CHAPTER ONE

INTRODUCTION

1.1 FIELD OF STUDY

There is no doubt that, the corrosion of reinforcing steel embedded in concrete considers a major problem worldwide. This problem takes place because of the effect of chlorides, sulphates or carbonation which attacks the concrete cover. It has been estimated that the annual cost of repair to UK concrete structures due to reinforcement corrosion is above £500 million, while in the USA, the associated repair due to reinforcement corrosion in concrete bridges alone has been estimated at $ 50 billion per annum (Wyatte, 1993).

In the Middle East, 74% of reinforced concrete structures show significant corrosion damage after as little as ten to fifteen years, due to the presence of salts such as chlorides and sulphates. The warm marine climate with saline ground conditions increase the corrosion problems. Corrosion control is made more difficult by the problems of curing concrete in hot, drying environments, and has led to very short lifetimes for reinforced concrete structures. Many structures have to be rebuilt every ten years of so unless extensive rehabilitation or repair is carried out (Rasheeduzzafar et al, 1992 and Lambert, 1995).

Chlorides are the principal cause of reinforcement corrosion in concrete structure. If the concentration of chlorides exceeds a threshold value, the passive oxide film on the surface of the reinforcement can be disrupted. In the presence of oxygen and moisture, corrosion then occurs. The chlorides may be introduced at the time of mixing (internal chloride) or penetrate once the concrete has hardened (external chloride). With internal chloride the amount of chloride which can become physically and /or chemically bound with the cement hydrates depends upon, principally, the cementitious, material and the total chloride content (Arya and Xu, 1995).

Steel embedded in good dense concrete is normally protected by the alkaline environment that is provided by the hydrated cement matrix and the pore solution phase which has a pH of around 13 to 14. In this condition, an invisibly thin passive layer is formed on the steel and this layer can be attacked and destroyed by the effects of chlorides ions and carbonation (Sideris and Savva, 2005). Once this layer gets damaged, an electrochemical processes of corrosion take place which leads to either localised attack (pitting) which cause the formation of rust which in turn causes expansive forces leading to cracking and spalling of concrete or uniform loss of thickness of steel (general corrosion) (RILEM Draft Recommendation, 1994).

There are different methods to inhibit or decrease the effect of corrosion of steel in concrete such as; patch repair, cathodic protection, cathodic prevention, coated steel with zinc or epoxy, admixed chemical corrosion inhibitors, corrosion inhibitors for remedial treatment of reinforced concrete in hardened state, electrochemical realkalisation and electrochemical chloride extraction (ECE). Some of these approaches have met with varying degrees of success; most are complicated and are practically not cost-effective (Ngala, 1995, Abdelaziz, 1998 and Page et al, 2000).

Patch repair method usually can be carried out with the removal of the deteriorated zones and cleaning of the steel surface. This method is expensive and may damage the structural integrity when large areas have to be treated. Repairs are often repeated every several years, which each successive repair being increasingly greater in magnitude. The presence of high levels of chloride ions remaining in concrete will allow the corrosion process to continue. The repair material also proves to be a problem since corrosion cells are in advertently created between steel embedded in the chloride-free repair material and the steel embedded in the existing chloride contaminated concrete. This result in corrosion damage along the periphery of the patch and eventually complete failure will occur within the surrounding material and the repair itself. It looks of interest to study alternative remedial measures which avoid the need of an extensive concrete removal or rebar cleaning (Alonso et al, 1996 and Daily and Somerville, 2000).

Corrosion inhibiting admixtures such as, sodium benzoate and sodium nitrite have been studied by many researches since 1970. Recent studies discussed other different corrosion inhibiting admixtures such as calcium nitrite and organic and inorganic inhibitors. The possible mechanism of corrosion inhibitors in reinforced concrete exposed to chlorides has been discussed by Hansson et al, 1998, Trepanier et al, 2001 and Giadis, 2004). The inhibitor can delay the onset of corrosion by a) reducing the rate of ingress of aggressive ions (chlorides) through increasing the rate of chemical binding of chlorides and/or raising the chlorides threshold value for corrosion initiation, and b) reducing the rate of corrosion once it is initiated. However, there is a lack of experimental evidence to confirm these above mentioned mechanisms.

Brown et al (2001) and Giadis (2004) have investigated the effect of calcium nitrite inhibitor on slump and setting time of concrete. Their results have shown the addition of this inhibitor has led to decreasing the slump and accelerating the initial and final setting time. However, there is a lack of information in literature regarding the other aspects of fresh concrete, flowability, rate of flowability loss and rheology of concrete containing corrosion inhibiting admixtures (CIA).

Hansson et al (1998) and Berke and Hicks (2004) have recently studied the effect of calcium nitrite as corrosion inhibiting admixtures (CIA) on the compressive strength of OPC concrete. They found that the inclusions of calcium nitrite on OPC concrete had led to a slight increase in the compressive strength of concrete. An opposite finding was obtained by Batis et al (1996) when they have used sodium benzoate as CIA. However, the effectiveness of CIA on the other mechanical properties of concrete such as tensile and bond strength have not been fully investigated yet.

Moreover, up to the author’s knowledge, there is no attempt has been carried out in literature to elaborate the effectiveness of corrosion inhibiting admixtures (CIA) on pore structure, cement-phase composition and permeation properties of concrete. If such elaborations are available, the mechanism of CIA on the corrosion activity of reinforcement would be clearly understood. So there is a need for carrying out such study to find a scientific explanation for the mechanism of CIA and then provide a reasonable explanation to its effectiveness on various fresh and mechanical properties of OPC matrix.

Gowripalan and Mohamed (1998) discussed the effect of steel coating (zinc rich) on corrosion potential of normal strength concrete and high strength concrete. Broomfield et al (1996) reported that the steel coating (zinc rich) improved the bond strength between steel and concrete by more than 20% in the high strength steel and more than 120% in the case of mild steel when compared to uncoated steel, while Gaidis and Rosenberg (2001), conformed that, the steel coating reduced the bond between the steel and concrete. However, the microstructure of the interfacial zone between concrete and steel have not deeply investigated and understood.

There are several alternative methods available for remedial treatment of chloride-contaminated reinforced concrete. Some of which involve the use of surface-applied corrosion inhibitors such as calcium nitrite (CN), sodium nitrite and sodium mono-fluro phosphate (MFP) that are intended to penetrate the concrete cover to the reinforcing steel thus modifying the electrochemical behavior of the reinforcing steel (Douch et al , 2005 and Chaussadent et al , 2006).

Ngala et al, 2002 and Ngala et al, 2003 have investigated the role of MFP and CN, respectively on the corrosion of embedded steel in concrete using two different solutions of either 15% MFP or 15% CN, which were applied repeatedly for 700 days to reinforced concrete specimens of 0.65w/c. The treated specimens were contaminated with various level of chloride contamination (0, 0.6, 1.2 and 2.4%, by weight of OPC). It was noted that the higher chloride content, the lower the effective of MFP and CN on the corrosion rate and the efficiencies of MFP and calcium nitrite on corrosion activity were comparable. These findings agree with the results obtained earlier carried out by Page et al (2000).

However, there is still a lack of information regarding the efficiency and mechanism of MFP and CN as a surface-applied corrosion inhibitor and its impact on the various corrosion activity aspects (such corrosion potential and corrosion current density) and microstructure. Moreover, there is a need to study the effectiveness of MFP and CN on electro-chemical activity of reinforcing steel embedded in OPC matrix especially that collaborated with cement replacement materials, namely silica fume and fly ash. Where, such replacement materials are commonly used nowadays and strongly recommended by specifications and concrete technologists for manufacturing reinforced concrete that would expose to sever environments, e.g. chlorides. Furthermore, understanding the impact of MFP and CN on the microstructure of cover concrete could be a useful approach to understand the mechanism of such treatment.

Due to chloride-induced corrosion, there are two rehabilitation methods currently available that are capable of stopping corrosion once it has been initiated: the conventional treatment of cathodic protection and the electrochemical chloride extraction. Both techniques normally use an impressed current that transforms the corroding steel from a collection of anodic and cathodic sites to a cathode with the addition of an external electrode and power supply to the surface of the concrete (Ali et al, 1992 and Buenfeld and Broomfield, 2000).

In cathodic protection, a current density of 3 to 20 mA/m^2 of concrete surface is typically applied for the remaining lifetime of the contaminated structure. Electro-chemical chloride extraction, however, uses higher current densities over shorter time periods, typically 0.5 to 5 A /m^2 of concrete surface for 4 to 8 weeks (Sharp et al, 2002). The resulting effect is that chlorides are removed from the concrete rather than migrating only a short distance away from the reinforcing steel. The primary advantage of electrochemical chloride extraction is that it reduces the long-term personnel and maintenance cost associated with cathodic protection (Green et al, 1993) and Marcotte et al (1999- a).

Marcotte et al (1999- a) studied the effect of ECE treatment on corrosion rate of reinforced OPC mortar made with 0.5 w/c ratio, 1/3 cement / sand ratio, 2% admixed NaCl and exposed to external chloride ingress of 1 mol/L NaCl. After approximately 10 months, linear polarization resistance measurements were performed on those specimens prior to ECE treatment. The extraction treatment was performed using an impressed current density of 1 A/m^2 for 8 weeks with 0.1 mol/L sodium borate as an electrolyte and platinized mesh as an external anode. Their results indicted that specimens exposed to external ingress chlorides exhibited lower corrosion rate than those made with admixed chlorides and the corrosion rate measurements remained significant high even after 31 days of ECE treatment. These findings confirmed the results reported by Green et al (1993), who observed that, prior to the application of the extraction treatment, the corrosion rates were 80to350 mA/m^2, whereas immediately after the treatment, the corrosion rate was 3.2 A/m^2 and dropped to 80 mA /m^2 after 21 days of treatment. They concluded that the extraction treatment did not significantly reduce the corrosion rate of reinforcement in the period up to 21 days after the treatment was halted.

Polder (1996) studied the efficiency of ECE treatment using different electrolytes, water and sodium borate and various cement types (OPC, slag cement). He reported that no influence on the chloride removal efficiency was found when the electrolyte and cement type were changed. On contrary, Sharp et al (2002) noted that, in specimens made with OPC, 0%-52% of the chlorides were removed during ECE treatment, whereas 33%-76% of the chloride were removed from the specimens made with type II cement. These observations agrees with those obtained by Orellan et al (2004), where their results showed that about 40% of the initial chloride was removed within 7 weeks after ECE treatment using calcium hydroxide as an electrolyte.

The efficiency of ECE using impressed current densities of 1 and 5 Ampere/ m^2 for 10, 20 and 31 days as period of treatment applied on reinforced OPC mortar was recently investigated by Toumi et al (2007). They observed that, ECE can significantly reduce the amount of chloride ions and increase the amount of the potassium and sodium ions in the region of the reinforcement.

On the other hand, several attempts have been carried out to investigate the microstructure of concrete treated with ECE. Marcotte et al (1999- b) studied the effect of ECE treatment on concrete microstructure using scanning electron microscopy. An impressed current density of 1 A/m^2 was used. They revealed that both chlorides and C-S-H were not detectable on the transition zone around reinforcement after the extraction treatment. The pore structure of untreated and treated OPC concrete made with w/c ratio = 0.4, admixed sodium chloride of 2.5% was also assessed by Siegwart et al (2003). They found that the pores in the untreated specimen were less frequent and larger than those in the treated specimen and the surface close to the anode in the treated specimen had the lowest total number of pores. However, the effect of using ECE with different impressed current densities on the microstructure of concrete still needs more clarifications.

It seems from the available data in literature that most studies were concerned with the short-term effectiveness of ECE on reinforcement corrosion, while, up to the authors' knowledge, there is a lack of information regarding the long-term effect of

ECE on corrosion rate after halting ECE process. It is thought that chloride ions can re-diffuse towards reinforcement after stopping ECE treatment. If such phenomenon occurs, this means that the passive film created on reinforcement surface due to ECE would be disrupted again. Thus, reinforcement corrosion might take place and remedial treatment measures have to be considered. However, this believe has to be confirmed by an experimental proof.

Moreover, there is still a need to signify the factors affecting ECE processes, such as, density of impressed current, duration of ECE treatment, type of electrolyte, cement type and source of chlorides (admixed and ingress). Where, there is a lack of information regarding the efficiency of ECE on SRC concrete and contradictory results regarding the effects of these parameters on the corrosion rate of reinforcement imbedded in treated concrete. Furthermore, the impact of ECE treatment on cement-phase composition and crystal structure of the transition around reinforcement still needs for more clarifications, to have a good understanding to the mechanism and effectiveness of ECE and to determine any possible side-effect of such treatment.

1.2 PURPOSE OF STUDY

The main objectives of this study can be summarized as follows:

1- To investigate the role of corrosion inhibiting admixtures on cement –phase composition, pore structure and permeation characteristic of OPC matrix and signify the importance of using corrosion inhibiting admixtures on reducing the corrosion activity of reinforcing steel.

2- To clarify the role of corrosion inhibiting admixtures on mechanical properties (compressive, tensile and bond strength) and fresh parameters (setting time, initial flowability, rate of flowability loss and rheology) of OPC matrix.

3- To clarify the influence of steel coating on corrosion activity of reinforcement, bond strength and microstructure of interfacial zone between steel and concrete.

4- To investigate the corrosion activity of reinforced OPC matrixes made with or without silica fume and fly ash and contaminated with different chloride contents prior to and after the application of MFP and CN.

5- To determine the factors affecting the efficiency of adopting MFP and CN as remedial treatment and to study the impact of MFP and CN on crystal and cement-phase composition of the interfacial zones around reinforcement.

6- To assess the long-term effect of ECE after halting the treatment on corrosion rate of re-passivated reinforcement, i.e. to study the possibility of occurrence of re-diffusion of chloride ions towards reinforcement after halting ECE treatment.

7- To signify the factors controlling the efficiency of ECE treatment and to clarify the effect of ECE on the microstructure of interfacial zone around reinforcement and chloride profile of cover zone.

1.3 OUTLINE OF THESIS

This thesis is divided into seven chapters, following this introduction (chapter 1). A review of literature is presented in chapters 2. This review presents a general review in the field of durability of reinforced concrete and the different methods to inhibit or decrease the corrosion, and their impacts on the various fresh and hardened properties of concrete.

Chapter 3 gives a brief description of the over-all experimental program, under taken together with details, mix proportions, specimens' preparation and testing techniques used throughout this investigation.

Chapter 4 shows the results and discussion of corrosion inhibiting admixtures by studying the effect of corrosion inhibiting admixtures (calcium nitrite and sodium benzoate) on fresh properties of mortar (flowability, flowability loss, rhoelogy and setting time). The effect of these inhibitors on corrosions behavior, mass transport, pore structure, microstructure and mechanical properties of mortar (compressive strength, tensile strength, bond strength) are also presented. This chapter also outlines the results and discussion of coating steel by studying the effect of coated steel on microstructure, bond strength between steel and surrounding matrix and corrosion behavior of steel embedded in OPC matrix.

Chapter 5 describes the results and discussion of corrosion inhibitors for remedial surface treatment of reinforced mortar by discussion the effect of different inhibitors types (calcium nitrite (CN), sodium mono fluro-phosphate (MFP) on corrosion rate, potential, mass transport and microstructure of mortar specimens. The influence of cement replacement materials on efficiency of these inhibitors is also presented.

Chapter 6 involves the results and discussion of electrochemical chloride extraction (ECE) treatment by studying the effects of cement type (OPC, SRC), initial chloride content and ingressed chloride content on this treatment. The effects of different current densities, various duration of treatment and several electrolyte types (water, calcium hydroxide) on efficiency of ECE treatment are also presented. A comparison between all methods studied to delay corrosion of steel embedded in mortar matrix was assessed in end of this chapter.

Chapter 7 shows the general conclusions and recommendations for further work.