

**UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF
NATURAL & APPLIED SCIENCES**

**CORROSION RESISTANCE OF REINFORCEMENT
STEEL EMBEDDED IN CHLORIDE CONTAMINATED
CONCRETE WITH AND WITHOUT METAKAOLIN**

**M. Sc. THESIS
IN
CIVIL ENGINEERING**

**BY
FATİH KARABOĞA
OCAK 2012**

**Corrosion Resistance of Reinforcement Steel Embedded in
Chloride Contaminated Concrete with and without
Metakaolin**

**M.Sc. Thesis
in
Civil Engineering
University of Gaziantep**

**Supervisor
Assoc. Prof. Dr. Erhan GÜNEYİSİ**

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OCAK 2012**

REPUBLIC OF TURKEY
UNIVERSITY OF GAZIANTEP
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES
CIVIL ENGINEERING DEPARTMENT

Name of the thesis: Corrosion Resistance of Reinforcement Steel Embedded in Chloride Contaminated Concrete with and without Metakaolin

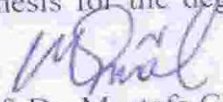
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Exam date: 25/01/2012

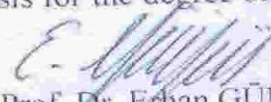
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ABSTRACT
**CORROSION RESISTANCE OF REINFORCEMENT STEEL EMBEDDED
IN CHLORIDE CONTAMINATED CONCRETE WITH AND WITHOUT
METAKAOLIN**

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M.Sc. in Civil Engineering

Supervisor: Assoc. Prof. Dr. Erhan GÜNEYİSİ

January 2012

52 Pages

One of the most remarkable drawbacks of the reinforced concrete structural elements is the corrosion of reinforcement. Especially, in marine structures or in such environments where chloride contamination risk exist this issue gains much importance. In this study, chloride contamination of the concrete was implemented by adding 0%, 1.5%, 3%, and 5% NaCl by weight of the total binder content, into concrete. To assess the influence of metakaolin (MK) incorporation on the corrosion resistance of the chloride contaminated concrete, 5% and 15% MK replacement levels by the total weight of the binder were assigned in concrete production. The corrosion behaviors of reinforcing bars embedded in concretes were monitored through accelerated corrosion test, corrosion current density and the corresponding corrosion rate by linear polarization technique (LPR). Moreover, the electrical resistivity of concrete was measured. Analysis of the test results indicated that MK was proved to be very effective in inhibiting the active corrosion of concrete even at severe chloride contamination levels.

Keywords: Accelerated corrosion, Chloride contamination, Corrosion rate, Electrical resistivity, Linear polarization, Metakaolin

ÖZET
KLORÜR KİRLENMESİNE MARUZ BIRAKILMIŞ METAKAOLİN
İÇEREN VE İÇERMİYEN BETON İÇERİSİNDEKİ DONATININ
KOROZYON DİRENCİ

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Yüksek Lisans Tezi, İnşaat Mühendisliği

Danışman: Doç. Dr. Erhan GÜNEYİSİ

Ocak 2012

52 Sayfa

Donatı korozyonu betonarme yapı elemanlarının en önemli dezavantajlarından biridir. Özellikle, deniz yapılarında veya klorür kirlenme riskinin yüksek olduğu ortamlarda bu durum daha da önem kazanır. Bu çalışmada, betona, toplam bağlayıcı miktarının %0, %1,5, %3 ve %5 oranlarında NaCl katılması ile klorür kirlenmesi sağlanmıştır. Metakaolin katkısının korozyon direnci üzerindeki etkisini irdelemek amacıyla, bu malzeme toplam bağlayıcı miktarının %5 ve %15 oranında çimento ile yer değiştirilerek kullanılmıştır. Beton içerisindeki donatı çubuklarının korozyon direnci; hızlı korozyon deneyi, lineer polarizasyon yöntemiyle korozyon akımının ölçülmesi ve buna bağlı korozyon hızının belirlenmesiyle değerlendirilmiştir. Ayrıca, betonların elektriksel direnci de ölçülmüştür. Deney sonuçları metakaolinin ciddi klorür kirlenme seviyelerinde bile aktif korozyonunun önlemesi bakımından oldukça etkili olduğunu göstermiştir.

Anahtar kelimeler: Hızlı korozyon, Klorür kirlenmesi, Korozyon hızı, Elektriksel direnç, Lineer polarizasyon, Metakaolin

*To my darling parent, daughter
and wife*

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor Associated Prof. Dr. Erhan GÜNEYİSİ for his continual encouragement helps and supervision.

I would like to express my deep appreciation to Assoc. Prof. Dr. Mehmet GESOĞLU, Research Asst. Kasım MERMERDAŞ for their invaluable guidance, helps and advices. I would also like to thank to those who took part in completion of this thesis.

My special thanks are reserved for my parents, my daughter NİL GÖKÇEN KARABOĞA and my wife ÖZLEM KARABOĞA for sacrificing their usual family time for my studies.

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LIST OF SYMBOLS/ ABBREVIATIONS

AC Alternative current

ACTIV Accelerated corrosion test with impressed voltage

CH Calcium hydroxide

CSH Tobermorite gel

DC Direct current

FA Fly ash

GGBFS Ground granulated blast furnace slag

LPR Linear polarization resistance

MK Metakaolin

OPC Ordinary Portland cement

R/C Reinforced concrete

RHA Rice husk ash

SF Silica fume

β_a Anodic tafel slope

β_c Cathodic tafel slope

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CHAPTER 1

INTRODUCTION

1.1 General

Reinforced concrete (R/C) is the most commonly used composite material in structural practices due to ease in applications and lower cost of construction. Besides, the reinforced concrete structures offer good service under certain environmental conditions. The worldwide demand for high performance concrete with improved corrosion resistance has increased and it is expected that it will be widely used in construction industry during next decades. The corrosion resistance of concrete has an important effect on the durability, and hence its performance. Therefore, it can be said that concrete performance depends mainly on the environmental conditions and the quality of the concrete.

The presence of chloride ions plays a major role in the mechanism of reinforcement corrosion, and hence it is very important issue for the durability and service life of R/C structures (Pradhan and Bhattacharjee, 2009). The existence of chlorides within reinforced concrete accelerates the initiation of the reinforcement corrosion and results in severe deterioration of concrete structures. Once the chloride content at the reinforcement reaches a threshold value and if enough oxygen and moisture are present, the reinforcement corrosion will be initiated (Chen and Mahadevan, 2008). When the corrosion is initiated, active corrosion results in a volumetric expansion of the rust around the reinforcing bars against the surrounding concrete (Tuutti, 1982).

It is known that, in well designed and high quality concrete, the risk of corrosion is expected to be minimal since it provides the chemical and physical conservation to the embedded steel reinforcement bars. The corrosion of rebar in concrete is generally considered as an electrochemical process (Hope et al., 1986; Liu and Weyers, 1998; El-Gelany, 2001; Elsener, 2002; Maheswaran and Sanjayan, 2004). Therefore, the use of electrochemical techniques for the appraisal of corrosion behavior of R/C in this regard, becomes a prominent field of durability study.

Metakaolin (MK) obtained through proper calcinations of kaolin and having pozzolanic properties has been used as an additive for cement (Pera, 2001). The studies, regarding the improvement of the mechanical, shrinkage, and some durability properties of the concrete by MK have been carried out by the researchers (Ding and Li 2002; Poon et al., 2006; Wild et al., 2006; Güneyisi and Mermerdaş, 2007; Kim et al., 2007). Nevertheless, there is still a gap in the literature regarding the corrosion resistance of the concretes modified with MK. Batis et al. (2005) studied the effect of metakaolin on the corrosion resistance of cement mortar. They used a poor Greek kaolin with low kaolinite content. The Greek kaolin was thermally treated and ground to the appropriate fineness. Moreover, a commercial metakaolin of high purity was also used. Several mixture proportions were used to produce mortar specimens, where metakaolin replaced with either sand or cement. For the evaluation of the corrosion of metakaolin, the following criteria considered: corrosion potential, mass loss, electrochemical measurements of the corrosion rate by the linear polarization method, and carbonation depth. They reported that the use of metakaolin, either as a sand replacement up to 20% w/w, or as a cement replacement up to 10% w/w, improved the corrosion behavior of mortar specimens.

In this thesis, the effectiveness of MK replacement by weight of the total binder content on the corrosion behavior and electrical resistivity of chloride contaminated concretes were investigated experimentally. For this purpose, two replacement levels of MK were assigned to produce mineral admixed concretes. For comparison, a reference plain concrete group was produced, as well. To evaluate the degree of the deterioration of the chloride contamination, four sodium chloride concentrations (0%, 1.5%, 3%, and 5%) were considered. Corrosion behavior of reinforcing bars embedded in concretes was monitored through accelerated corrosion test and linear polarization resistance (LPR) test at different, respectively. Moreover, being an important indicator of reinforcing steel corrosion, the electrical resistivity of concrete was also measured at the end of the specified curing periods.

1.2 Outline of the Thesis

Chapter 1-Introduction: Scope and objective of the thesis are given.

Chapter 2-Literature review and background: A literature survey was carried out on the utilization of metakaolin for enhancing durability properties of concrete. Moreover, the studies regarding the corrosion of reinforcement embedded in concrete were also investigated.

Chapter 3-Experimental study: Materials, mixtures, casting, and test methods are described.

Chapter 4-Test results and discussions: Indication, evaluation, and discussion of test results are given.

Chapter 5-Conclusion: Conclusions of the thesis are presented.

CHAPTER 2

LITERATURE REVIEW AND BACKGROUND

2.1 Corrosion

Concrete can be considered as a good medium for protecting the embedded steel in concrete against corrosion due to its high pH value. High alkalinity of the concrete is resulted from KOH and NaOH which are formed during hydration. Around the reinforcing steel embedded in concrete, a thin passivation layer of iron oxide provides a protection against corrosion. However, this protection keeps on while a high level of pH can be maintained. On the other hand, carbonation or chlorides may pass through the oxide film which causes the decrease in the alkalinity and the steel corrosion. The period up to start of corrosion is named “the initiation phase” shown in Figure 2.1 (Tuutti, 1982).

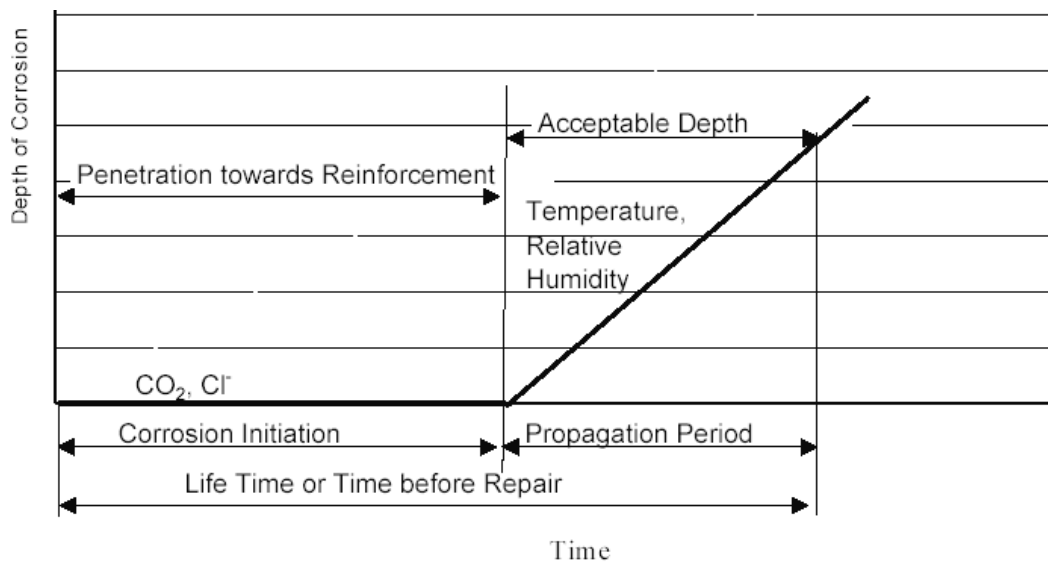
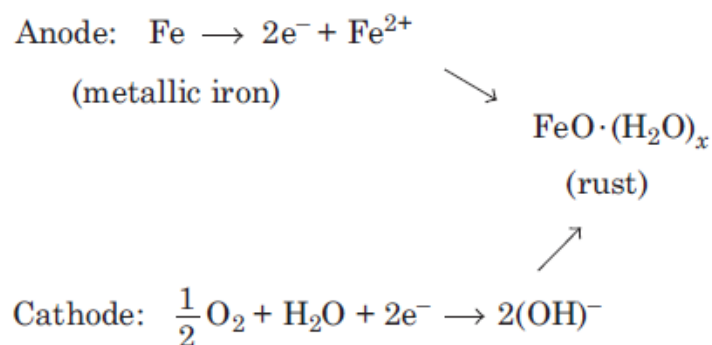


Figure 2.1 Initiation and propagation periods for corrosion in a structure (Tuutti, 1982)

2.1.1 Corrosion mechanism

Corrosion of reinforcement embedded in concrete is known to be an electrochemical process. The electrochemical potentials to form the corrosion cells can be yielded in two ways (Mehta, 2006).

1. *Formation of composition cells:* when two dissimilar metals are embedded in concrete, such as steel reinforcement and aluminum pipes, or when remarkable variations exist in surface characteristics of the steel.
2. *Formation of concentration cells:* In the environs of reinforcing steel, concentration cells may be formed due to differences in the concentration of dissolved ions, such as chlorides and alkalies. As a result, one of the two metals becomes cathodic and the other anodic. The basic chemical changes taking place at the cathodic and anodic regions are given below (see also Figure 2.2).



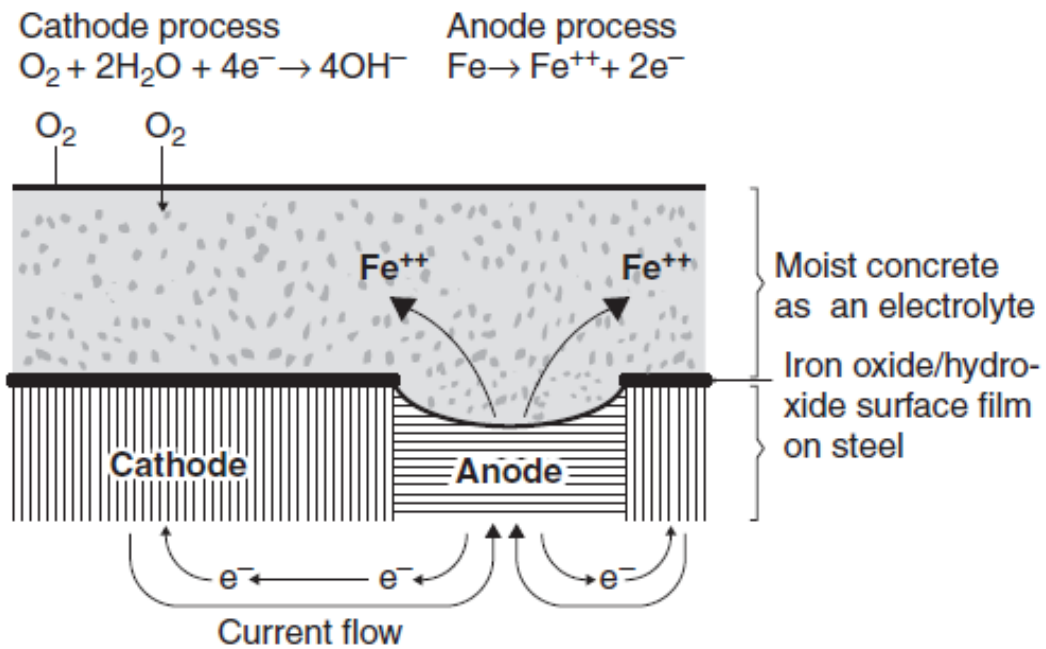


Figure 2.2 Electrochemical process of corrosion (Mehta, 2006)

For various pH levels in concrete, the corrosion rate changes in the subsequent manner (Bhaskara and Maheshwari, 1987):

- a) if pH is greater than 10, no corrosion risk occurs,
- b) if pH is between 4 and 10, the corrosion rate can be considered as stable, and
- c) if pH is less than 4, corrosion rate becomes fast.

2.1.2 Corrosion damage on R/C structures

One of the most important durability issue with reinforced concrete is deterioration of R/C structural elements due to the reinforcement corrosion (Wallbank, 1989; Watson, 1990). Since steel corrodes, the cross-sectional area of the reinforcement decreases. The corrosion products occupy a larger volume than the steel reinforcement which exerts significant tensile forces on the concrete cover. When the expansion becomes excessive, concrete cracking will occur (Güneyisi et al., 2005). As a result, bonding between the concrete and reinforcement is diminished.

In the Figure 2.3, some examples to structural elements exposed to corrosion damage are illustrated.



a)



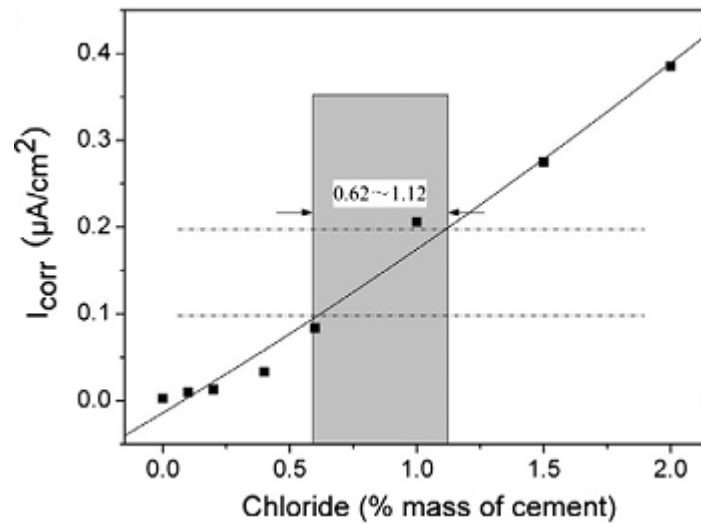
b)

Figure 2.3 Spalling of concrete cover due to corrosion damage on a) bridge girders and b) Bridge column (<http://www.mto.gov.on.ca/english/transtek/roadtalk/rt17-1/index.shtml>; http://onlinemanuals.txdot.gov/txdotmanuals/sic/bridge_columns.htm)

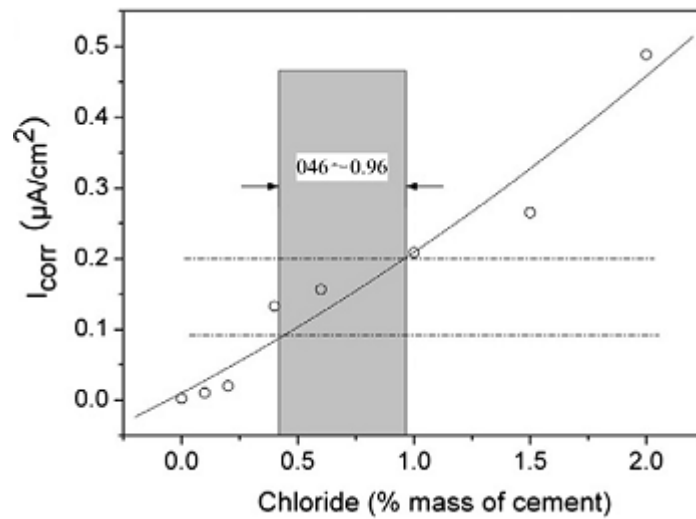
2.1.3 Effect of chloride contamination on corrosion

Chlorides, water, and oxygen are the aggressive agents penetrating into concrete through the porous media existing within the paste matrix. Mainly, the quality of concrete affects the penetration rate. Moreover, the ratio of water-binder content of the concrete and the existence of preventive agents such as mineral admixtures or chemical inhibitors may retard or decelerate the chloride permeation. The main penetration action of chloride ions into the pore system are the capillary water absorption in partially saturated concrete and diffusion of the chloride ions in the fully saturated concrete. Diffusion of chloride ions can be described as a mass transfer of free chloride ions in the pore solution having a net flow from zones of higher concentration to lower concentration (Kropp et al., 1995). Although the chloride penetration into concrete is sophisticated transport mechanisms, Fick's law of diffusion is applicable to assess this penetration.

Xu et al. (2011) studied the effect of different types of salts being chloride sources for evaluating corrosion threshold values of steel reinforcement embedded in concrete. They reported that the increase in the amount of chloride resulted in the rise of i_{corr} and risk of corrosion of reinforcement (Figure 2.4).



a)



b)

Figure 2.4 Corrosion current varied with the increases of chloride for the concretes contaminated with a) sodium chloride and b) calcium chloride (Xu et al., 2011)

In Figure 2.5, the corrosion damage in bridge piers due to severe chloride attack is shown.



Figure 2.5 Bridge pier under severe chloride attack
(<http://www.compositesworld.com/articles/composite-vs-corrosion-battling-for-marketshare>)

2.2 Protecting reinforcing steel against corrosion

There have been many methods for avoiding the corrosion since the late 1960s. These methods may be broken into four categories, regarding the protection principle (Kepler et al., 2000):

- a) *Alternative reinforcement and slab design* is based on the isolation of steel from the concrete through special materials. Hence, forming a barrier for chloride ions
- b) *Barrier methods* provide protection of R/C from corrosion by means of obstructing the reach of corrosive agents to the steel. Therefore, corrosion initiation can be avoided

- c) *Electrochemical methods* are based on utilization of electrical current. The protection of reinforcement is provided by external anode, even when the concentration of chloride ions is higher than the threshold value and
- d) *Corrosion inhibitors* provide protection by increasing the threshold concentration level, through enhancing the permeability characteristics of the concrete.

Utilization of mineral admixtures or corrosion inhibitors may be considered as alternative methods of corrosion control. The use of mineral admixtures can be preferable because of lower cost and simplicity of usage (Tommaselli et al., 2009).

2.2.1 Chemical corrosion inhibitors

Inhibitors are such chemicals reacting with the surface of metal, or the media to which the metallic surface is exposed. The inhibitors provide the surface a significant level of protection. The influence mechanism is mainly based on adsorption of the inhibitors on the surface. The surface is protected through formation of a thin film which is distributed from a solution. Sometimes, they may be used for production of protective coat. The effectiveness of the inhibitors is due to slowing down the corrosion processes by either:

- a) Providing a high electrical resistance to the metallic surface
- b) Reducing the ionic diffusion to the metallic surface, and
- c) Changing the anodic or cathodic polarization slopes to higher values (β_a , β_c).

Tommaselli et al. (2009) studied the influence of corrosion inhibitors in saturated Ca(OH)_2 solutions acidified by acid rain components. They analyzed the effect of

NaNO₂ and Na₂MoO₄ as inhibitors (Figure 2.6 and Figure 2.7). They concluded that at low rates of concentrations (0.013% total solution mass), Na₂MoO₄ was observed to be more effective than NaNO₂, however their prevention effect was determined to have similar trend at high concentrations.

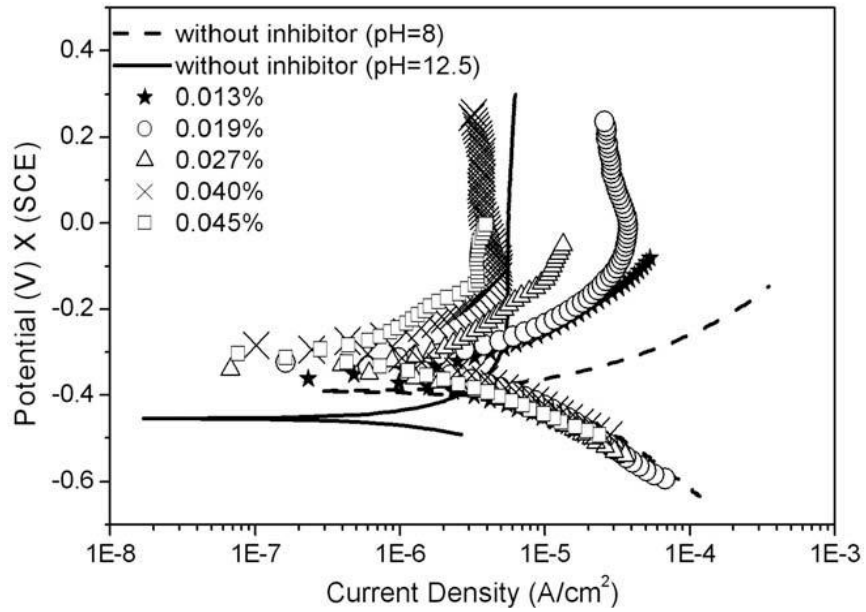


Figure 2.6 Potential vs. current density reinforcement in saturated Ca(OH)₂ solution with various concentrations of NaNO₂ (Tommaselli et al., 2009)

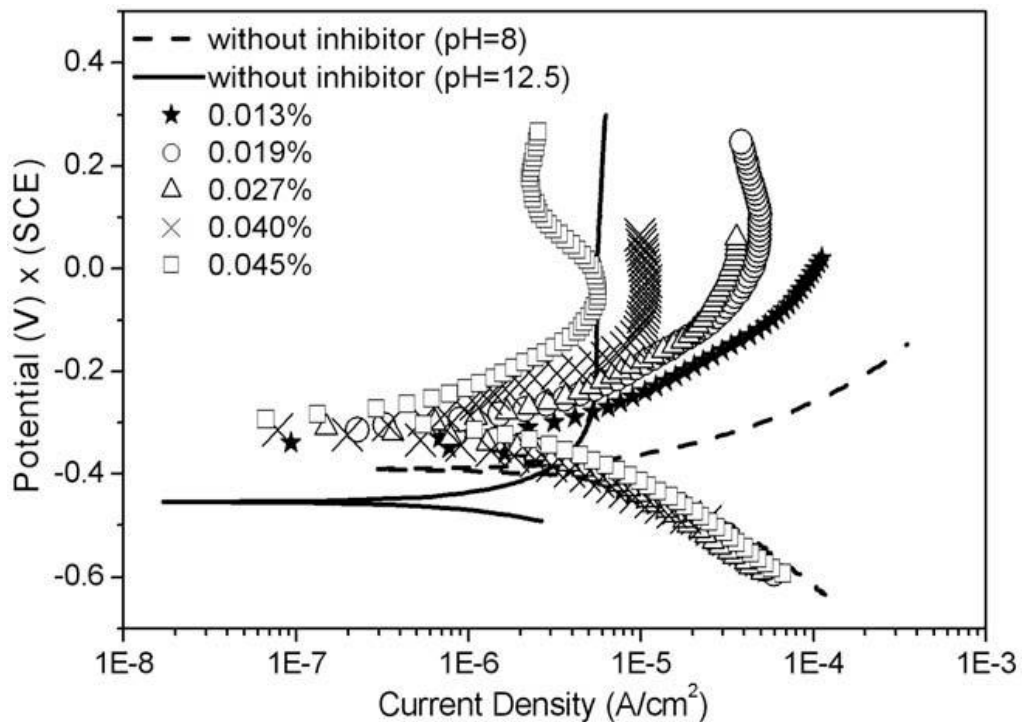


Figure 2.7 Potential vs. current density reinforcement in saturated $\text{Ca}(\text{OH})_2$ solution with various concentrations of Na_2MoO_4 (Tommaselli et al., 2009)

2.2.2 Use of mineral admixtures for corrosion protection

For a few decades, there have been intensive studies performed on utilization of mineral admixtures and their effectiveness on decreasing chloride ingress and diffusion into concrete. Those studies focused on the type of mineral admixture, percent substitution levels with total binder content, curing and exposure conditions etc. Generally, concrete containing pozzolanic admixtures demonstrate improved permeability and diffusion coefficients comparing for plain concretes (Ding and Li, 2002; Chindapasirt et al., 2004; Sun et al., 2004; Güneyisi and Mermerdaş, 2007; Chindapasirt and Rukzon, 2008)

Chindapasirt and Rukzon (2008) investigated the effect some waste by-products, namely, fly ash (FA) and rice husk ash (RHA) on the strength, porous structure and

corrosion behavior of mortars. They used ternary blends of these mineral admixtures. They stated that the corrosion resistance due to chloride ion induction of mortar observed by accelerated corrosion with impressed voltage was improved considerably. That was resulted from use of ternary and binary blend of ordinary portland cement. The resistance of ternary blend of mortar was measured to be higher than that of binary mortar mixes. The results also illustrated that the use of ternary blend ordinary Portland cement, rice husk ash and fly ash was very efficient in enhancing chloride induced corrosion of mortar (Figure 2.8).

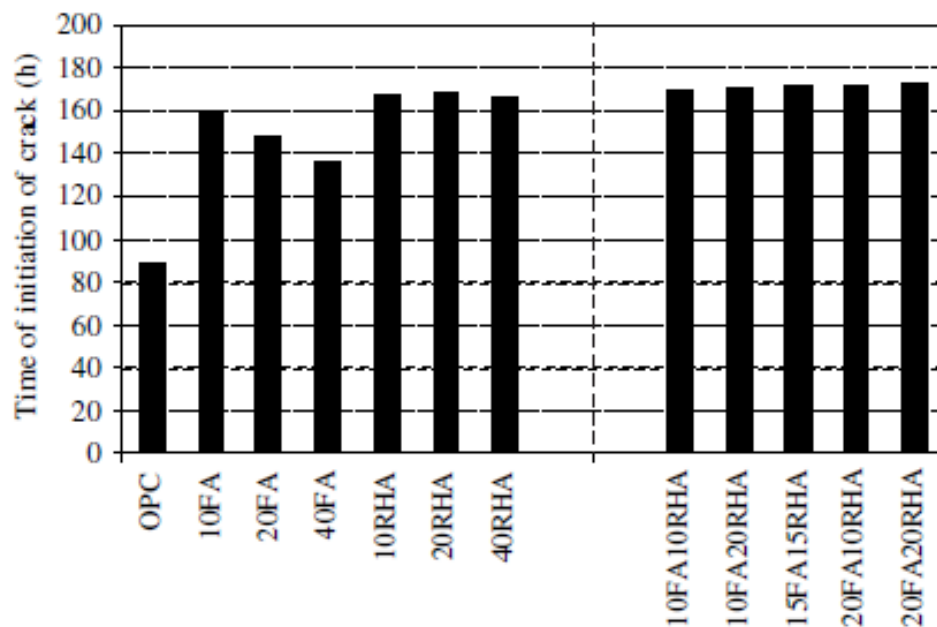


Figure 2.8 Crack initiations of mortars in accelerated corrosion test with impressed voltage (Chindaprasirt and Rukzon 2008)

2.3 Mineral admixtures

Mineral admixtures, additions, or supplementary cementitious materials have been used for provision the means to improve the properties of concrete whether fresh or hardened. In some instances, they may reduce the cost of concrete as well as

recycling the waste materials. In general, the mineral admixtures are defined as finely ground siliceous materials added to enhance the fresh properties of concrete and the performance of hardened concrete.

The most commonly used mineral admixtures for enhancing the properties of concretes are as follows :

- Rice husk ash,
- Ground granulated blast furnace slag,
- Silica fume,
- Metakaolin, and
- Fly ash, etc.

SEM micrographs of some mineral admixtures are given in Figure 2.9 (<http://www.fhwa.dot.gov/>)

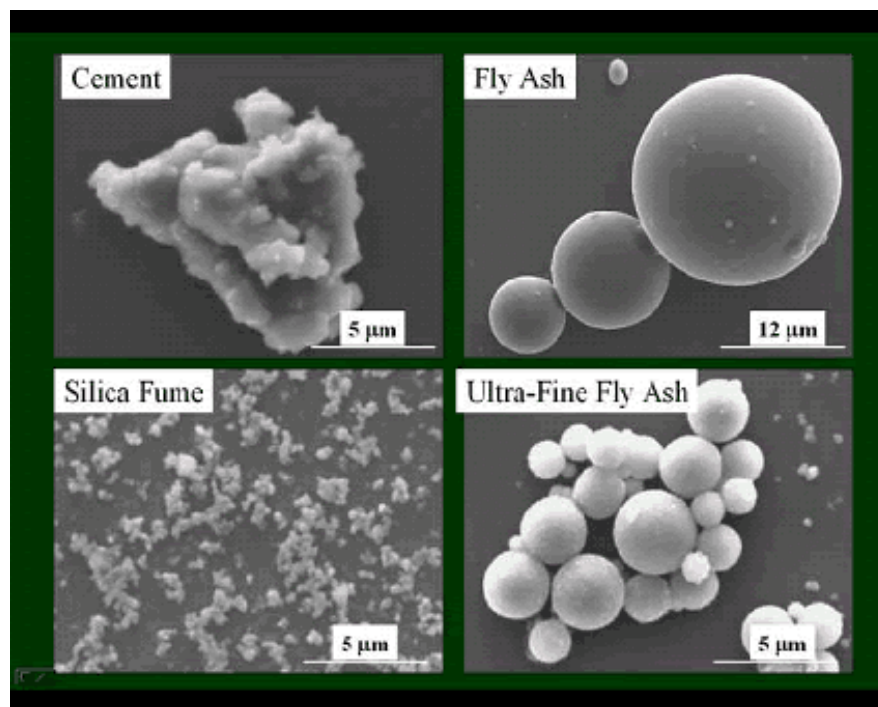


Figure 2.9 SEM images illustrating the size difference of various cementitious materials (<http://www.fhwa.dot.gov/pavement/pccp/pubs/04150/chapt11.cfm>)

2.3.1 Silica fume (SF)

Silica fume which is also known as condensed silica fume or micro-silica is a waste by-product from the production of ferrosilicon alloy. It is a very fine powder having a relatively great specific surface area when compared to other mineral admixtures. It has spherical particles much smaller in size than portland cement. The range of diameters is between 0.02 μm and 0.5 μm . Silica fume contains up to 95% noncrystalline amorphous SiO_2 . The improvements of the properties of concrete as a result of use of silica fume are as follows:

- High strength,
- Lower heat of hydration,
- Reduced permeability,
- Resistance in environmental effects such as freeze-thaw effects, and
- Increased resistance against chemical attacks.

The enhancement of these properties may be attributed to denser microstructure of cement paste matrix and improvement of interfacial transition zones (Neville, 1995; Ding and Li, 2002).

2.3.2 Fly ash (FA)

Fly ash is one of the most commonly used mineral admixtures in concrete related studies. It is a fine, glassy powder produced in coal-fired power generation plants. In those plants millions of tons of fly ash are produced annually. There are two types of FA, Class C and Class F. The particles of Class F FA has are covered in a kind of melted glass. However, Class C FA has a higher percentage of calcium oxide, and is more commonly used for structural concrete.

FA is a relatively cheap replacement material when compared to SF. It enhances mechanical properties of concrete as well as providing segregation resistance, and ease of pumping of the fresh concrete. This material can also be used as an ingredient in structural fills.

Use of fly ash in concrete dates back to late 1920s. It is now being used worldwide. It mostly consists of silica, alumina and iron. When it is introduced to lime and water, it forms additional CSH gel in the cement matrix. Moreover, decrease in segregation of the concrete mixture can be attained using fly ash. The internal friction can be reduced due to the spherical shape of the particles. This increases the concrete's consistency, hence mobility and providing longer pumping distances. As a result of improved workability the need for water dramatically decreases. SEM image of fly ash particles is illustrated in figure 2.10 (PCA, 2003).

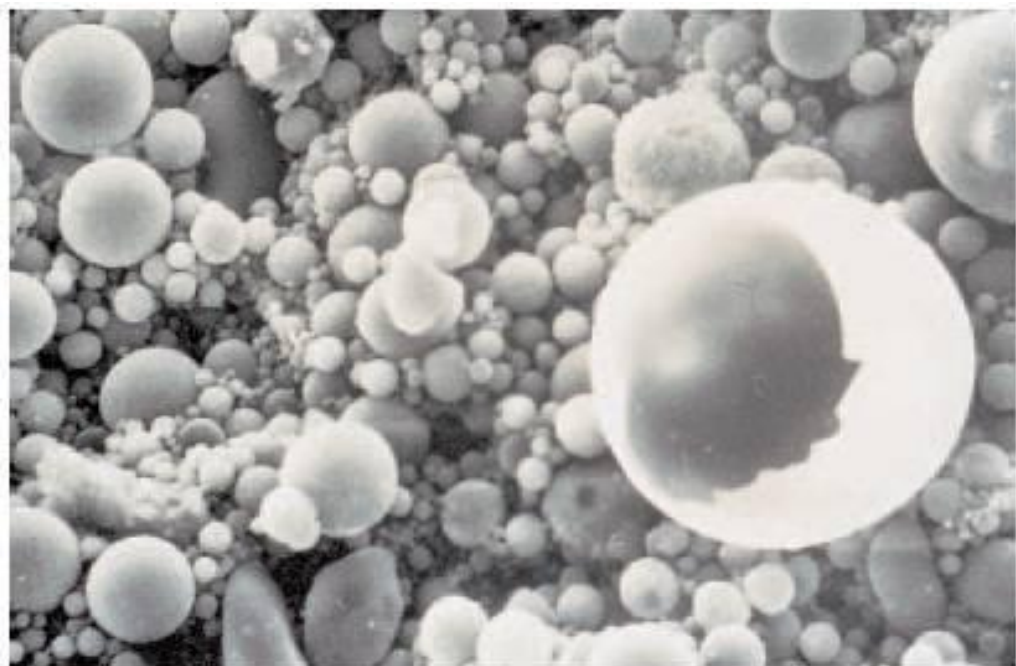


Figure 2.10 SEM image of fly ash particles at 1000 magnification (PCA, 2003)

2.3.3 Rice husk ash (RHA)

Being produced in millions of tons, rice husk is a type of waste material which can be utilized in concrete technology. 20 kg of rice husk can be extracted from processing of approximately 100 kg of rice. 80% of rice husks contain organic materials (Mehta, 1992). RHA is produced by burning rice husk. One of the most important characteristics of RHA is its pozzolanic property as due to the amorphous phase content. Rice husk ash is a highly reactive pozzolanic material convenient to be utilized as a cement substituting material. High amount of SiO_2 , vulnerability of RHA to react to lime depends on a combination of two factors. These factors are the quantity of non-crystalline silica content and degree of fineness (Mehta, 1992). SEM image of rice husk ash particles is given in Figure 2.11 (<http://mse.utoronto.ca>).

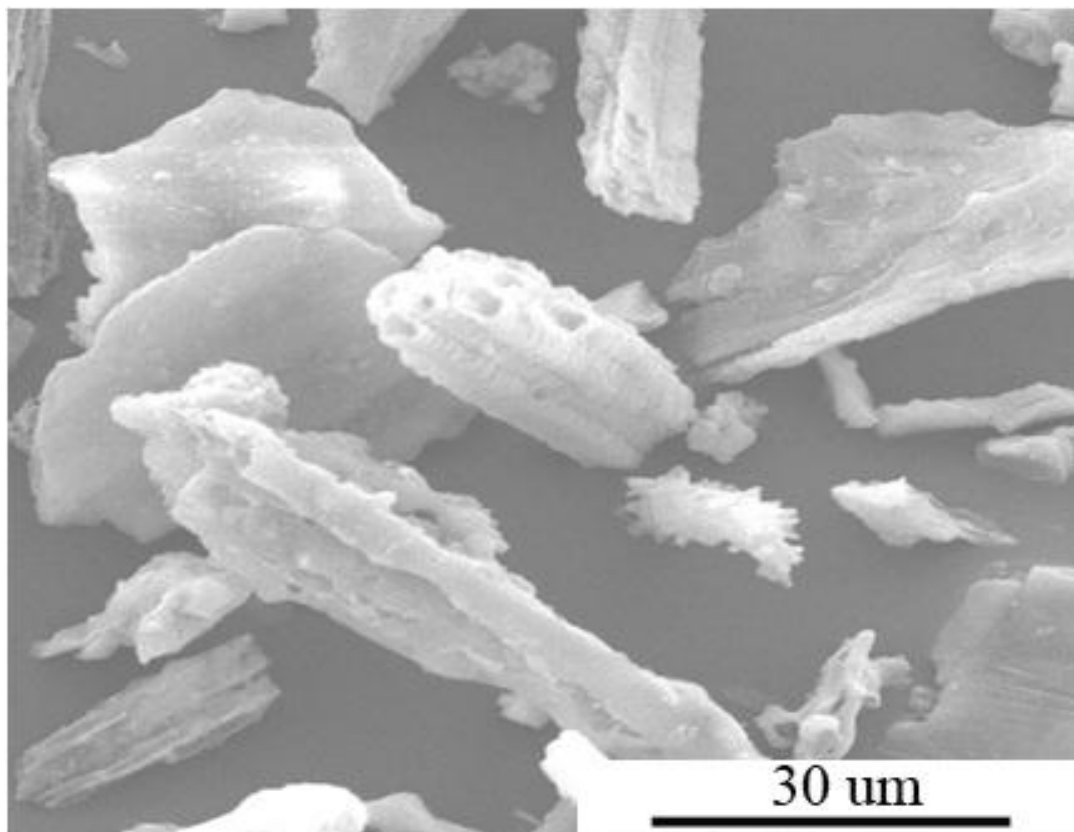


Figure 2.11 SEM micrograph of RHA (<http://mse.utoronto.ca>)

2.3.4 Ground granulated blast furnace slag (GGBFS)

Like aforementioned mineral admixtures, GGBFS is also one of the byproduct mineral admixtures used in concrete. This material is obtained from steel industry. Blast furnace slag consisting of calcium silicates and other bases is a non-metallic product that is developed in a molten condition. The rate of cooling influences the features of the slag. If it is allowed to cool slowly, the crystallization occurs and the material with no cementing property is obtained. On the other hand, if the cooling rate is rapid enough to below 800 °C, glassy cementitious material is formed. A subsequent grinding operation is applied to have a powder material to be utilized for either manufacture of blended cement or mineral admixture. Up to 90% of GGBFS is smaller than 45 microns. This material has been used for many years as a cement replacement material in concrete production, either as a mineral admixture or as a component of blended cement. The particles of GGBFS have sharp, rough and edged shapes as shown in Figure 2.12 (PCA, 2000).

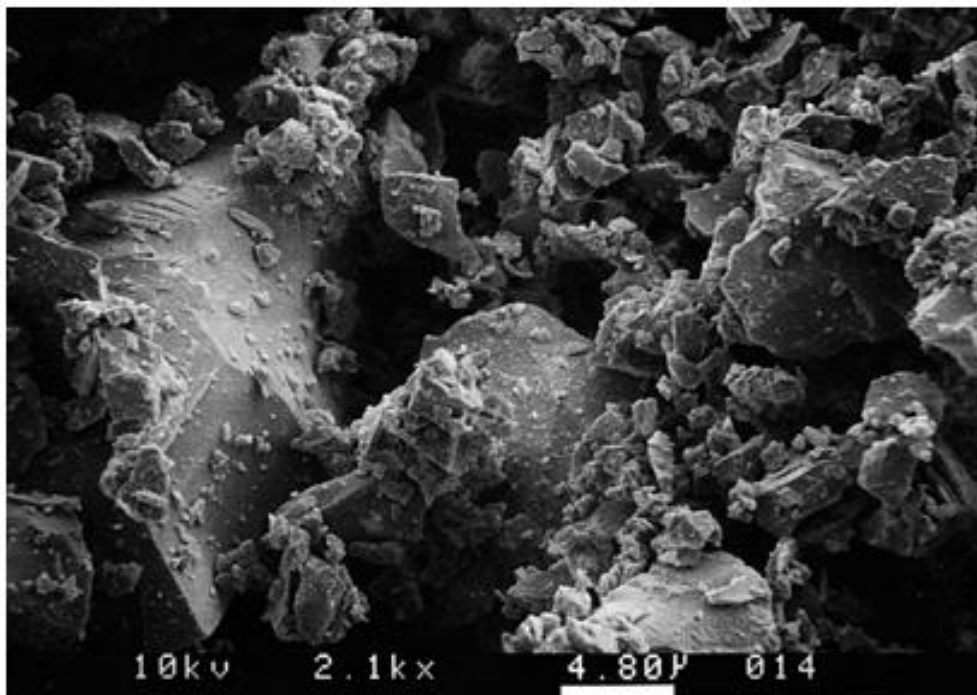


Figure 2.12 SEM image of GGBFS particles at 2100 magnification (PCA, 2000)

2.3.5 Metakaolin (MK)

Metakaolin is an ultrafine pozzolana, obtained by calcinations of pure kaolinite at temperature ranging from 650 to 900 °C to destroy the crystalline structure during driving off the chemically bound water (Snyder, 2000; Sabir et al., 2001; Brooks and Johari, 2001). Unlike industrial by-products such as silica fume, fly ash, GGBFS, MK is refined carefully to lighten its color, remove inert impurity, and control particle size. The particle size of MK is generally less than 2 µm, which is significantly smaller than that of cement; though not as fine as SF (Bissonette et al., 1999; Brooks and Johari, 2001; Benboudjema, 2005). Moreover, the use of MK in concrete in its present form is considered to be a relatively new concept (since the mid 1990s) (Benboudjema et al, 2005). MK attracted the interest of the researchers in that its reactivity in the consumption of calcium hydroxide (CH) to form additional CSH. Thus, metakaolin improves the long-term mechanical and durability properties. Furthermore, due to its micro filling effect, it enhances early age strength (Cook, 1986).

2.4 Metakaolin as a supplementary cementitious material

In the literature, it has been stated that concrete modified with metakaolin has superior engineering properties that can be comparable with silica fume concrete, (Dunster et al., 1993; Kristof et al., 1993). This results from the characteristics of its chemical composition, fineness, and poorly crystalline nature (Frias and Cabrera, 2001). The research work about the use of metakaolin deals with two main areas. In the first one, the calcination procedure in other words the dehydroxylation/amorphization treatment of the kaolin, and the formation of the metakaolin have been studied by researchers (Frias and Cabrera, 2001 Gamiz et al., 2005). The second one deals with physical and chemical contribution of MK on the

properties of mortar and concrete (Neville and Brooks, 1990 ; Dunster et al., 1993; Caldarone et al., 1994; Zhang and Malhotra, 1995; Khatib and Wild, 1996; Wild et al., 1996; Ding and Li, 2002; Lee et al., 2005; Batis et al., 2005; Revilla et al., 2006).

Research related to the effectiveness of metakaolin on the concrete performance is in progress because of the fact that metakaolin is a relatively new mineral admixture for concrete industry, especially its present form. Metakaolin is also considered as an alternative supplementary cementing material. It is comparable to silica fume in pozzolanic reactivity, but is lower in price (Revilla et al., 2006).

2.4.1 Effect of MK on the properties of mortar and concrete

There is a general agreement that the long-term deterioration of many structures is generally due to the ingress of aggressive species into concrete. There are number of factors affecting the concrete performance, such as environmental conditions and quality of the concrete. The performance of concrete depends on the continuation of hydration reactions. This continuation is related to the chemical and physical properties of cement as well as the amount and the type of supplementary cementing materials. The other important factors are w/cm ratio and the early age curing conditions (Khatri et al., 1997). It is obvious that those factors are essential to obtain the durable concrete structures.

The primary factors that are considered for the contribution of metakaolin in concrete are as follows :

- The micro filling effect due to high degree of fineness,
- The pozzolanic property of metakaolin, and
- The dilution effect.

Need for high performance in concrete and environmental impacts make the use of mineral admixtures inevitable. Therefore, it could be said that, metakaolin would soon be a popular supplementary cementing material for concrete industry.

2.4.2 Effect of metakaolin on corrosion resistance

The studies regarding the effect of MK on the corrosion resistance of the cementitious composites, such as mortar and concrete is very limited. Batis et al. (2005) carried out a study on the influence of metakaolin on the corrosion behavior of mortars. They prepared several mixtures where metakaolin replaced either cement or sand. They exposed the mortar specimens to the corrosive environment of either partial or total immersion in 3.5% w/w NaCl solution. According to their experimental test results, it was concluded that the use of metakaolin, either as a sand replacement up to 20%, or as a cement replacement up to 10%, improved the corrosion behavior of mortar specimens. However, in case of using greater percentages of metakaolin had no positive effect (Figure 2.13)

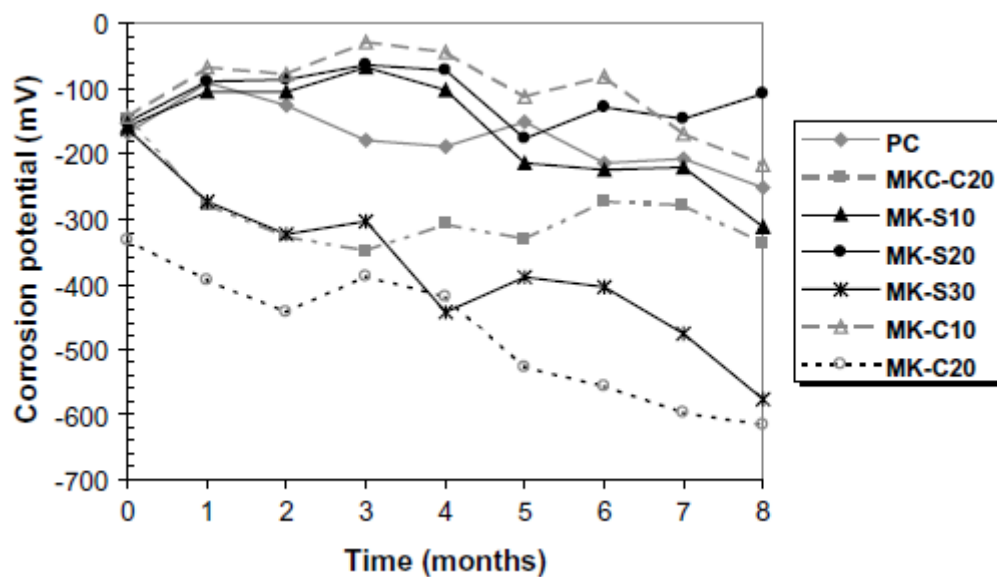


Figure 2.13 Corrosion potentials of specimens immersed in sodium-chloride solution (Batis et al., 2005)

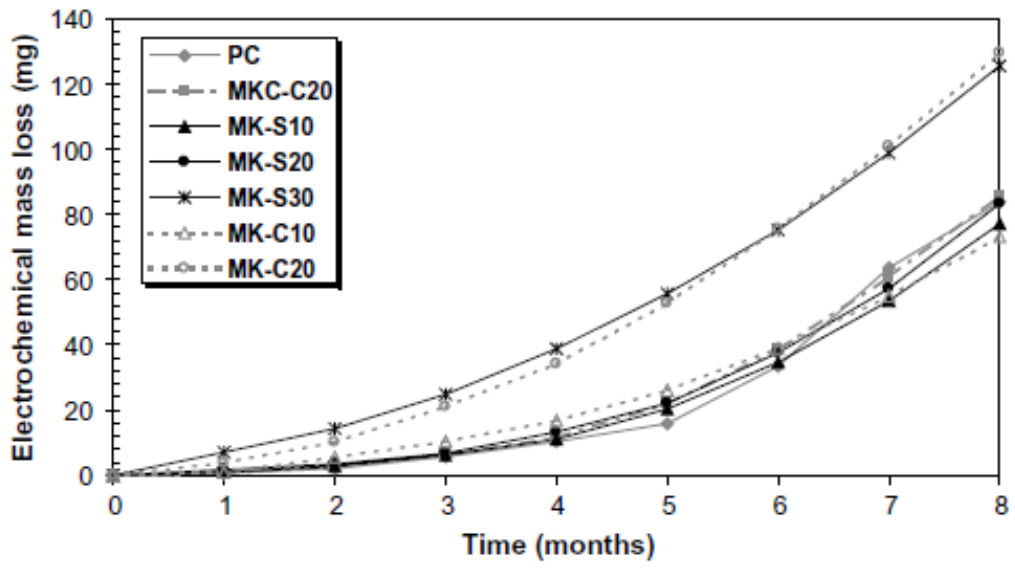


Figure 2.14 Electrochemical mass loss of mortar specimens immersed in sodium-chloride solution (Batis et al., 2005)

CHAPTER 3

EXPERIMENTAL STUDY

3.1 Materials

The materials used in this study were Portland cement, metakaolin (MK), fine and coarse aggregates, and superplasticizer. Portland cement (CEM I 42.5R) conforming to the TS EN 197-1 (European EN 197-1), commercial grade MK was utilized as cementitious materials. The physical properties of Portland cement and MK as well as the chemical compositions are given in Table 3.1.

Fine aggregate was comprised of crushed sand and river sand while the coarse aggregate was river gravel with a maximum nominal particle size of 22 mm. Aggregates were supplied from local sources. Specific gravity, fineness moduli and the sieve analysis of the aggregates are presented in Table 3.2. Moreover, grading of aggregates is shown in the Figure.3.1. Grading of the aggregate mixture was kept constant for all concretes. Sulphonated naphthalene formaldehyde type water-reducing admixture with specific gravity of 1.19 was used to achieve the slump value of 10 ± 2 cm for the proper consistency.

Table 3.1 Chemical composition and physical properties of portland cement and metakaolin

Item	Portland cement	Metakaolin
CaO (%)	63.60	0.78
SiO ₂ (%)	19.49	52.68
Al ₂ O ₃ (%)	4.54	36.34
Fe ₂ O ₃ (%)	3.38	2.14
MgO (%)	2.63	0.16
SO ₃ (%)	2.84	-
K ₂ O (%)	0.58	0.62
Na ₂ O (%)	0.13	0.26
Loss of ignition (%)	2.99	0.98
Specific gravity (g/cm ³)	3.13	2.5
Specific surface area (m ² /kg)	339	12000

Table 3.2 Specific gravity, fineness modulus and sieve analysis of the aggregates

Sieve size (mm)	Fine aggregate		Coarse aggregate	
	River sand	Crushed sand	No I	No II
31.5	100	100	100	100
16.0	100	100	100	27.7
8.0	99.7	100	31.5	0.6
4.0	94.5	99.2	0.4	0
2.0	58.7	62.9	0	0
1.0	38.2	43.7	0	0
0.50	24.9	33.9	0	0
0.25	5.40	22.6	0	0
Fineness modulus	2.79	2.38	5.68	6.72
Specific gravity	2.66	2.45	2.72	2.73

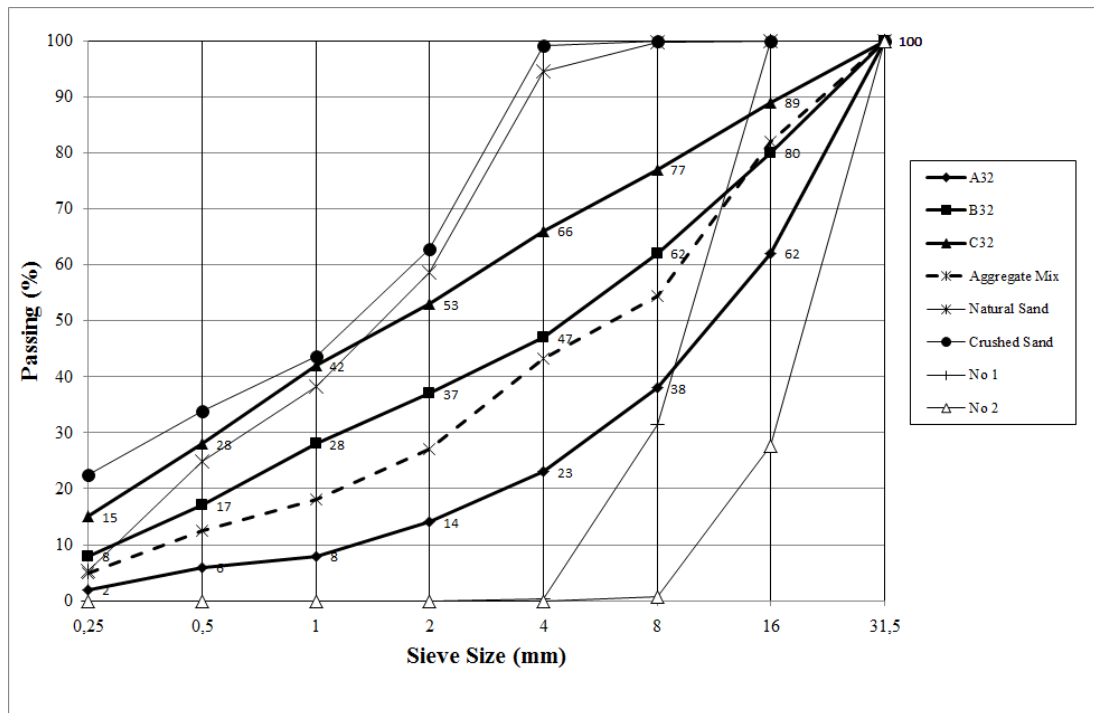


Figure 3.1 Grading of the aggregates

3.2 Mix proportioning and test specimens

Concrete mixtures with water-to-binder (w/b) ratio of 0.40 and metakaolin(MK) substitution levels of 5% and 15% were designed. To develop the metakaolin modified concrete mixtures, the Portland cement was partially replaced with MK by weight of the total binder content. The details of the concrete mixtures as well as 28 and 90 day compressive strength values were given in Table 3.3. The chloride was added in concrete as sodium chloride of analytical reagent grade. For production of chloride contaminated concrete, the chloride concentrations of 0%, 0.91%, 1.82%, 3.03% corresponding to 0%,1.5%, 3%, and 5% NaCl concentration by mass of cement were used. Thus, totally twelve different mixtures were prepared in this study.

The specimens for the accelerated corrosion and linear polarization resistance tests were Ø100x200 mm cylindrical concrete specimens. Φ16 mm diameter reinforcing steel bar was centrally embedded in concrete. The steel bar was embedded into the concrete cylinder such that its end was at least 30 mm from the bottom of the cylinder. The exit of the steel bar from the concrete cylinder was coated with epoxy to avoid crevice corrosion. For electrical resistivity measurements of concretes, Ø100x200 mm concrete cylinders without reinforcement were also used. For each test two specimens were utilized.

After casting the concrete specimens, they were covered with a plastic sheet and left in the casting room for 24 h. Then, the specimens were demoulden and transferred to lime saturated water for curing.

Table 3.3 Mixture proportions and compressive strengths of the concretes

Mix proportions (kg/m ³)	Materials		Control	5MK	15MK
	Cement		420	399	357
	Water		168	168	168
	Metakaolin(MK)		0	21	63
	Coarse Aggregates	No1	753	749	742
		No2	263	262	259
	Fine aggregates	Natural Sand	593	589	581
		Crushed Sand	182	180	178
	Superplasticiser		2.94	5.04	8.4
Compressive Strength (MPa)	at 28 days		63.8	67.7	72.4
	at 90 days		67.8	71.0	77.6

3.3 Test methods

3.3.1 Accelerated corrosion test (ACT)

ACT is a rapid corrosion testing method used for comparing the corrosion behaviour of plain and MK incorporated concretes with different chloride contamination levels. Figure 3.2 is a schematic representation of the experimental set up for the ACT. The specimens were immersed in a 5% NaCl solution leveling the midheight of the cylindrical specimens. The steel bar which is considered as working electrode was connected to the positive terminal of a DC power source. The negative terminal was connected to counter electrode (stainless steel plates) and it was placed near the specimen in the 5% NaCl solution. In this system, the steel plates are the cathode while the steel bar is the anode, and the % NaCl solution is the electrolyte. An anodic potential of 30V was impressed to initiate the corrosion process. The reason for using a high impressed voltage is to shorten the test period by accelerating the corrosion process. In Figures 3.3 and 3.4, the photographic views of the specimens after termination of the test and the experimental set up are shown.

The specimens were observed to see how long it takes for corrosion initiation of the surface cracks. Recording of the variation of the current with time was achieved through a data logger connected to a computer (Figure 3.4). The abrupt increase in the current indicates the crack initiation. The time to failure of the specimens and change of current with time was determined for all concretes. Two specimens from each mixture were tested at the age of 28 days.

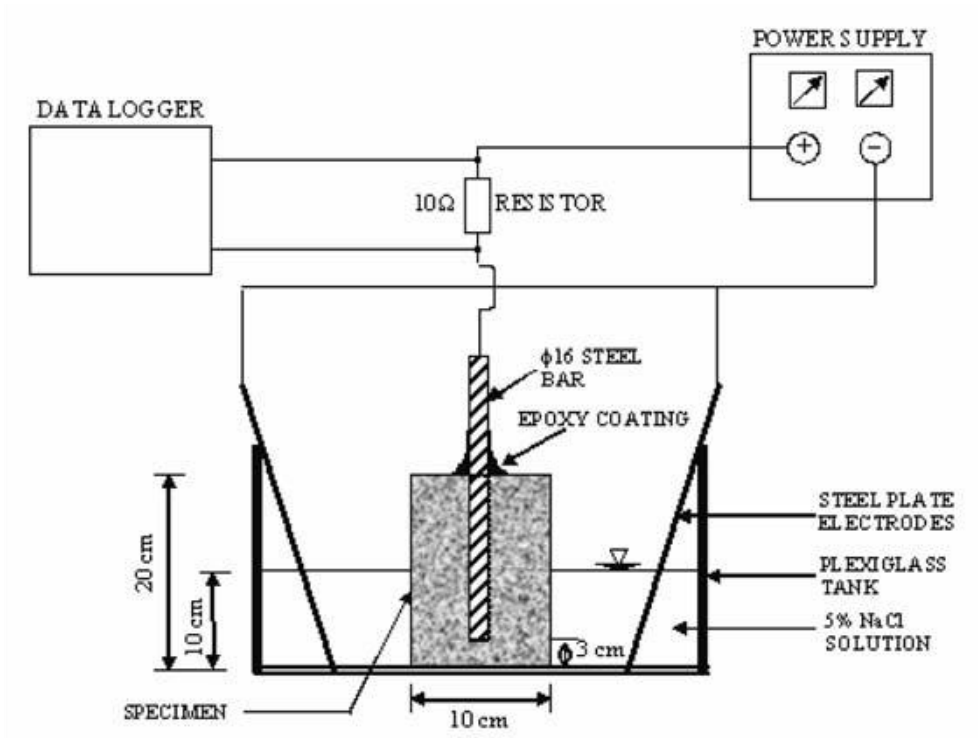


Figure 3.2 Schematic view of the ACT set up



Figure 3.3 Typical corrosion specimens after finishing ACT

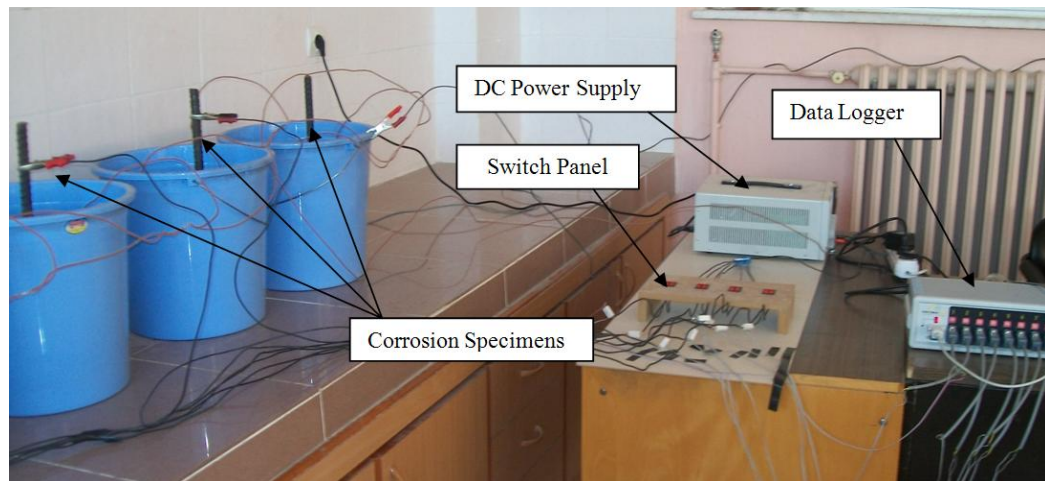


Figure 3.4 Photographic view of accelerated corrosion test set up

3.3.2 Corrosion current density by linear polarization resistance (LPR) technique

The term linear polarization refers to the linear regions of the polarization curve, in which slight changes in current applied to corroding metal in an ionic solution cause corresponding changes in the potential of the metal (Liu , 1996). This technique uses a single voltage scan or ramp programmed from an initial potential to a final potential (range generally limited to +/- 20mV vs. open circuit at E_{corr}) that progresses at a defined step height per step time. Technique also referred to as LPR, provides capability to calculate corrosion rate. The linear polarization resistance method has been considered to be a relatively simple and reliable technique to assess the rate of corrosion reinforcement in concrete (Andrade et al., 1986; Maslehuddin and Al-Amoudi, 1992).

Corrosion current density (I_{corr}) value of less than $0.1 \mu\text{A}/\text{cm}^2$ indicates negligible corrosion, while a value greater than $0.3 \mu\text{A}/\text{cm}^2$ indicates active corrosion

(Rodriguez et al., 1994). Therefore, in this investigation, an I_{corr} value of $0.3 \mu\text{A}/\text{cm}^2$ was considered as the threshold criterion for corrosion initiation.

The corrosion current density was measured using the DC linear polarization resistance method with lower potentials. The resistance to polarization (R_p) was determined by conducting a linear polarization scan in the range of ± 25 mV of the open circuit potential at a scan rate of 0.1 mV per second. The corrosion current density (I_{corr}) will be then calculated using the Stern–Geary Formula: $I_{\text{corr}}=B/R_p$, where B is a constant based on the anodic and cathodic Tafel constants (β_a and β_c) (Stern and Geary, 1957). B is calculated by the formula: $B= (\beta_a \cdot \beta_c)/(2.303(\beta_a + \beta_c))$. The value of B was taken as 26 mV considering steel in active condition (Maslehuddin and Al-Amoudi, 1992). Lambert et al. (1991) have indicated a good correlation between the corrosion current density determined by the linear polarization resistance method and gravimetric weight loss using these values. According to Faraday’s law, the following equation can be applied to calculate the corrosion rate (CR) in mm/yr (Ismail and Ohtsu, 2006).

$$\text{CR}=3.27 \times I_{\text{corr}} \times \text{E.W.}/d \quad (3.1)$$

where E.W. is the equivalent weight of steel in gm and d is the density of reinforcing bar in gm/cm^3 .

In this study, VersaSTAT 3 a potentiostat/galvanostat with an optional frequency response analyzer (FRA) contained in a single unit was used to polarize the steel at a rate of 0.1 mV/s. Tafel constants were utilized in the calculation of the corrosion current density. As well as corrosion current density, CR values of each mixture were

also calculated and presented. The test set up is schematically illustrated in Figure 3.5. In Figure 3.6, the photographic view of the potentiodynamic test set up was also presented.

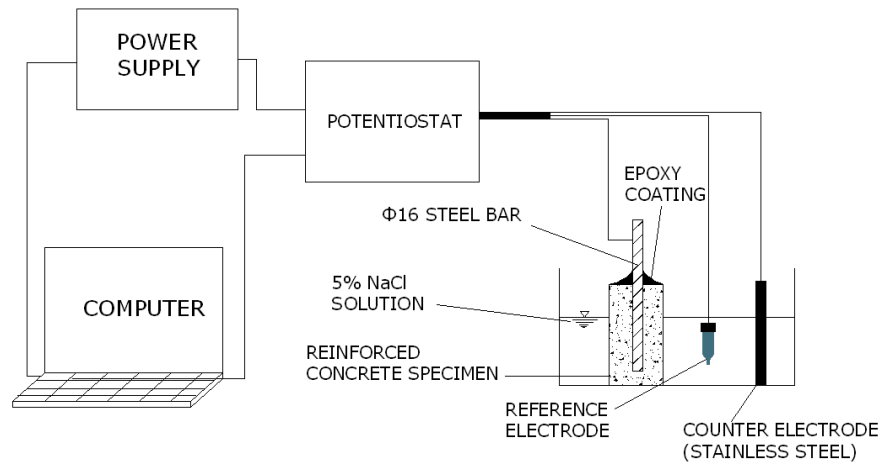


Figure 3.5 Schematic presentation of the linear polarization resistance test set up

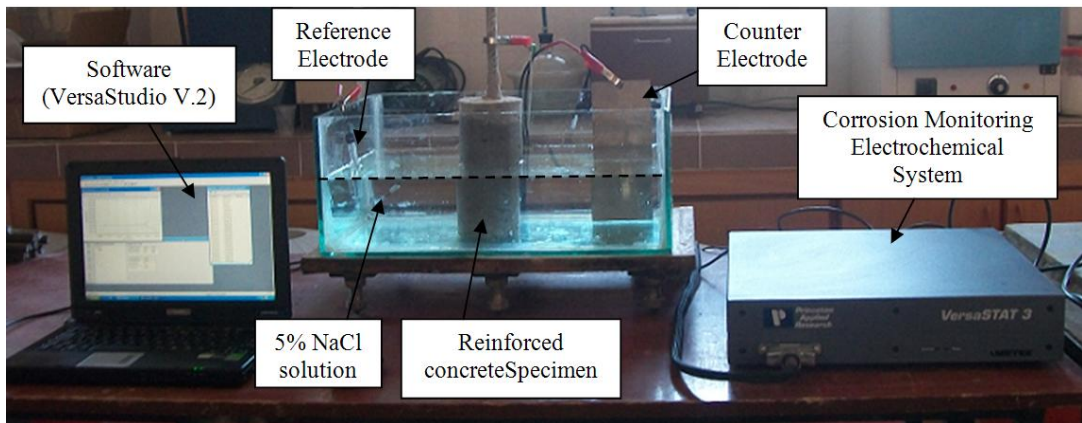


Figure 3.6 Photographic view of the potentiostat/galvanostat test set up

3.3.3 Electrical resistivity

Commercially available non-destructive testing RM-8000 model resistivity meter was used, which produced frequency-independent resistivity measurement for evaluating the resistivity of concretes (Gowers and Millard, 1999). The test is performed on Ø100x200 mm cylinder specimens. For this purpose, two electrodes of the resistivity meter are placed in the holes drilled to a depth of 8 mm in concrete and filled with conductive gel. The spacing between electrodes is 50 mm (Figure 3.7.). During the test, a small alternative current is applied between probes and the resultant potential difference is measured across the probes. The resistivity R of the concrete, for a semi-infinite geometry, is then determined. Two measurements are taken on the side face of each specimen, and the averages of four readings on two specimens are reported. No measurements were made on the top and bottom faces of the cylinders to avoid variations induced by bleeding and repetitive vibration, respectively.



Figure 3.7 Photographic view of the ER test device

CHAPTER 4

TEST RESULTS AND DISCUSSIONS

4.1 Accelerated corrosion test

The accelerated corrosion behavior of steel bars embedded in plain and MK incorporated concrete specimens subjected to different chloride contamination conditions were studied by impressing a constant anodic potential. The current required to maintain the fixed potential was plotted against time and the typical curves of corrosion current versus time for 15MK concretes with and without chloride ions are illustrated in Figure 4.1. As seen from Figure 4.1, current–time curve had a tendency of steady low rate of increase in current for a few days for 0% chloride contamination level. However due to the addition of 3.03% chloride ion, this duration was significantly shortened and rapid increase in current due to the formation of the surface cracks in specimens was detected until failure of the specimen. The sudden rise of the current intensity was observed to coincide with the cracking of the specimen. Thus, it was reported that this curve can be utilized to determine the corrosion time of the specimen when the specimen cracked due to corrosion and the current started to increase sharply (Güneyisi et al., 2005). Figure 4.2 presents the average corrosion times required to crack the plain and MK concretes contaminated with different levels of chloride. Time to cracking in plain concretes was in 5-102 hrs (0.2-4.25 days) whereas that in 5MK and 15MK concretes were 18-120 hrs (0.75-5 days) and 25-130 hrs (1-5.5 days), respectively. The resistance of concretes was seemed to be improved by inclusion of MK, especially at

higher rate. The increase in the chloride concentration resulted in sharp decreases in the times of failure, especially for the plain concrete group. When 0.91% chloride contamination is considered, the reductions in time to failure were observed to be 59% and 31% for 5MK and 15MK concretes, respectively, while it was measured as 78% for control concrete.

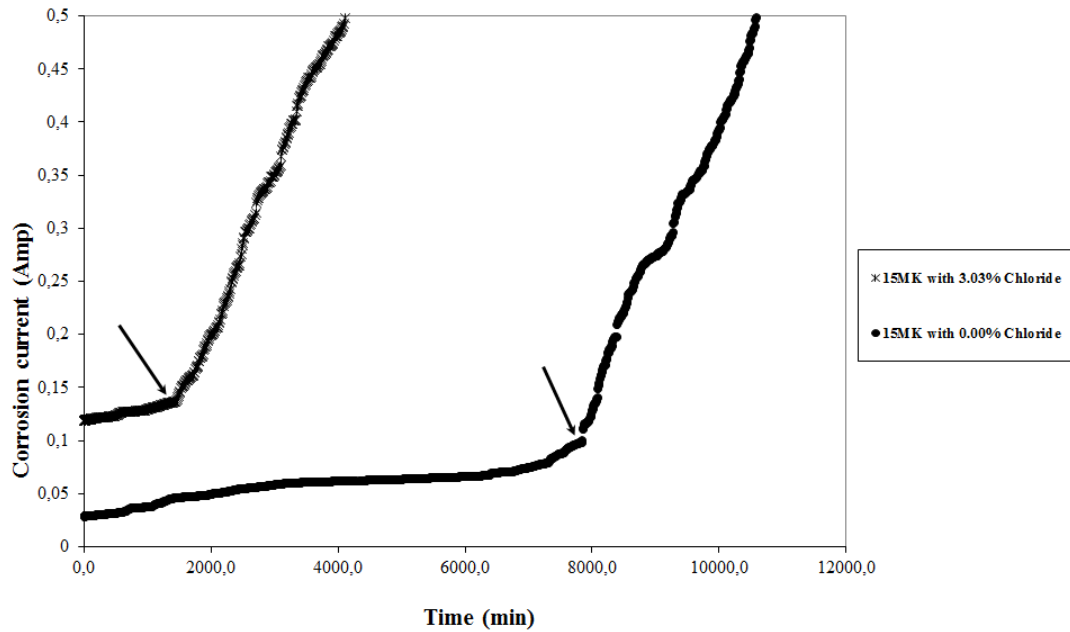


Figure 4.1 Typical time-current for the concretes containing %15 MK

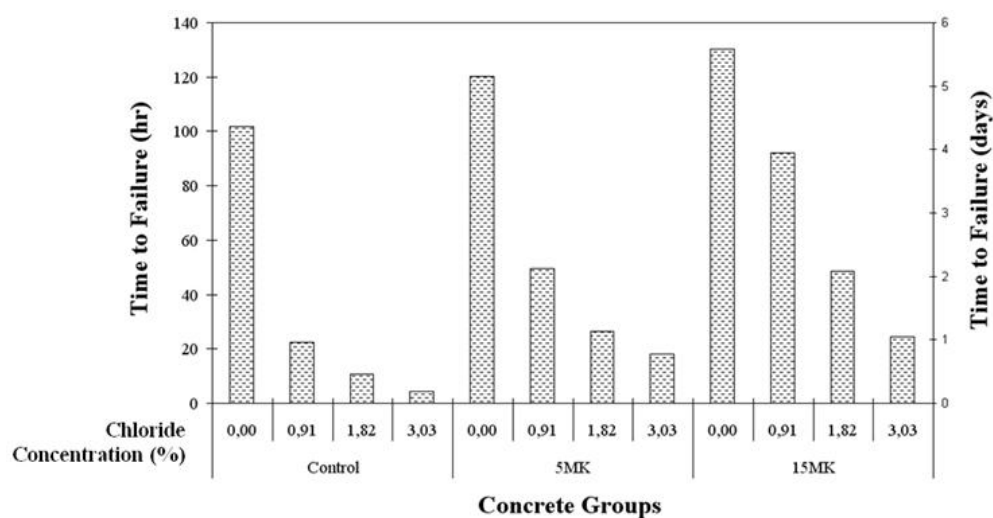


Figure 4.2 Effects of MK replacement and chloride contamination levels on the average time required to crack the specimens under accelerated corrosion test

4.2 Corrosion current density and corrosion rate

The progress of the corrosion and consequently the performance of the MK admixed concretes can be monitored by means of the corrosion current density measurement. In Figures 3-4, the corrosion current densities and the corresponding corrosion rates of the concretes were illustrated, respectively. Negligible and active corrosion zones were bordered by dotted horizontal lines in Figure 4.3. It can clearly be seen from the figure that there is a systematic decrease in the corrosion current density of the concretes due to the increase in the amount of chloride admixed. In previous studies, it was reported that when chloride concentration increases in both exposure media or in concrete itself, the corrosion current density increases and concrete becomes more vulnerable to corrosion (Liu, 1996; Ismail and Ohtsu, 2006; Fajardo et al., 2009; Pradhan and Bhattacharjee, 2009). The effect of chloride concentration on control concrete is more pronounced than MK concretes. At 1.82 % and 3.03% chloride concentration levels, plain concrete showed active corrosion behavior, whereas MK concretes generally stayed in moderate corrosion region. 5MK concrete with 3.03% chloride concentration slightly exceeded the threshold corrosion current density ($0.3 \mu\text{A}/\text{cm}^2$). On the other hand, 15MK concrete without chloride contamination seemed to have negligible corrosion. For a given chloride concentration level, the utilization of MK especially at 15%, provided good performance to the concrete in terms of corrosion. This situation can be attributed to the contribution of MK in both chloride binding capacity and the improvement in cement paste matrix. Silica fume (SF) is one of the most important supplementary cementing materials used for production of concretes with improved mechanical and durability properties. In some studies, it was proposed that this material has similar or better contribution for providing additional performance to concrete when compared to MK (Poon et al., 2006).

However, Thomas et al. (2011) stated that the chloride binding was highest with metakaolin and lowest with silica fume due to the distinction in the amount of the alumina content. This situation can be considered as an evidence for superior performance of the concretes including MK for corrosion behavior when considering the other mineral admixtures.

To visualize the effect of corrosion on the mass loss of the reinforcement, the corrosion rate was also calculated and presented in Figure 4.4. The corrosion rates were varied between 0.0025-0.0058 mm/yr, 0.0015-0.0035 mm/yr, and 0.0013-0.0032 mm/yr for control, 5MK, and 15MK concretes, respectively. The highest corrosion rates at each chloride concentration level were observed at control concrete. The corrosion rate values obtained for 5MK and 15MK concretes were close to each other at the same level of chloride content. MK concretes with the highest chloride content had the corrosion rates over 0.003 mm/yr. Nevertheless, the plain concrete even at 0% chloride reached to that value. The corrosion rate of plain concrete was observed to reach 0.006 mm/yr due to the inclusion of chloride ions. Ismail and Ohtsu (2006) studied corrosion rate of ordinary and high-performance concrete subjected to chloride attack by AC impedance spectroscopy. They produced high performance concrete with 550 kg/m^3 including 10% silica fume (water/binder=0.3), however, ordinary portland cement concrete had 300 kg/m^3 cement (water/binder=0.6). They concluded that, HPC specimens show lower corrosion rates, compared with OPC specimens. The lower w/c ratio and the use of silica fume could result in a lower corrosion rate. In this study, MK exhibited similar performance in terms of mitigation the effect of corrosion.

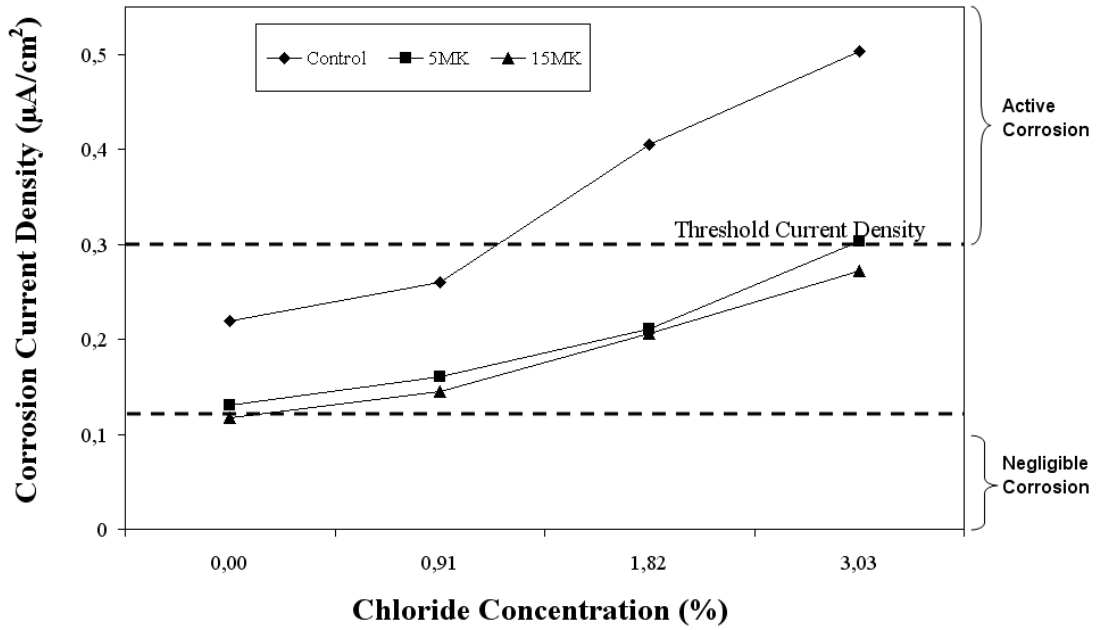


Figure 4.3 Change of the corrosion current density with the change in level of chloride contamination

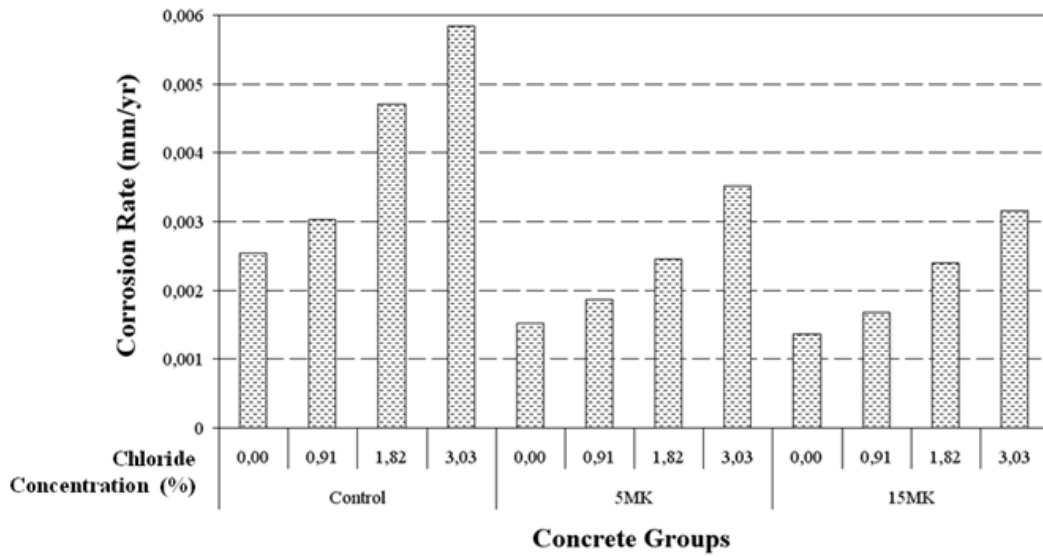


Figure 4.4 Corrosion rates of the concretes with respect to the level of MK used and the chloride contamination level

4.3 Electrical resistivity

The data concerning the variation of electrical resistivity with chloride contamination and MK incorporation level are shown in Figure 4.5. The electrical resistivity values

of plain, 5MK, and 15MK concretes were ranged between 7.5-14.5, 9.6-15.2, and 13.2-22.9 kohm-cm, respectively, depending mainly on the level of chloride concentration. The results revealed that the amount of MK and the level of contamination had significant effect on electrical resistivity values. When a constant chloride contamination level is considered, the increase in the amount of MK resulted in increase in the resistivity values. Gesoğlu and Özbay (2007) used multisystem blends of fly ash, ground granulated blast furnace slag, and silica fume for concrete production and they reported that, using mineral admixtures enhances the electrical resistivity of the concretes with increasing the cementitious materials content. From Figure 4.5, it was also noted that the increase in the level of chloride contamination, dramatically reduced the electrical resistivity of the concretes. For example, 15MK concrete with no chloride content had 22.9 kohm-cm resistivity, while 0.91% chloride addition resulted a decrease to 18.9 kohm-cm.

Wee et al. (2000) explained the lower chloride permeability of concretes containing mineral additives in terms of the lower ionic conductivity (OH^- ions) of the pore fluid and the denser microstructure of the cement paste which may also explain the higher electrical resistivity of these concretes. Therefore, it can be inferred that the higher the ionic conductivity due to the introduction of chloride ions, the lower the electrical resistivity resulting in the susceptibility to initiation of corrosion. However, it should be noted that utilization of MK provides an improvement in electrical resistivity of the concretes as a result of chloride binding property (Thomas et al., 2011). Thomas et al. (2011) reported that the cement pastes incorporating MK had remarkable chloride binding capacity due to high alumina content (45% Al_2O_3). MK also provides a denser structure to concrete by microfilling and secondary pozzolanic reactions (Wild et al., 1996; Poon et al., 2006). Moreover, Güneyisi et al. (2005)

stated that the increase in the electrical resistivity with strength of concrete was mainly due to the denser microstructure of concrete.

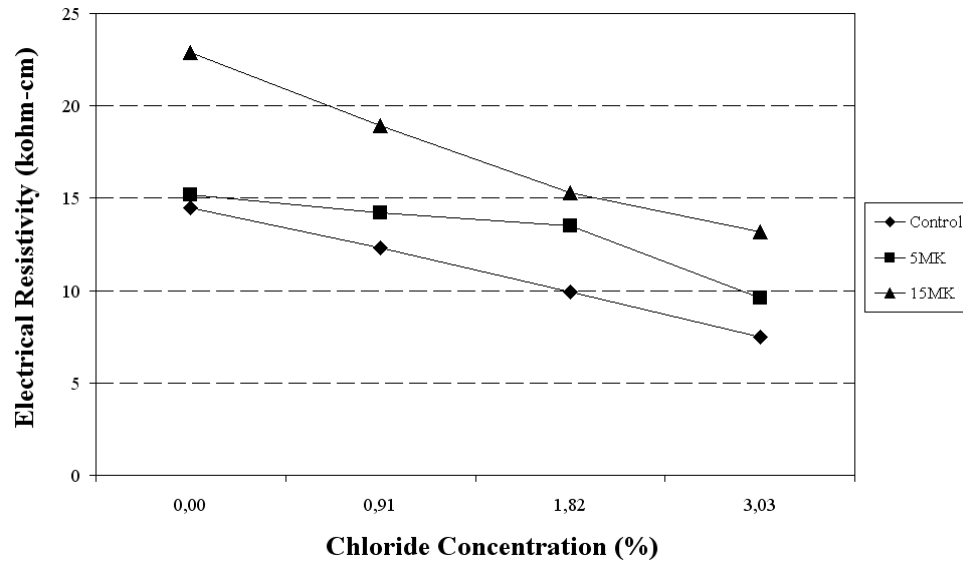


Figure 4.5 Variation in electrical resistivity of the concretes with chloride contamination levels

CHAPTER 5

CONCLUSION

Based on the findings presented in this study, the following conclusions can be drawn.

- Times to failure in chloride contaminated concretes were shortened as the chloride concentration increased. The shortest failure time was observed at control concrete with 3.03% chloride content (5 hours). However, the longest time was observed at 15MK concrete (132 hours). It was observed that there are large differences between time to failure values of the plain and MK concretes. This situation implies that the utilization of MK is effective for enhancing the corrosion resistance to concrete.
- The minimum corrosion current density values were measured 15MK concretes, irrespective of the chloride contamination level. The values obtained for 5MK concretes were fall between those of plain and 15MK concretes. However, 5MK concretes demonstrated a close trend to that of 15MK. For example, at 0.91% chloride contamination level, corrosion current densities of control and 5MK concretes were 1.80 and 1.11 times that of 15MK concrete, respectively. When the chloride concentration increased to 1.82%, these ratios become 1.97 and 1.02 for control and 5MK concretes, respectively.
- Corrosion rates of the concretes seemed to have similar trends with the aforementioned findings. The highest corrosion rate was measured as 0.0058

mm/yr in control concrete at 3.03% chloride contamination. However, use of MK provided approximately 50% reduction in corrosion rate.

- Increased level of chloride contamination resulted in significant reduction in electrical resistivity of concretes. The lower the electrical resistivity the higher the corrosion risk occurs in reinforced concrete. However, the utilization of MK notably improved electrical resistivity of the concretes, especially at 15% level of replacement.

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