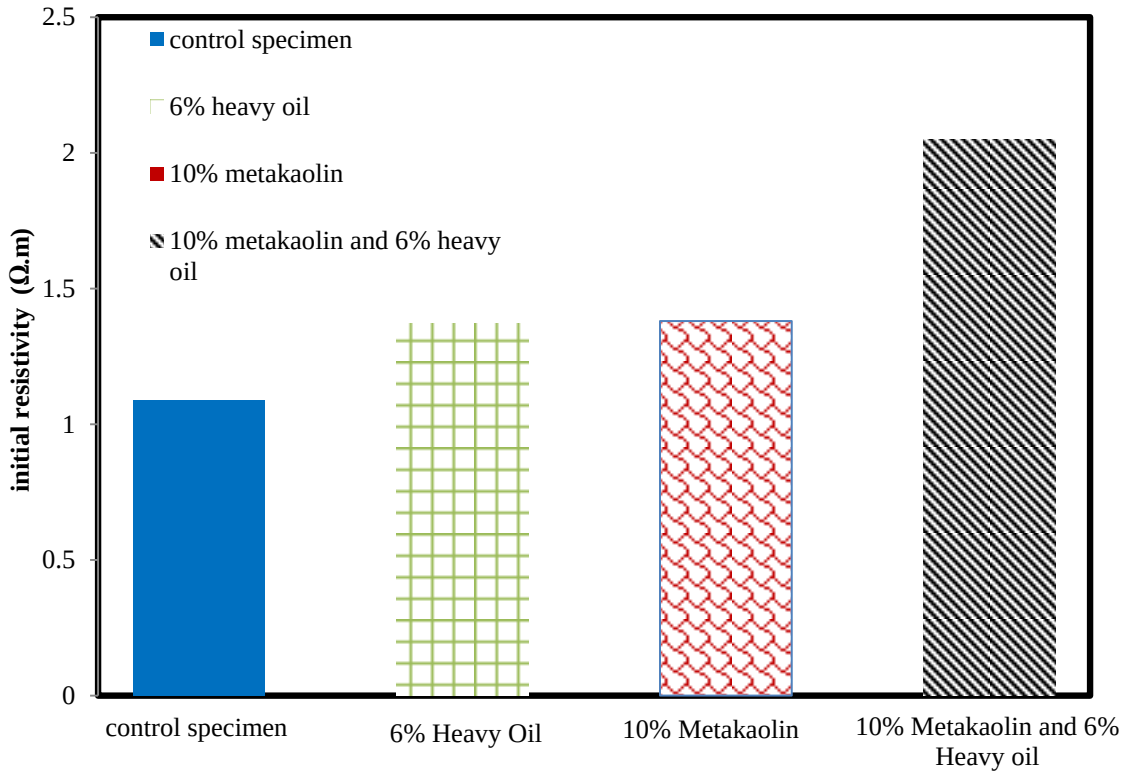


Figure 5.2 Comparison of initial resistivity of control specimen with 4% heavy oil contaminated specimen and 4% heavy oil with 10 % metakaolin specimen

5. 3- Contamination Effect on the Piezoresistive Properties of Oil Well Cement

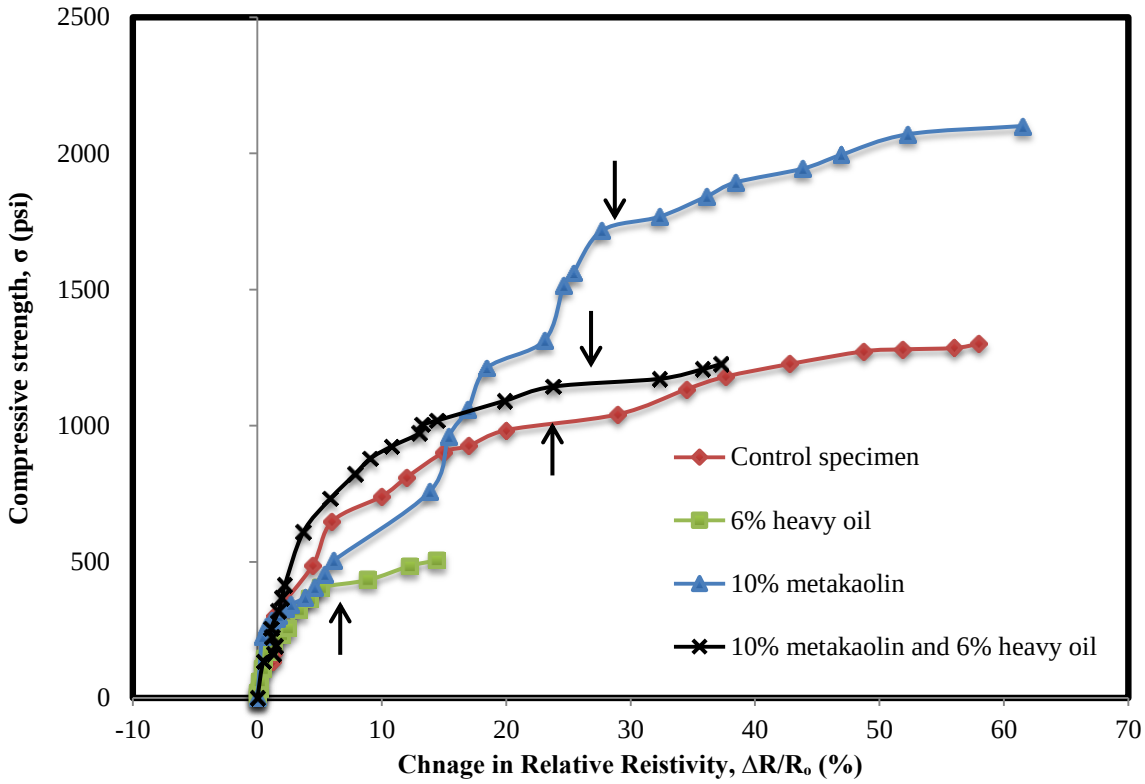


Figure 5.3 Piezoresistivity change due to the effect of contamination and metakaolin

One day Compressive strength versus change in relative resistivity of the control specimen, 6% heavy oil, 10% metakaolin, and the combination of 6% heavy oil with 10% metakaolin were tested. From Figure 5.3, it can be understood that the addition of 6% heavy oil changed the piezoresistive behavior of the oil well cement. change in relative resistivity for the contaminated specimen was about 14% at the peak and for the control specimen it was about 60%, four times higher than of the contaminated specimen. The addition of the 10% metakaolin did not significantly change the change in relative resistivity for a 1 day old specimen at the peak load as compared to the control specimen,

and both showed a piezoresistivity of about 60%, however, 1 day compressive strength increased by 62%. The specimen made with 6% heavy oil and 10% metakaolin improved the piezoresistive and sensing properties of the contaminated oil well cement and increased the change in relative resistivity by almost 2.6 times from 14% to 37%.

5. 4- Cement and casing interface failure

Not all the time failure in the oil well happened due to the compressive failure of cement. Many type of earlier failure could in the oil well cement was attributed to the cement/casing interface failure which increase the surge of study in this field.

Change in the electrical resistivity used as an index to in order to correlate the interface loss between the cement and casing, in this part 5/8" unthreaded rod were used. Rod was loaded and the amount of shear stress was calculated based on the amount of force using the Eq (5-1):

$$\tau = \frac{F}{2\pi r h}, \tag{5-1}$$

where :

τ: shear stress applied on the interface,

F: horizontal force applied on the casing,

r: radius of casing,

h: length of the rod embedded inside the cement.

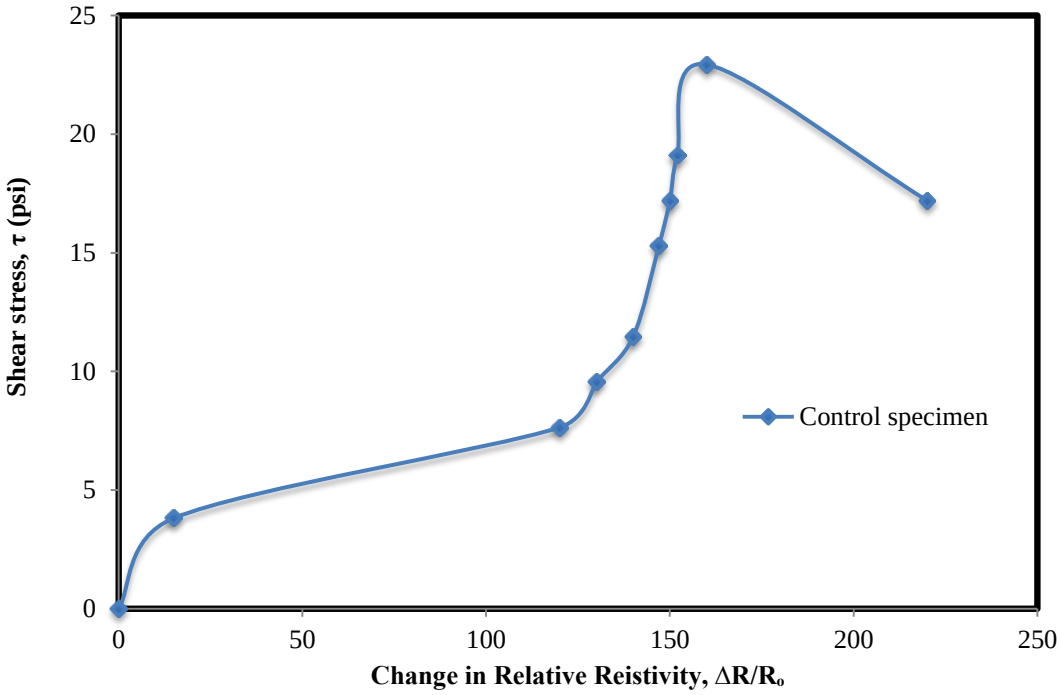


Figure 5.4 Control specimen 1 day

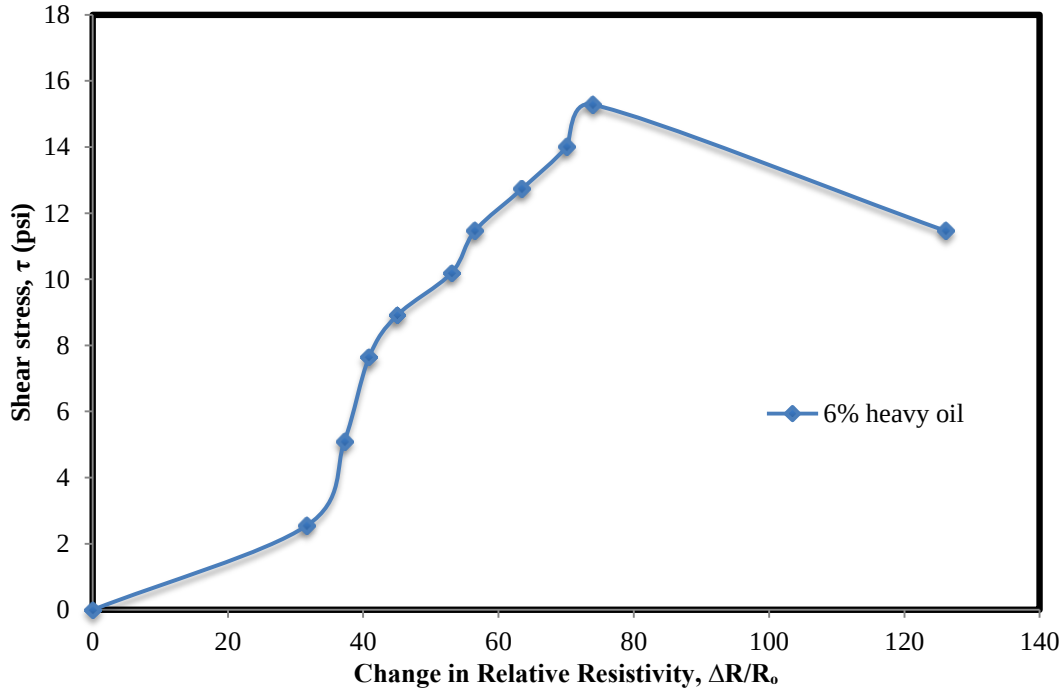


Figure 5.5 1 day 6% Heavy oil 1 day cured specimen

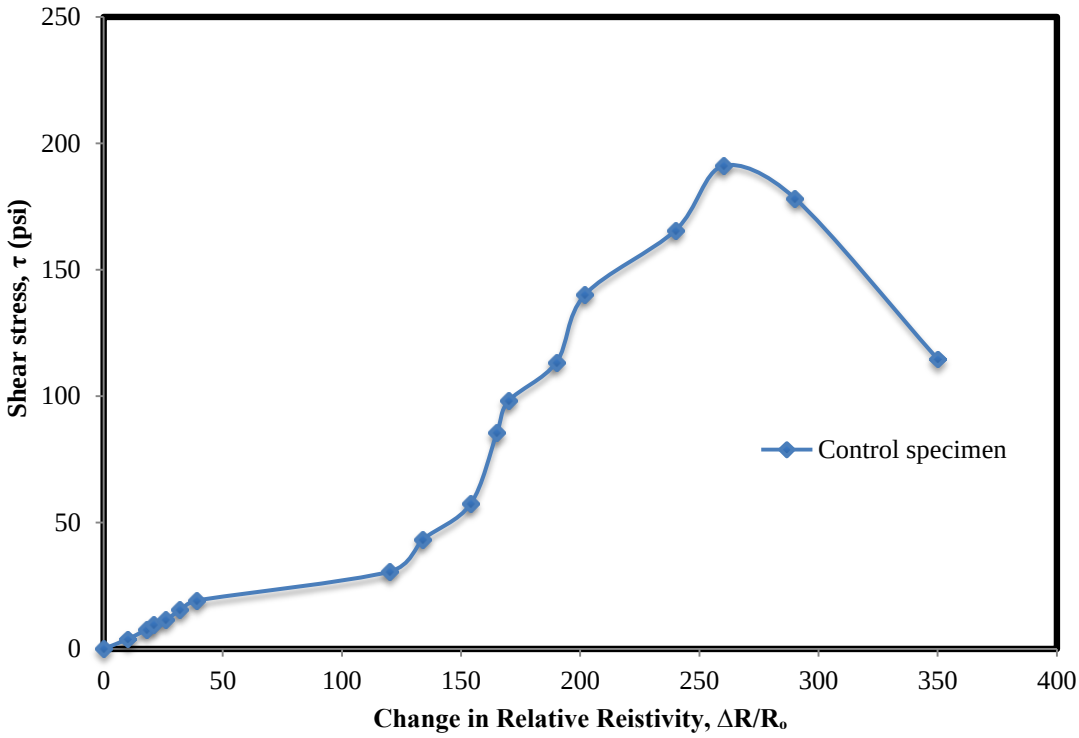


Figure 5.6 control specimen 28 days cured

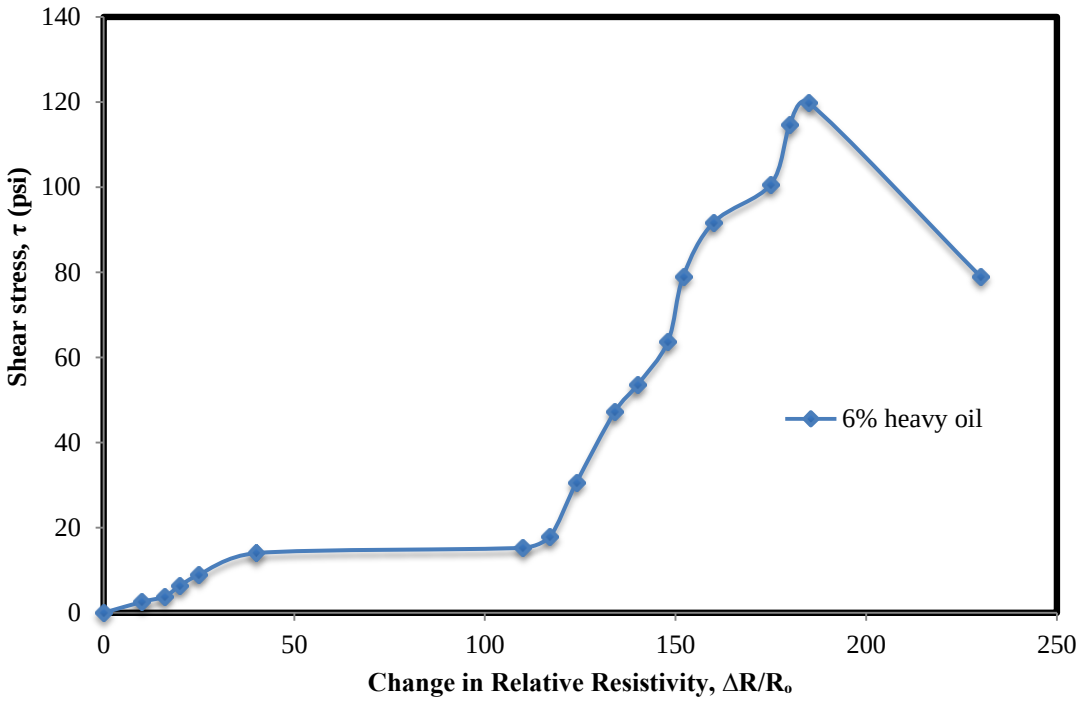


Figure 5.7 6% Heavy oil specimen 28 days cured

Control specimen after 1 day and 6% heavy oil contaminated was tested. From Figure 5.4 and Figure 5.5, it can be understood that the electrical resistivity of the specimen increased by applying stress, and undergoing a sudden increase could be due to the weakening of the bonding due to the shrinkage. After this level of stress, the interface resists to applied force and the resistivity of the specimen starts increasing up to the peak load causes the interface to fail. After this point, the rod slides inside the slurry and resistivity experiences another sharp increase and drop in the force carried by the cement/casing interface. Form Figure 5.4 and Figure 5.5 ,it can be understood that addition of 6% heavy oil reduced the piezoresistivity of the specimen at the peak load from 159% to 74%. The addition of heavy oil also reduced the shear strength of the cement interface from 23 psi to 15 psi. Figure 5.6 and Figure 5.7 showed 28 day cured specimen loading under the same condition. General trend of the graph is the same as the 1 day specimen except that the first jump in the value of change in relative resistivity was higher due to the fact that curing time in air was higher, specimen underwent a higher amount of drying shrinkage and autogenous shrinkage, which caused higher weakening effect in the cement/casing interface. After that sudden increase, the change in relative resistivity was increased up to the failure of interface. 28 days cured specimen showed that addition of 6% heavy oil reduced the piezoresistivity of the specimen at the peak load from 260% to 185%, it also reduced the shear strength of the cement interface from 191 psi to 119 psi.

5. 5- Summary

The following conclusions are taken from the above discussions:

1. Contamination tracked in the oil well cement by means of initial resistivity; from the study it can be understand that addition of Heavy oil by 6% increase the initial resistivity 27%.
2. Contamination also decreased the 1 day Piezoresistivity of cement at the peak load by 75% also the compressive strength was decreased by 75%.
3. Addition of Metakaolin to the contaminated specimen increased both the compressive strength and sensing properties of it by 120% and 150% respectively.
4. Sensing properties of the oil well under the anchor test at the peak load is reduced by 54% and 29% after 1 and 28 days of curing respectively.
5. oil contamination reduced the shear strength of the cement/casing bonding by 37% at both 1 day and 28 days old specimens

6- Conclusion and Recommendation

Cement which fills the area between the formation and casing play a key role in productivity of the oil well. Rheology, strength and integrity of the cement are major requirement for a successful cementing. During this study a practical method for monitoring and characterizing behavior of the oil well from the initial mix up to hardening and its service life were developed. Smart cement with the high sensing properties was characterized based on the different curing and loading condition.

6. 1- Conclusion

Based on this study the following conclusions were obtained:

1- Impedance spectroscopy test has proven that 300kHz of frequency would almost eliminate the effect of contact resistance

2- Hydration has been characterized by electrical resistivity for OWC and metakaolin added mix.

3- Resistivity of the specimens cured under saturated sand increased up to 20 times, while resistivity of the specimens cured in air increased up to 300 time as compared to the their initial respectively.

4- Addition of 10% metakaolin increased the initial resistivity of the specimen by 25%.

5- Addition of 5% and 10% metakaolin increased the piezoresistivity effect under the compressive loading respectively by 35% and 50% at 14 days, and 45% and 68% after 4 months of curing.

6- Curing age increases the piezoresistivity of the specimen in the range of 25 to 40% with higher effect on the metakolin specimens.

7- RI_{24} was used as an index to predict the compressive strength and improvement of compressive strength for control and the metakaolin specimen.

8- Contamination tracked in the oil well cement by means of initial resistivity; from the study it can be understand that addition of Heavy oil by 6% increase the initial resistivity 27%.

9- Contamination also decreased the 1 day Piezoresistivity of cement at the peak load by 75% also the compressive strength was decreased by 75%.

10- Addition of Metakaolin to the contaminated specimen increased both the compressive strength and sensing properties of it by 120% and 150% respectively.

11- Sensing properties of the oil well under the anchor test at the peak load is reduced by 54% and 29% after 1 and 28 days of curing respectively.

12- Oil contamination reduced the shear strength of the cement/casing bonding by 37% at both 1 day and 28 days old specimens.

6. 2- Recommendation

Based on the experiments were done, the following recommendation can be inferred:

1- Oil well drilled up to thousands of meters, this would make it difficult to monitor the cement quality. Electrical resistivity is a simple and applicable method for monitoring behavior of cement through its life-time.

2- Since electrical resistivity of each material is unique, electrical resistivity can be used as a method to study the effect of different types of matrials on the cement and also track the contamination in the oil well cement.

3- Electrical resistivity (RI_{24}) could be an applicable method for predicting the compressive strength of the oil well cement from its initial electrical properties.

4- The change of relative resistivity of cement at the failure point is around 80 times higher than the strain; hence, this method has appropriate sensitivity to detect damage and failures of well cement.

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