



HOKKAIDO UNIVERSITY

Title	Corrosion Resistance of Steel Reinforcement in Fly Ash Concrete under Chloride Penetration
Author(s)	Zafar, Idrees
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第12023号
Issue Date	2015-09-25
DOI	https://doi.org/10.14943/doctoral.k12023
Doc URL	https://hdl.handle.net/2115/59931
Type	doctoral thesis
File Information	Idrees_Zafar.pdf



**CORROSION RESISTANCE OF STEEL REINFORCEMENT
IN FLY ASH CONCRETE UNDER CHLORIDE
PENETRATION**

塩分浸透を受けるフライアッシュコンクリートの鉄筋腐食抵抗

Idrees Zafar

**DIVISION OF FIELD ENGINEERING FOR THE ENVIRONMENT
GRADUATE SCHOOL OF ENGINEERING
HOKKAIDO UNIVERSITY**

September, 2015

**CORROSION RESISTANCE OF STEEL REINFORCEMENT
IN FLY ASH CONCRETE UNDER CHLORIDE
PENETRATION**

塩分浸透を受けるフライアッシュコンクリートの鉄筋腐食抵抗

Idrees Zafar

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Examination Committee

Prof. Takafumi Sugiyama

Prof. Hiroshi Yokota

Prof. Tatsuya Ishikawa

DIVISION OF FIELD ENGINEERING FOR THE ENVIRONMENT
GRADUATE SCHOOL OF ENGINEERING
HOKKAIDO UNIVERSITY

September, 2015

ABSTRACT

Japan is now among the world's leading coal importers to fulfil its power generation demand and is generating more than 10 million tons of coal ash as a by-product from coal fired thermal power plants every year. The quantity of coal ash produced is estimated to increase due to the construction of new coal fired power plants to meet the power generation demands. To cope with the expected increase in the generation of coal ash in the future, the increase in its effective utilization in concrete, apart from dams and cement industry, is one of the important issues under focus. The increase in the utilization of fly ash in reinforced concrete structures like bridges and high rise buildings requires the durability aspect of the concrete to be tested. Specifically, in the region like Japan which is surrounded by sea and has harsh winter conditions (Hokkaido), the corrosion resistance of embedded steel subjected to salt attack becomes a primary concern. In this regard, the current study is focused on various stages of corrosion i.e. corrosion initiation, corrosion propagation, corrosion under flexural cracking in fly ash concrete with a main aim to understand the mechanism of corrosion in fly ash concrete and to recommend the increase in the usage of fly ash as a partial replacement of ordinary Portland cement in concrete to the construction industry.

In the first stage we evaluated the performance of fly ash concrete against the corrosion initiation subjected to chloride ion ingress. According to JIS A 6201, fly ash Type II which is recommended for use in concrete was used in this research. Two different replacement ratios of fly ash as a partial replacement to cement i.e. 15% and 30% at a constant water to binder ratio of 0.5 under different curing period of 28 days and 91 days with deformed and plain rebars were tested against 10% NaCl solution exposure. A lead-lead oxide (Pb/PbO_2) electrode was embedded in all the specimen series to reliably detect the corrosion initiation of rebars in fly ash concrete along with combination of alternating impedance spectroscopy. The experimental results have shown that the corrosion resistance was exceptionally improved for fly ash concrete with 30% cement replacement and combination of long curing and plain rebars. The increased corrosion resistance for fly ash concrete is mainly attributed to the pozzolanic reaction and high concrete resistance as compared to normal concrete. The fly ash concrete specimens having a cover depth of 20 mm with plain bar and curing of 91 days have not shown corrosion initiation even after 7 years exposure to salt solution and are still under monitoring. The long curing period for fly ash concrete resulted in a dual beneficial effect of delaying the onset of corrosion due to lowered diffusion coefficient and pushing the chloride threshold values of fly ash concrete close to that of normal concrete. On the other hand the 28 day curing period for fly ash concrete led to the reduction in the corrosion initiation time along with the chloride threshold values. After 28 days of curing, the chloride threshold value for 30% replacement of fly ash was 0.41% by mass of binder, compared to 0.71% for normal Portland cement concrete. The chloride threshold value for fly ash concrete after 91 days of curing, however, was increased to 0.66% by mass of binder. In addition it was also observed that the longer curing for fly ash concrete has resulted in better performance against corrosion than just increasing cover depth.

In the second stage the fly ash concrete was tested during the propagation period of corrosion from moderate to high corrosion rate. The corrosion state of the reinforcement in concrete containing 15% and 30% of fly ash as a partial replacement of cement was analyzed within specified limits of corrosion current density ($0.5\text{--}1.0\text{ }\mu\text{A}/\text{cm}^2$). Four different series of reinforced concrete specimen based on the fly ash replacement ratio and curing period were tested against the salts solution exposure. All the reinforced concrete specimens were subjected to 10% NaCl solution to de-passivate the reinforcement bars. The specimens were of the same configuration as used for the initiation stage and an alternating current impedance spectroscopy was used to obtain the impedance data at regular intervals of two weeks. It was observed that

activation polarization was found to be the governing mechanism of rebar corrosion irrespective of the fly ash addition. Furthermore the fly ash concrete with a long curing had depicted the extended time period to reach the specific degree of corrosion but had also shown the highest surface corroded area and increased the probability of pitting corrosion.

In the third stage an effort was made to clarify the performance of fly ash concrete in the presence of cracks against corrosion, under static loading conditions. The specimens were subjected to 10% NaCl solution under repeated wet and dry cycles for 106 days. A specially designed apparatus was used to generate the cracks and to keep the specimens under constant bending moment. The uniqueness of this apparatus is the application of salt solution only in the limited region i.e. crack mouth. The results have shown that the presence of cracks, irrespective of the fly ash replacement as a part of cement, can adversely affect the corrosion resistance of rebars embedded in concrete when exposed to wet and dry cycles under static loading. However, fly ash concrete has shown suppressed values of corrosion current density values as compared to normal Portland cement concrete under cracked conditions and is mainly because of high resistivity as well as the self-healing effect for fly ash concrete as compared to the normal concrete. It is inferred that the fly ash replacement as a part of cement in concrete with cracks can effectively reduce the severity of concentrated diameter loss of rebar under the exposure of saline solution through wet and dry cycles.

Furthermore the corrosion monitoring of the steel reinforcement in a RC waste water outlet structure incorporating fly ash cement, located at an electric power generation plant which is still in service for last 40 years was done. The electrochemical data has shown that the reinforcement in real structure incorporating fly ash are still in the passive state clearly indicating the high durability of fly ash against corrosion. The corrosion evaluation of real structures in service is of utmost importance from practical point of view.

Dedication

To my beloved family

Acknowledgement

Up and above anything else, praises are due to Almighty Allah alone, the omnipotent, and the omnipresent.

It is matter of great pleasure and honor for me to express my heartiest gratitude and appreciation to respected and learned research supervisor Prof. Takafumi SUGIYAMA, under whose kind supervision and sympathetic attitude, the present research was completed. His guidance enabled me to treat this work objectively and comprehensively.

I am sincerely grateful to all esteemed members of the doctoral committee, Prof. Hiroshi YOKOTA and Prof. Tatsuya ISHIKAWA for their comments and advices.

Sincere appreciation goes to MEXT (Ministry of Education, Culture, Sports, Science and Technology, Japan) for awarding highly prestigious “Monbukagakusho Scholarship” to support this study in Hokkaido University.

Honest gratitude must be extended to Dr. Kazunori SHIMURA and Dr Michael Ward HENRY. To all students and staff of the Environmental Material Engineering Laboratory at Hokkaido University, the author wishes to express his sincere appreciation for the friendly and supportive atmosphere that certainly helped him to carry out this research in a pleasant working environment.

Earnest thanks must go to the author’s colleagues, especially Mr. Junro FURUMURA, Mr. Motoki KANEKO, Mr. Tatsuya NAKATA and Mr. Eitaro MOMONO, the former undergraduate and graduate students in Environmental Material Engineering Laboratory. Their support contributes in many ways for the completion of this study.

No acknowledgement would ever adequately express my obligation to my parents and wife who have always wished to see me flying high up at the skies of success. Without their prayers, sacrifices and encouragements the present work have been a merry dream.

List of Publications

International Journal

1. Idrees Zafar and Takafumi Sugiyama, “Laboratory Investigation to Study the Corrosion Initiation of Rebars in Fly ash Concrete”, Magazine of Concrete Research, 2014, 66(20): 1051-1064.

International Referred Conference Proceedings

2. Idrees Zafar and Takafumi Sugiyama, “Study on the effect of Bending Crack on Corrosion of Rebars in Fly Ash Concrete”, in proceedings of “The 6th International Conference of Asian Concrete Federation, ACF 2014”, September 21-24, 2014, Seoul, Korea. 1111-1113
3. Idrees Zafar and Takafumi Sugiyama, “Experimental Factors with regard to Increased Corrosion Resistance in Fly Ash Concrete”, in “EURO COAL ASH 2014”, October 14-15, 2014, Munich, Germany. 251-264
4. Idrees Zafar and Takafumi Sugiyama, “Study on the Corrosion of Rebars in Fly Ash Concrete during Moderate to High Corrosion Rate”, in proceedings of “Fourth International Symposium on Life-Cycle Civil Engineering, IALCCE 2014”, November 16-19, 2014, Waseda University, Tokyo, Japan. 1538-1543

Presentation

5. Idrees Zafar and Takafumi Sugiyama, “Study on the Progressive Corrosion State of Rebars in Concrete based on Corrosion Current Density measurements”, in “1st International Doctoral Symposium with partner Universities, Structural and Hydraulic Engineering. Disaster Presentation, Mitigation and Restoration”, February 7-8, 2013, Hokkaido University, Sapporo, Japan.
6. Idrees Zafar and Takafumi Sugiyama, “Study on the Initiation and Propagation of Reinforcement Corrosion in Fly Ash Concrete Subjected to Chloride Ingress”, in “Ecoba Coal ash Research Workshop”, October 13, 2014, Munich, Germany.
7. Idrees Zafar, Motoki Kaneko and Takafumi Sugiyama, “Study on Moderate to High Corrosion State of Rebars in Fly Ash Concrete due to Chloride Penetration”, in “NACE International East Asia & Pacific Rim Area Conference & Expo 2013”, November 19-21, 2013, Kyoto, Japan.

Others

8. Motoki Kaneko, Idrees Zafar and Takafumi Sugiyama, “ Study on the effect of Bending Crack on Corrosion of Reinforced steel in Concrete”, in proceedings of “The Annual Conference of Japan Society of Civil Engineers, Hokkaido Branch, No. 70: E07. ”, February 01, 2014, Sapporo, Japan.
9. Eitaro Momono, Takafumi Sugiyama and Idrees Zafar,” Corrosion diagnosis of doubly reinforced RC slab by using half-cell potential method”, in The 69th Annual meeting of Cement and Concrete Engineering, 12-14 May, 2015, Tokyo, Japan.
10. Jhutan Chandra Kuri, Idrees Zafar and Takafumi Sugiyama, “ Application of X-ray CT to the Observation of Cracking in a Corroded RC Bridge Slab”, in the 2nd International Conference on the Tomography of Materials and Structures, ICTMS 2015, 29 June – 3rd July, Quebec, Canada.

Table of Contents

ABSTRACT	i
Dedication	iii
Acknowledgement.....	iv
List of Publications.....	v
Table of Contents.....	vi
List of Figures	ix
List of Tables	xii
CHAPTER 1 INTRODUCTION.....	1
1.1. GENERAL	1
1.2. THEORITICAL BACKGROUND	1
1.2.1. Fly Ash	1
1.2.2. Corrosion of steel in concrete.....	2
1.2.3. Chloride-induced corrosion in concrete	4
1.2.4. Corrosion stages	5
1.2.5. Corrosion initiation of rebar in concrete (Chloride Threshold Values).....	6
1.2.6. Corrosion of rebars during propagation stage	7
1.2.7. Corrosion of rebars in cracked concrete	8
1.3. RESEARCH OBJECTIVES	9
1.4. THESIS STRUCTURE	9
CHAPTER 2 MATERIALS AND METHODS.....	12
2.1. Materials and mix proportions	12
2.2. Specimen configuration	13
2.3. Embedded reference electrode	16
2.4. Electrochemical measurements.....	17
2.5. Determination of chloride ion concentration	20
2.6. Calculation of hydroxide content	20
2.7. Measurement of surface corroded area	21
2.8. Crack formation	22
2.9. Crack width measurement.....	23
2.10. Exposure conditions.....	23

2.11. Measurement of attack penetration	23
2.12. In-Service Reinforced Concrete Waste Water Outlet Structure	24
CHAPTER 3 CORROSION INITIATION OF REBARS IN FLY ASH CONCRETE.....	26
3.1. Performance of Embedded Reference Electrode	26
3.2. Time to Initiate Corrosion	33
3.3. Chloride Threshold Level.....	34
3.4. Steel-Concrete Interface	35
3.5. Probabilistic Analysis for Corrosion initiation.....	37
3.6. Summary	39
CHAPTER 4 CORROSION OF REBARS IN FLY ASH CONCRETE FROM MODERATE TO HIGH CORROSION RATE.....	40
4.1. Half-Cell Potential Measurements	40
4.2. Corrosion Current Density Measurements	42
4.3. Specific Concrete Resistance Measurements	43
4.4. Relationship between Corrosion Potential and Corrosion Current Density.....	45
4.5. Corroded Surface Area and Attack Penetration of Concrete Specimens	47
4.6. Summary	49
CHAPTER 5 CORROSION OF REBARS IN CRACKED FLY ASH CONCRETE.....	50
5.1. Crack Width Variation.....	50
5.2. Electrochemical Measurements	50
5.3. Chloride Ion Concentration.....	53
5.4. Surface Corroded Area and Attack Penetration	54
5.5. Summary	55
CHAPTER 6 CORROSION MONITORING OF REAL REINFORCED CONCRETE STRUCTURES	56
6.1. In-Service Reinforced Concrete Waste Water Outlet Structure	56
6.1.1. Electrochemical Measurements	56
6.1.2. Chloride ion Concentration Analysis	56
6.1.3. Verification for Corrosion Reinforcement with regard to service life	57
6.2. Summary	60

CHAPTER 7 CONCLUSION AND FUTURE WORKS.....	61
REFERENCES.....	63

List of Figures

Figure 1.1 Schematic illustration of chloride induced corrosion in concrete.....	4
Figure 1.2 Typical deterioration levels for a steel reinforced concrete structure suffering from corrosion.	5
Figure 1.3 Specific volumes of the corrosion products of iron.	6
Figure 1.4 Schematic diagram for corrosion induced cracking in concrete.	7
Figure 1.5 Outline of Thesis Chapters.....	10
Figure 2.1 (a) Test specimen setup showing corrosion monitoring system, placement of rebars (UP and DO) and application zone of 10% NaCl solution (b) Cross section of test specimen showing the position of plain rebars and electrode (c) Embedded Reference Lead Electrode (d) Placement of electrode in formwork (All units in mm)CT Number profile of concrete.....	15
Figure 2.2 (a) Test specimen setup showing placement of rebars along with the application zone of 10% NaCl solution (b) Cross section of test specimen showing details of rebars (units in mm).....	16
Figure 2.3 (a) Test specimen setup showing corrosion monitoring by corrosion meter (b) Schematic view for the measurement positions done by corrosion meter	18
Figure 2.4 (a) Schematic diagram for half-cell potential measurement relative to a reference electrode (b) Measurement of half-cell potential relative to Pb/PbO ₂ for F30Z (1) specimen.	19
Figure 2.5 (a) Schematic diagram showing the location of the point drilled (R side) for chloride analysis (b) Slicing of slat application zone (L side) Preparation of mortar beam for flexural test.	21
Figure 2.6 Apparatus showing the specimens in a three point bending mode along with the application of 10% NaCl solution during wet and dry cycle	22
Figure 2.7 (a) Three measurement points on the surface of tension fiber along the length of crack (b) Five measurement locations for each measurement point.	22
Figure 2.8 (a) Corrosion monitoring of a RC waste water outlet structure (b) Location of electrochemical measurements (A-D) and drilled cores (1-2) for chloride analysis....	25
Figure 3.1 Measurement of Half-cell Potential values by Embedded Lead Electrode of (a) N50P, (b) F15D, (c) F30D, (d) F30DL, (e) F30P and (f) F30PL series.	28

Figure 3.2 (a): Half-Cell Potential measured by Corrosion Meter of F30DL (2) Specimen and (b): No Visible Corrosion Products on the Reinforcement of F30DL (2) Specimen, (c): Half-Cell Potential measured by Corrosion Meter of F30DL (4) Specimen and (d): Visible Corrosion Products on the Reinforcement of F30DL (4) Specimen	30
Figure 3.3 Measurement of Specific Concrete Resistance at different Locations for F30DL (4) Specimen	30
Figure 3.4 Measurement of Specific Concrete Resistance at UM for (a) N50P, (b) F15D, (c) F30D, (d) F30DL, (e) F30P and (f) F30PL Series	32
Figure 3.5 Threshold Values for Half Cell potential and Polarization resistance for Fly ash concrete.....	34
Figure 3.6 Chloride Threshold Values for all the specimen series.	35
Figure 3.7 Corrosion Products attached to the concrete interface at (a) ribs for deformed bar and (b) air void for plain bar.....	36
Figure 3.8 Probability of corrosion initiation estimated by Monte-Carlo simulation.	38
Figure 4.1 Trend of half-cell potential measurements for (a) N2Z, (b) F15Z, (c) F30Z and (d) F30ZL series.	41
Figure 4.2 Time period for initiation and propagation period for N2Z, F15Z, F30Z and F30ZL series.	41
Figure 4.3 Trend of corrosion current density measurements for (a) N2Z, (b) F15Z, (c) F30Z and (d) F30ZL series.....	43
Figure 4.4 Trend of Specific concrete resistance for (a) N2Z, (b) F15Z, (c) F30Z and (d) F30ZL series	45
Figure 4.5 (a) Relationship between E_{corr} and I_{corr} for all the specimen series (b) Relationship between E_{corr} and I_{corr} during Active state of corrosion.....	46
Figure 4.6 Relation between Corroded Surface Area and Attack Penetration.	47
Figure 4.7 Corroded Surface of UP rebar: (a) N2Z (4), (b) F30ZL (4), UP rebar of F30ZL (1) specimen after cutting and removal of corrosion products in (c) and (d) respectively.	48
Figure 4.8 Histogram for the Diffusion Coefficient and Chloride Concentration.	48
Figure 5.1 Crack width variation at the end of specified cycles for (a) N2C2 and (b) F30C2 Specimen.	51
Figure 5.2 Trend of half-cell potential against time for (a) N2C and (b) F30C series.....	52
Figure 5.3 Trend of corrosion current density values against time for (a) N2C and (b) F30C Series	52
Figure 5.4 Semi-log plots of half-cell potential versus corrosion current for the steel embedded	

in N2C, F30C, N2Z and F30ZL series.	53
Figure 5.5 Distribution of chloride ion concentration: from exposed surface (a) N2C2 and (b) F30C2 specimen.	53
Figure 5.6 Plot between estimated mean corrosion depth and measured mean corrosion depth of all specimen series	54
Figure 5.7 Plot between surface corroded area and mean corrosion depth.	54
Figure 5.8 Rebar surface after removal of corrosion products (a) N2C4 and (b) F30C4 specimen.	55
Figure 6.1 The presence of fly ash particle by scanning electron microscope	56
Figure 6.2 Half-Cell Potential (E_{corr}) and Corrosion Current (I_{corr}).	57
Figure 6.3 The profiles of chloride ion concentration for core specimens.	57
Figure 6.4: The predicted profiles of chloride ion concentration after a service life of 50, 100 and 125 years for normal concrete and fly ash concrete.	59

List of Tables

Table 1.1 Specifications for four types of fly ash according to JIS A 6201	2
Table 2.1 Properties of fly ash used in this study	12
Table 2.2 Physical Properties of Ordinary Portland cement, Fine and Coarse Aggregates.....	13
Table 2.3 Mix Proportions of Concrete Specimens for all Corrosion Stages.....	13
Table 2.4 Configuration of Concrete Specimens for Initiation	14
Table 2.5 Configuration of Cracked Concrete Specimens	16
Table 2.6 Average Initial Crack width for C, CT and CB series	23
Table 2.7 Details of the waste water outlet structure.....	24
Table 3.1 Average values of T_i , D_o , C_s , CTL and CH for all specimen series	33
Table 3.2 Input parameters for Monte Carlo Simulation in terms of Log-Normal Probability	38
Table 3.3 Comparison of Experimental and Predicted values of T_i	38
Table 6.1 Predicted chloride ion concentration values at cover depth after certain period of service life	60

CHAPTER 1

INTRODUCTION

1.1. GENERAL

Corrosion of reinforcement in concrete has been established as one of the main deterioration mechanism which outlines the service life of reinforced concrete structures. The major source of steel reinforcement corrosion is the presence of chlorides either from contaminated aggregates, chloride containing admixtures, penetration from sea or ingress of de-icing salt. The chlorides ions diffuse into concrete, mount up near the surface of the reinforcing bars causing the passive film around the reinforcement, because of high alkaline environments, to break down and subsequently initiate the corrosion of reinforcing steel. The corrosion will proceed, provided with favorable conditions, forming the expansive corrosion products and generating the cracks along the reinforcement, and subsequently, spalling of the concrete cover may occur. The bare steel reinforcement will corrode further causing the reduction in the rebar cross section. Finally, the loss of cross section of the reinforcement will lead to reduction of the load bearing capacity.

In last few years the incorporation of supplementary cementitious materials like fly ash, silica fume and slag in concrete, has been proposed as one of the effective methods to reduce the corrosion induced damage in concrete structures [1-2]. Fly ash, among the rest of cementitious materials is the common pozzolan and used worldwide in blended cements. It is generally recognized that the inclusion of fly ash in concrete improves its resistance against chloride-induced corrosion of steel reinforcement by reducing its permeability, particularly to chloride ion transportation and increasing the resistivity of the concrete [3]. Recent advanced technique with X-ray CT employed for the microstructure evolution in cementitious materials led to better understanding of fly ash concrete [4-5].

In addition it is evident that the replacement of ordinary Portland cement with industrial by-products like fly ash, silica fume and slag is highly beneficial from the stand point of cost, economy, energy efficiency and overall ecological and environmental benefits. Coal-fired thermal plants play a vital role in the consistent supply of electric energy in Japan, and to keep the plants functional, the key component i.e. coal is imported from overseas markets. Consequently, a vast amount of coal ash is produced annually as industrial by-product and is expected to increase due to the construction of new coal fired power plants to meet the power generation demands. To cope with the expected increase in the generation of coal ash in the future, the increase in its effective utilization in concrete, apart from dams and cement industry, is one of the important issues under focus. The increase in the utilization of fly ash in reinforced concrete structures like bridges and high rise buildings requires the durability aspect of the concrete to be tested. Specifically, in the region like Japan which is surrounded by sea and has harsh winter conditions (Hokkaido), the corrosion resistance of embedded steel subjected to salt attack in reinforced concrete structures becomes a primary concern.

Furthermore the corrosion monitoring of the real reinforced concrete structures in service is also highly important to minimize the economic losses due to corrosion of steel reinforcement. The detailed analysis of real structures, in the light of laboratory testing, is necessary to determine the cause and mechanism of corrosion, so that those factors should be eliminated to prevent further corrosion damage in real reinforced structures.

1.2. THEORITICAL BACKGROUND

1.2.1. Fly Ash

Fly ash sometimes also known as flue ash primarily comes from coal-fired electric generating power plants. The coal is provided in various mills within power plants so as to

pulverize it to fine powder before burning. During the coal combustion process, glassy aluminosilicate spherical particles i.e. fly ash remain in suspension within the flue gas from the boiler and are ultimately collected by electrostatic precipitators and stored in silos.

According to ASTM C 618, fly ashes can be divided into two main classes, F and C, based on their chemical composition resulting from the type of the coal burned. The sum of silicon dioxide (SiO₂), aluminum oxide (Al₂O₃) and iron oxide (Fe₂O₃) should be more than 70% and 50% of the total mass for class F and C respectively. Generally class F fly ash is formed from anthracite or bituminous coals, whereas class C Fly ash is formed from lignite or sub-bituminous coals. The information of the silica, alumina, and iron oxide content of the ash indirectly indicates the behavior of fly ash in concrete. Another important parameter includes the calcium oxide content, fineness, and loss on ignition (LOI, an indicator of carbon content) of the ash.

JIS A 6201 is the standard which details the use of fly ash for concrete in Japan. According to the latest modification in JIS A 6201 (1999), fly ash is categorized into four types named as Type I, Type II, Type III and Type IV [6]. Some of the major properties of these types are summarized in Table 1.1. Among these Type II is recommended for the use in concrete as an admixture.

Table 1.1 Specifications for four types of fly ash according to JIS A 6201

Property		Type I	Type II	Type III	Type IV
Ignition loss (%)		3 or less	5 or less	8 or less	5 or less
Specific surface area (cm ² /g)-Blaine method		5000 or over	2500 or over	2500 or over	1500 or over
Activity Index (%)	28 days	90 or over	80 or over	80 or over	60 or over
	91 days	100 or over	90 or over	90 or over	70 or over
Specific Gravity (g/cm ³)		1.95 or over			
Silicon dioxide: SiO ₂ (%)		45 or over			
Hygroscopic moisture (%)		1 or less			

1.2.2. Corrosion of Steel in Concrete

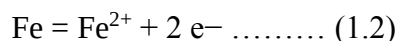
Iron and plain carbon steels are thermodynamically unstable materials. Nature will bring these materials back to their original and thermodynamically stable forms, specifically oxides, i.e. rust. Under neutral and alkaline environments, as in concrete, the corrosion process requires the presence of both water and oxygen. The process of corrosion is provided by electrochemical reactions, i.e. chemical reactions involving transfer of electrons and electric charges at the interface between the metal and the concrete. Different types of iron oxides may be formed depending on exposure conditions:



This overall reaction may be divided into two reactions, called half-cell reactions, which are running simultaneously at adjacent locations, often very close to each other (microscopic distances), or separated by macroscopic distances. If the two half reactions occur at widely separated locations, it is termed a macro-cell corrosion and when it occurs sufficiently close

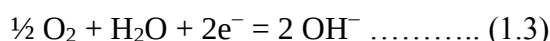
together, or essentially at the same location, they are defined as micro-cell corrosion. One of the half-cell reactions, called the anodic reaction, is the dissolution of iron, i.e. an oxidation of iron to form ferrous ions and leaving behind electrons in the metal:

Anodic reaction – oxidation of iron



Iron is oxidized from Fe (oxidation state 0) to Fe^{2+} (oxidation state +2). In the other half-cell reaction, called the cathodic reaction, the liberated electrons from the oxidation of iron are consumed by oxygen in the presence of water to form hydroxyl (OH^-). In this reaction oxygen is electrochemically reduced from O_2 (oxidation state 0) to OH^- (oxidation state -2):

Cathodic reaction – reduction of oxygen



If no external electric source of electrons exists, the anodic reaction must generate electrons at exactly the same rate as the cathodic reaction consumes them. The algebraic sum of these two reactions makes the total reaction, called the corrosion cell reaction:

Overall Corrosion Cell Reaction:



The potential-pH diagrams have been developed, using the Nernst Equation, which indicate the conditions under which the metal is likely to corrode or not. The thermodynamic domains of immunity, passivity and corrosion of iron and iron oxides in solution are depicted in equilibrium potential-pH diagrams, i.e. Pourbaix diagrams. [7].

For sound concrete, the pH of the pore solution ranges from 13.0 to 13.5. In this high alkalinity of the pore solution, the steel embedded in concrete is usually in the passive state which enables the formation of a protective iron oxide layer, i.e. passive film. This protective layer formed in concrete is commonly thin i.e. few nano meters. Indeed whatever the thickness of passive layer it cannot stop the corrosion process rather than reducing the intensity. Studies found that in the passive state generally the corrosion rate is $0.1 \mu\text{m}/\text{year}$ which could be at least three orders in magnitude is case of existence of no passive film [8]. The exact composition and microstructure of the protective film formed in concrete is expected to vary from that formed in aqueous solutions since the composition of the concrete pore solution is certainly chemically more complex. In addition, variations in the composition and pH of the concrete pore solution, oxygen and moisture availability and existence of cement hydration products will define the nature of the film. Furthermore, with time, a rather thick ($50\text{-}200 \mu\text{m}$) and porous layer of iron oxides combined with Portlandite [$\text{Ca}(\text{OH})_2$] has been observed [9].

1.2.3. Chloride-Induced Corrosion in Concrete

The active corrosion of steel in concrete proceed by breakdown of the protective passive film. This breakdown could occur over the whole surface of the steel due to fall in pH by carbonation or locally due to localized chemical attack by aggressive ion such as chloride. Among the causes of corrosion initiation in concrete, the most common is the presence of chloride ions through admixture, contaminants, marine environment, or deicing salts. Although various kinds of theory are reported, the actual and detailed mechanism of passive film breakdown is still unclear. However, the breakdown of passive layer is typically related to one of three main mechanisms; the penetration mechanism, the film breaking mechanism and the adsorption mechanism [10]. According to the penetration mechanism, chloride ions in the electrolyte infiltrate through the passive layer to reach the metal surface due to the high potential difference across the passive film. The film breaking mechanism, assumes that discontinuities in the passive film, such as cracks resulting from sudden change in corrosion potential, allow direct access of chloride ions to the reinforcement surface. Lastly the adsorption mechanism includes the adsorption of chloride ions to the passive film resulting in progressive thinning of the passive film until complete dissolution. The overall process of chloride induced pitting corrosion in concrete can be schematically represented by Figure 1.1.

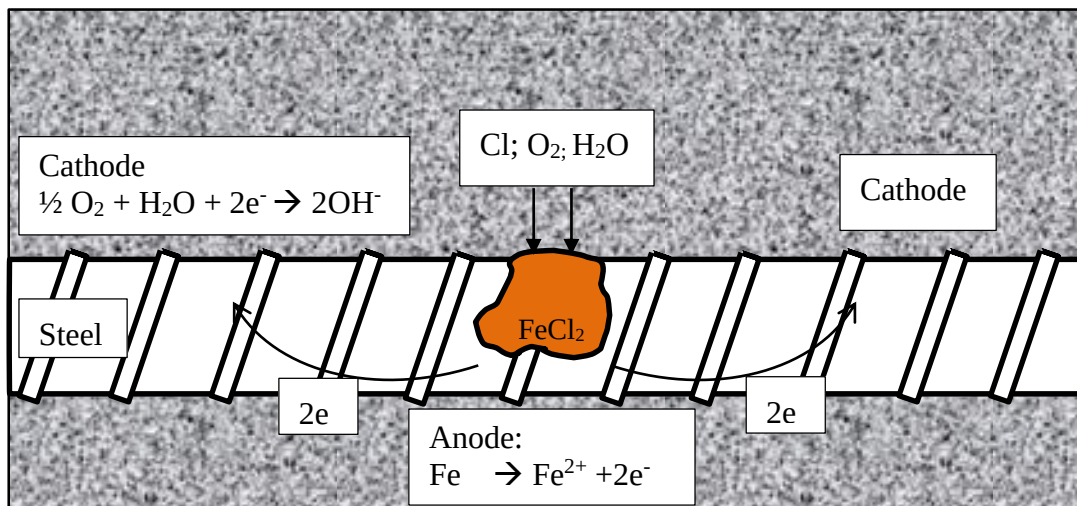


Figure 1.1: Schematic illustration of chloride induced corrosion in concrete

After breakdown of passive film this localized zone becomes anodic and it attracts more and more chloride ions toward this area than the surrounding cathodic areas as a result the local concentration of chloride ions are increased. The hydrolysis of the dissolved iron inside the pit occurs and the solution within the growing pit becomes progressively acidified [11]. In addition, a permeable layer of iron rust products is also formed on the metal surface which can significantly reduce the mass transport into and out of the pit and if provided with alkaline environments possibly repassivation can occur.

1.2.4. Corrosion Stages

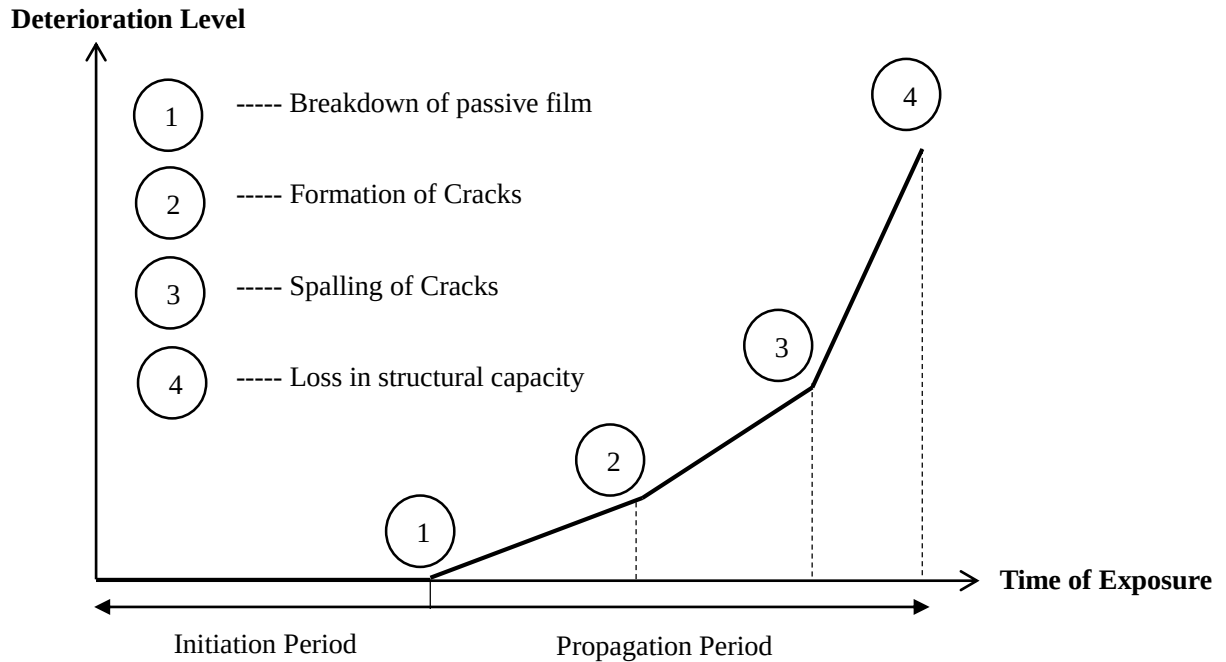


Figure 1.2: Typical deterioration levels for a steel reinforced concrete structure suffering from corrosion [adapted from 12].

Corrosion of reinforcement in concrete is generally divided into two stages, initiation stage and propagation stage. The initiation period is defined as the time until the reinforcement becomes de-passivated by the breakdown of protective passive layer which is formed on the rebars due to the alkaline environment in concrete. As soon as the concrete at the depth of the reinforcement contains a critical amount of free chlorides, corrosion of the rebars may occur. This limit state defines the beginning of the propagation period. Figure 1.2 shows the breakdown of the two stages. As shown by the figure during the propagation period the cracks start to appear which lead to the spalling of concrete cover. Once the reinforcement is exposed to the environment the corrosion rates increase rapidly and structural integrity is affected badly.

The most detrimental consequence of chloride-induced reinforcement corrosion is the build-up of voluminous, insoluble corrosion products in the concrete which leads to internal stresses and, eventually, to cracking and spalling of the concrete cover. Obviously once such damage is visually apparent, the reinforcement is prone to very rapid further corrosive attack because access to oxygen and moisture is no longer limited by diffusion through the concrete cover. All forms of iron oxide and hydroxide have specific volumes greater than that of steel but their volumes vary by a factor of more than five as indicated in Figure 1.3 [13].

Thus, the degree of damage to the concrete produced by a certain amount of corrosion will depend on the specific corrosion products formed and their distribution within the concrete cover as well as on the porosity and strength of the concrete itself.

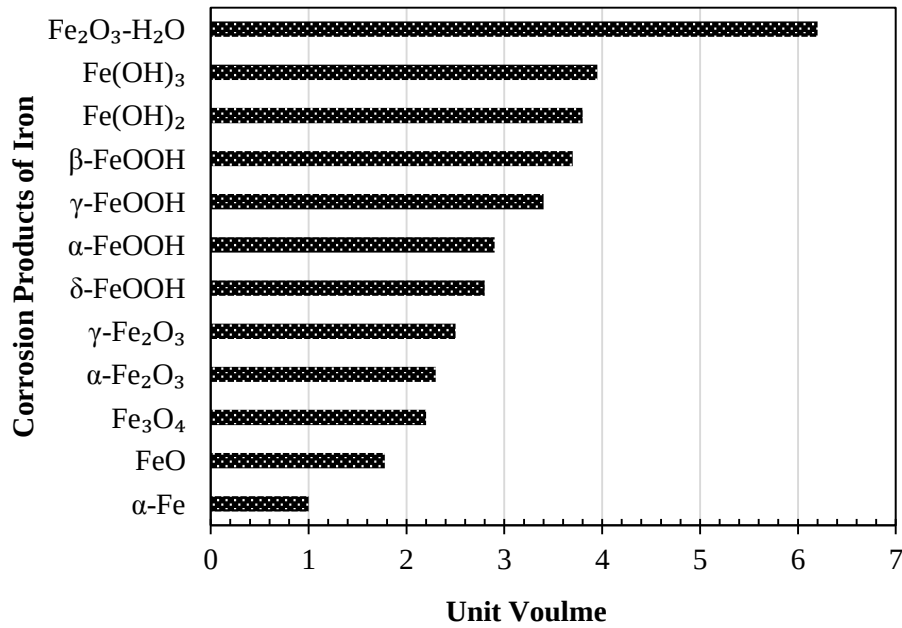


Figure 1.3: Specific volumes of the corrosion products of iron [Adapted from 13]

1.2.5. Corrosion Initiation of Rebar in Concrete (Chloride Threshold Values)

The chloride threshold level (CTL) can be defined as the critical chloride content at the depth of rebar in concrete which is necessary to initiate the corrosion process through local passive film breakdown [14]. The time period at which the chloride ions damage the passive film is termed as time to initiate corrosion (T_i). Both of the parameters, T_i and CTL are important for defining the time to first repair and service life of reinforced concrete structures [15].

Various laboratory studies have been done to determine the chloride induced corrosion initiation by monitoring half-cell potential of the reinforcement in concrete [15-17]. A method using embedded lead reference electrode inside concrete for determining the corrosion initiation of rebars in concrete has been proposed recently [19-20]. The embedded lead electrode monitors the half-cell potential of steel reinforcement and indicates initiation by a sharp drop of half-cell potential to a significant negative value. The stability of the lead electrode inside the Portland cement concrete and a given fly ash concrete has already been investigated by a recent study [20-21]. However, with the increase in the use of fly ash in concrete there is need to verify the effectiveness of this system for fly ash concrete.

Moreover, in past few decades a lot research has been done to determine CTL for Portland cement concrete [16, 17, and 22] but because of the different exposure environments, binder types, type of specimen and method applied to determine CTL values vary in a wide range. On the other hand few studies [23-24] have been done to determine the CTL values for fly ash concrete but the effect of curing on CTL for fly ash has not been studied yet. It is generally reported that the CTL values decrease with increase in the replacement of fly ash because of lowered pH of the concrete [25]. It is expected that with long curing, the increased degree of pozzolanic reaction will consume more amount of calcium hydroxide, further changing the alkali condition and as a result the CTL values might reduce more. Therefore, there is a requirement to validate the effect of fly ash replacement and curing on CTL for fly ash concrete.

Recent studies [26] have reported a range of values for T_i and CTL even for apparently similar specimens and recommended to treat both of these parameter as probabilistic in nature instead of a specific value. The randomness in the values of the T_i and CTL emphasize the use of probability based approach for durability analysis. The probability models normally used to

predict the service life in terms of corrosion initiation, assume a certain probability distribution for the above mentioned parameters [27]. However, there is limited data available on the effect of fly ash replacement, type of reinforcement and long curing on the type of probability distribution of Ti and CTL. Instead of using the normal probability distribution irrespective of the binder type and rebar type, there is a need to assess the best fit probability distribution for all the concerned parameters for fly ash concrete.

1.2.6. Corrosion of Rebars during Propagation stage

Generally, the corrosion initiation time is quite longer (decades) than that of the propagation stage (years) for the RC structures. In such situations, the accuracy of predicting the overall service life of the structure depends on the accuracy of predicting the initiation period [28]. However, few RC structures show corrosion initiation early in their service life with longer corrosion propagation stage which emphasis the need for accurate prediction of the variability in the corrosion propagation especially with the increase in the use of supplementary cementitious materials like fly ash in concrete. The early corrosion can occur in case of new structures with preexisting narrow cracking, which has caused corrosion to initiate relatively early.

Once corrosion has initiated, its propagation is governed mainly by the oxygen supply, moisture content and resistivity of concrete [29]. There are various damage indicators related to the progression of corrosion i.e. loss of rebar cross-sectional area, loss of bond strength between steel and concrete and corrosion-induced concrete cover cracking. The conceptual diagram of the corrosion induced cracking is shown in Figure 1.4.

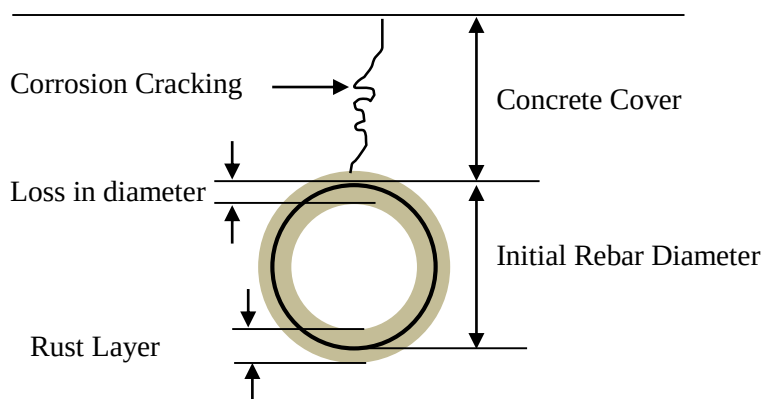


Figure 1.4: Schematic diagram for corrosion induced cracking in concrete

Corrosion acceleration by an impressed current technique is a common approach that has been used to study the propagation stage of corrosion-induced damage in concrete structures. The primary advantage of the method is to achieve the desired corrosion damage in short duration of time as compared to natural corrosion in RC structures. In this method a constant current ($5\text{--}200\ \mu\text{A}/\text{cm}^2$) is applied to achieve a certain degree of corrosion like corrosion stains, first visible crack or certain crack width. However, it has been pointed out that the commonly-used direct linear extrapolation of results acquired from accelerated testing to predict the behavior in real structures may be misleading [28 and 30]. Moreover, in real structures the values of corrosion rates higher than $1\ \mu\text{A}/\text{cm}^2$ are seldom measured, while the values between $0.1\text{--}1.0\ \mu\text{A}/\text{cm}^2$ are most frequent [31]. In addition the electrochemistry of the corrosion process in real structures is also different as compared to the impressed current method [32–33]. In this regard less data is available especially for the fly ash concrete at relatively small corrosion current density values ranging from $0.5\text{--}1.0\ \mu\text{A}/\text{cm}^2$. As per classification of corrosion rate by RILEM TC-154, $0.5\text{--}1.0\ \mu\text{A}/\text{cm}^2$ correspond to the range of moderate-high values of corrosion

rate [34].

1.2.7. Corrosion of Rebars in Cracked Concrete

The durability aspect of reinforced concrete is typically related to the concrete matrix, i.e. a dense microstructure will most likely show lower permeability and reduce the transport of corrosive agents to reinforcement. However, in real reinforced concrete structures it is certain to have cracks, either in form of the micro cracks between aggregate and cement paste or macro cracks encountered during the service life due to loading or degradation process. In addition, the increasing demands for greater loads, for example long-span bridges, make the structures prone to more cracking. Cracking adversely affects the serviceability and durability of a structure and particularly when exposed to marine environments because of the corrosion of rebars. The formation of cracks increases the transport properties of concrete because cracks space can behave as preferential passages so that the transportation of chloride ions by water or moisture movement may take only a few hours to reach the steel, while penetration of ions through the non-cracked concrete would take a longer time. Cracking has become critical feature of reinforced concrete structures and significant efforts have been done throughout the world to minimize the cracking problem in reinforced concrete structures. For the same reason, many codes and specifications have fixed the criteria of service life on the basis of allowable crack width [35-36].

Meanwhile, in last few years, the use of fly ash in concrete is becoming increasingly popular all over the world. The incorporation of fly ash in concrete can help to reduce the environmental impact of cement industry at a reduced or no additional cost [37]. Also it is generally recognized that the inclusion of fly ash in concrete improves its resistance against chloride-induced corrosion of steel reinforcement by reducing its permeability, particularly to chloride ion transportation and increasing the resistivity of the concrete [3]. According to a recent study, provided enough curing, the fly ash concrete showed the same chloride threshold values as that of normal Portland cement concrete for corrosion initiation [38]. It has also been shown that high volume of fly ash concrete has the ability to self-heal the cracks under moist conditions [39]. In addition Na et al. had shown that the self-healing performance in fly ash blended mixtures is dependent on the curing temperature, curing age and fly ash replacement ratio [40].

In recent years the effect of cracking on the penetration of chloride ion in concrete has been the focus of numerous studies [41-43]. All of these studies have clearly mentioned that the presence of cracks could add to an increase in the diffusion coefficient of chloride ion. Transport of chloride ions generally occurs by either capillary absorption, diffusion or both. It is thought that the capillary absorption occurs in dry concrete whereas diffusion can only occur when the crack space is saturated with water. Hence, the transport of ions by the absorption would be faster than that of diffusion. The degree of saturation inside the crack space is an important parameter in the transport of a solution in cracked concrete, along with the crack geometry. In the light of this it is expected that the different exposure conditions for the crack concrete, will lead to different chloride profile inside the crack space as well as in the perpendicular concrete matrix, resulting in different corrosion behavior.

In the past, a lot of research has already been done to study the effect of crack width on corrosion of rebars embedded in concrete [44-45]. But most of these studies have focused on normal Portland cement concrete and relatively less research has been done on the corrosion of rebars in fly ash concrete under cracked conditions [44]. Furthermore, in most of the laboratory investigations, the cracked samples have been fully submerged in the salt solution in the unloaded state which is quite different from the reality [46]. So there is a need to clarify the performance of fly ash concrete in cracked conditions under sustained loading.

1.3. RESEARCH OBJECTIVES

The general aims of this study are to investigate the corrosion behavior of steel reinforcement for different replacement ratios of fly ash concrete under salt attack, as the base line and compare with normal Portland cement concrete for various stages of corrosion process i.e. initiation of corrosion, propagation of corrosion and corrosion of rebar under cracked conditions. In addition an effort is made to relate the laboratory testing to the corrosion monitoring of real structures. In summary, this study has following main aims and objectives:

- 1) To establish a test method for reliable determination of corrosion initiation of rebars in fly ash concrete. In addition to clarify the effect of long curing for fly ash concrete on CTL values along with probabilistic analysis of CTL and Ti.
- 2) To determine the performance of fly ash concrete with different replacement ratios from moderate to high corrosion rate, under the application of saline solution.
- 3) To evaluate the effect of flexural cracks on the corrosion of rebars in fly ash concrete exposed to wet and dry cycle, under static loading.
- 4) To correlate the laboratory scale testing with corrosion monitoring of reinforcement in real structures incorporating fly ash.

1.4. THESIS STRUCTURE

This thesis is divided into seven chapters as explained below:

Chapter one gives a brief background to chloride induced reinforcement corrosion, its deterioration stages in concrete and introduction to fly ash along with the objectives of the present study and thesis layout.

In chapter two, the main experimental methods employed for investigating corrosion of steel reinforcement in fly ash concrete subjected to 10% NaCl solution are described. Electrochemical parameters like half-cell potential, corrosion current density and specific concrete resistance were measured to quantitatively evaluate the corrosion behavior of reinforcement in concrete during corrosion initiation, propagation and cracking stages especially for fly ash concrete.

Chapter three provides the results and discussions on the corrosion initiation of rebars in fly ash concrete. A reliable detection method for corrosion initiation of rebars in fly ash concrete was introduced. The results of fly ash replacement ratios, curing conditions and types of rebars on chloride threshold values were also discussed. In addition probabilistic analysis of time to initiate corrosion and chloride threshold values using monte - carlo simulation was also explained.

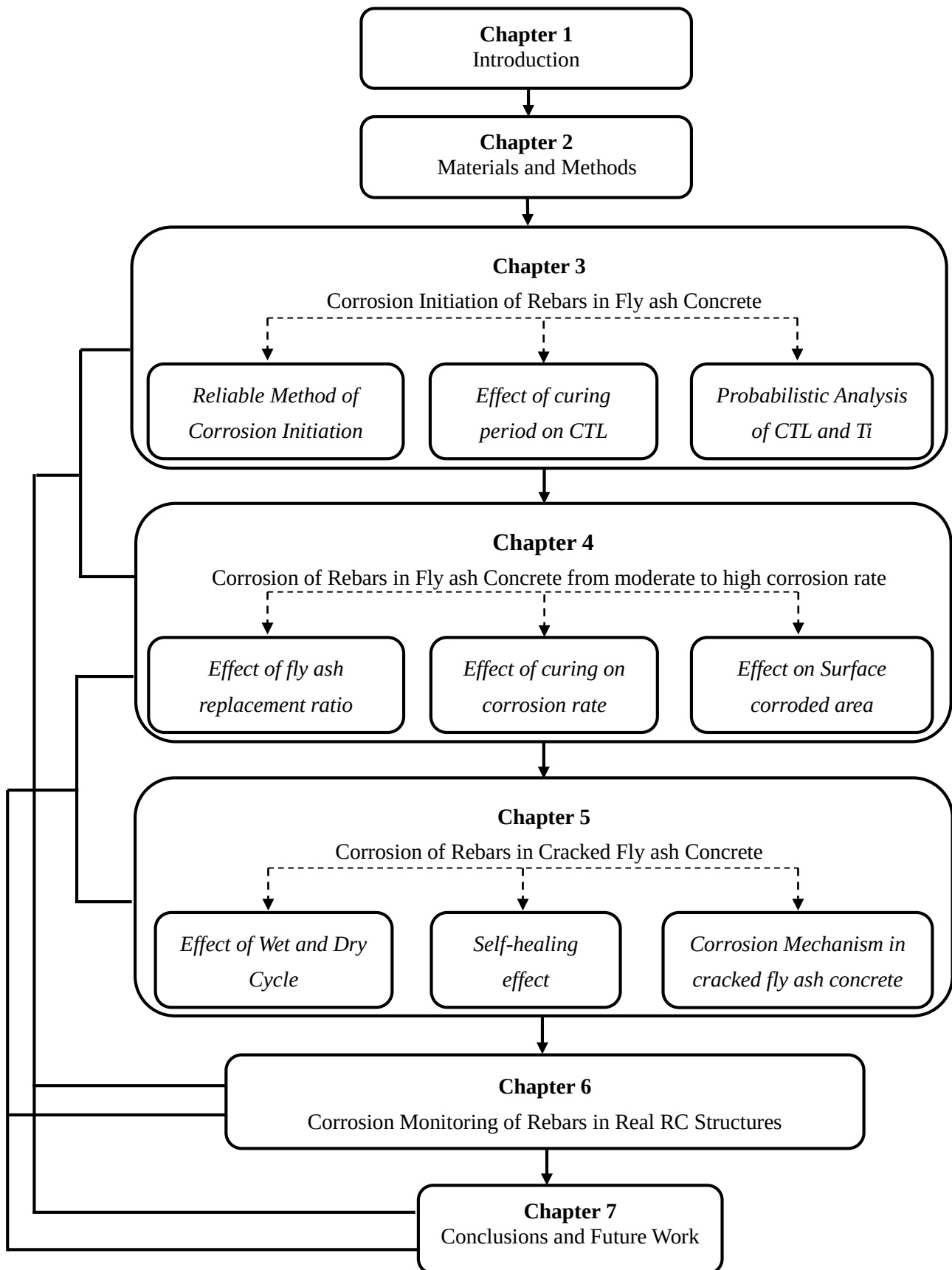


Figure 1.5 Outline of Thesis Chapters

Chapter four of thesis gives the corrosion characteristics of the steel reinforcement in fly ash concrete from moderate to high corrosion rate. The results, interpretation and major conclusions obtained from the experimental work are presented.

Chapter five deals with the corrosion behavior of steel reinforcement in cracked fly ash concrete subjected to saline solution with a combination of wet and dry cycle under sustained loading. The self-healing behavior for fly ash concrete under salt exposure was also discussed along with the results of mean corrosion depth of steel reinforcement for normal Portland cement concrete and fly ash concrete.

In Chapter six, the corrosion monitoring of reinforced concrete structures incorporating fly ash was analyzed. The apparent diffusion coefficient and chloride ion concentration were obtained from the chloride ion analysis of the cores taken from the real structure. The prediction of the service life using JSCE specifications was also done.

The seventh chapter gives a brief summary of the work, and major conclusions resulting from the present experimental investigation and also gives some recommendations for future work.

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials and Mix Proportions

In this research concrete specimens were casted with Ordinary Portland cement (C) and various fly ash (FA) replacement levels. Japanese Industrial Standard (JIS A 6201) Type II fly ash was used. Properties of fly ash are summarized in Table 2.1.

Table 2.1: Properties of fly ash used in this research

Fly ash type		JIS standard (A6201) Type II	Fly Ash Used
Composition and Chemical properties	Loss on Ignition (%)	5 (max)	2.4
	SiO ₂ content (%)	45 (min)	66.4
	Al ₂ O ₃ content (%)	-	18.88
	Fe ₂ O ₃ content (%)	-	3.63
	CaO content (%)	-	0.90
	MgO content (%)	-	0.54
	Others (%)		9.63
	pH	-	10.1
Physical Properties	Absorption using Methylene Blue (mg/g)	-	0.60
	Absorption using Methylene Blue (Japan Cement Association) (mg/g)	-	0.53
	Density (g/cm ³)	1.95 (min)	2.20
	Fineness	Blaine surface area (cm ² /g)	3990
		Retain on 45 μ m sieve (%)	13
	Flow (%)	95 (min)	104
	Activity coefficient (28 days) (%)	80 (min)	89
	Activity coefficient (91 days) (%)	90 (min)	114

The coarse aggregate (G) was crushed stone with a maximum size of 13 mm. The sand (S) from Mukawa River, Japan was used as a fine aggregate. The physical properties of Ordinary Portland cement, fine and coarse aggregates are potted in Table 2.2.

The concrete specimens for all the corrosion stages were prepared with a constant water to binder ratio (W/B) of 0.5. The target slump and target air content was 12 $\pm$ 1.5 cm and 5 $\pm$ 0.5 % respectively. The detailed mix proportions of all the concrete series are shown in Table 2.3. The reinforcement used for all the specimens was deformed steel bar having a diameter of

19 mm. Rebars were prepared by cutting to about 420 mm lengths. Both the ends of steel bars were coated by an epoxy.

Table 2.2. Physical Properties of Ordinary Portland cement, Fine and Coarse Aggregates

Material	Specific Gravity (g/cm ³)	Absorption (%)	Fineness Modulus
OPC	3.16	-	-
Fine Aggregate	2.61	2.85	2.68
Coarse Aggregate	2.68	1.62	6.10

Table 2.3. Mix Proportions of Concrete Specimens for all Corrosion Stages

Stage	Type	FA (C+FA)	s/a*	Unit Weight (kg/m ³)					Compressive Strength (MPa)	
		(%)	(%)	W	C	FA	S	G	28 days	91 days
Initiation	N50	0	43	162	324	-	793	1047	42.9	46.4
	F15	15	45	146	248	44	857	1044	35.1	41.2
	F30	30	45	145	203	87	852	1037	29.5	39.7
Propagation	N2Z	0	43	175	350	---	763	1000	45.1	49.6
	F15Z	15	43	170	289	51	765	1003	37.1	42.1
	F30Z	30	43	170	238	102	759	995	27.3	35.6
Cracking	N2	0	43	165	330	---	781	1024	40.7	45.8
	F30	30	43	162	227	97	774	1015	29.6	39.5

* s/a : sand/ aggregate. Target Slump: 12 ±1.5 cm and Target Air Content: 5 ± 0.5 %

2.2 Specimen Configuration

Corrosive behaviour of rebar in concrete is normally involved in uncertainties resulting in a different manner even with duplicated specimens of the same batch being tested concurrently. Then for the enhancement of the accuracy of the results duplicated specimens for all series were prepared and tested in this study. The concrete specimens for corrosion initiation were categorized into seven different series based on the various amounts of fly ash replacement, reinforcement type, curing period and concrete cover as summarized in Table 2.4. Five specimens per series were made to implement a probabilistic analysis. The detailed

configuration of the specimen is shown in Figure 2.1 (a) and (b). Each single specimen had two reinforcements named as UP (for 20 mm cover depth) and DO (for 25 mm cover depth) from the top surface. The nominal diameter of both plain and deformed bars was 19 mm. To avoid the accumulation of bleeding water underneath the reinforcement bars, concrete was placed in lengthwise direction. Every specimen was water cured for a specified period of time as mentioned in Table 2.4. After the curing period, all the sides (except top and bottom) of the specimens were sealed with a butyl tape of aluminum coating to allow the penetration of species only from the top surface. A canister, 50 mm x 100 mm in cross section, was glued at the midpoint of the top surface as shown in Figure 2.1(a). Subsequently, 10 % NaCl solution was poured in that container and specimens were placed in a temperature controlled room. The level of salt solution was maintained at a height of 50 mm to avoid the losses by evaporation.

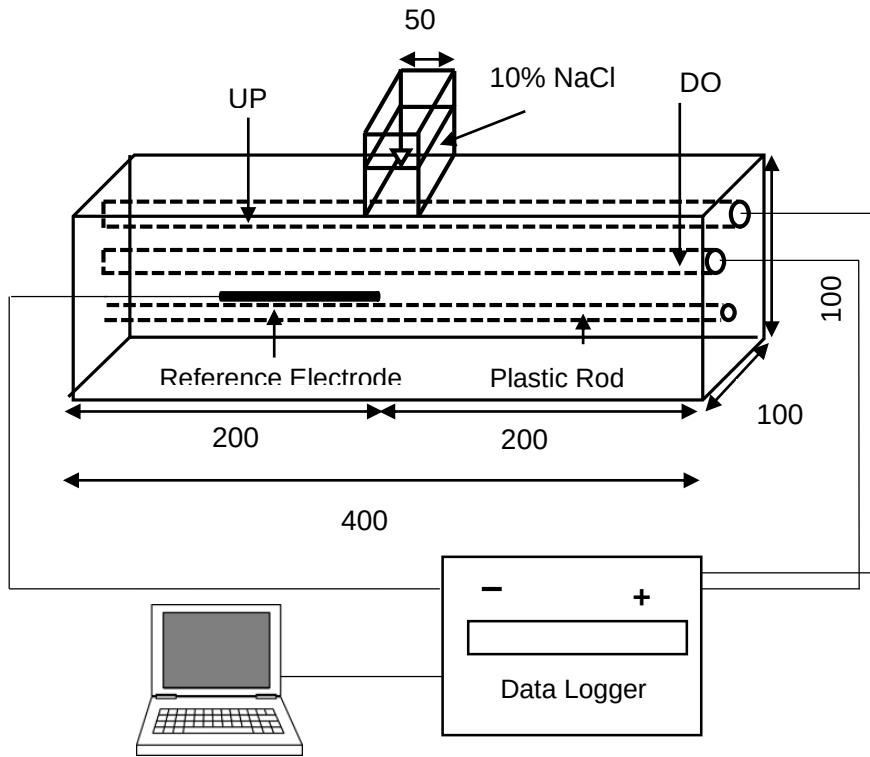
Table 2.4. Configuration of Concrete Specimens for Initiation

Specimen	Fly Ash Replacement (%)	Reinforcement Type	Curing Period (Days)	Concrete Cover* (mm)
N50D	0	Deformed	28	20, 25
N50P	0	Plain	28	20, 25
F15D	15	Deformed	28	20, 25
F30D	30	Deformed	28	20, 25
F30DL	30	Deformed	91	20, 25
F30P	30	Plain	28	30, 35
F30PL	30	Plain	91	20, 25

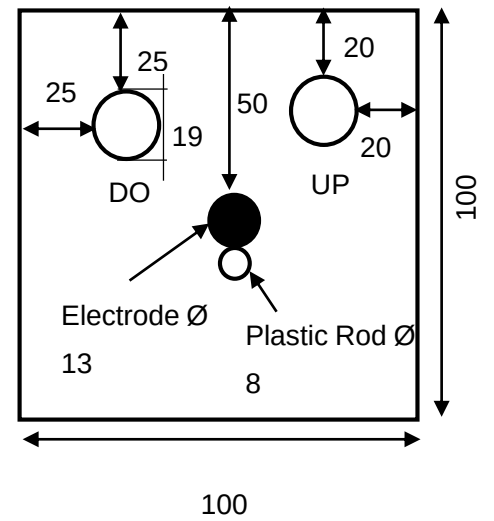
* First and second numbers correspond to the concrete cover of UP and DO bars respectively.

Four different series of specimen (N2Z, F15Z, F30Z and F30ZL) were prepared to study the corrosion resistance of rebars during corrosion propagation i.e. moderate to high corrosion rate. Fly ash concrete specimens were made by replacing 15% and 30% ordinary Portland cement with fly ash, named as F15Z and F30Z respectively. All specimen series were cured for 28 days except F30ZL series which was cured for 91 days. A total of twenty specimens were prepared comprising five from each series. The detailed configuration of the specimens is shown in Figure 2.2.

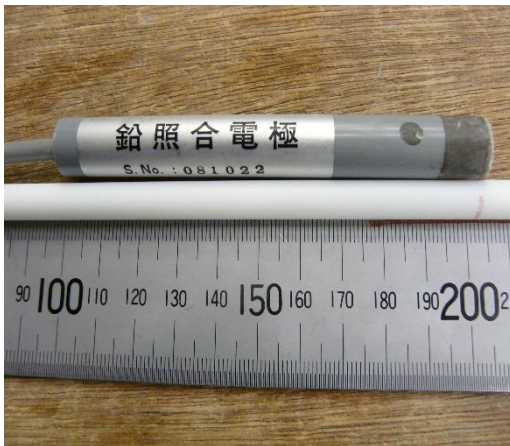
A total of eight prisms (100 x 100 x 400) mm were prepared to compare the corrosion behaviour of fly ash concrete with normal Portland cement concrete. Fly ash concrete was produced by replacing 30% ordinary Portland cement with fly ash. The detailed configuration of the specimens is explained in Table 2.5. The cross section of the specimens is same as that of shown in Figure 2.2 (b).



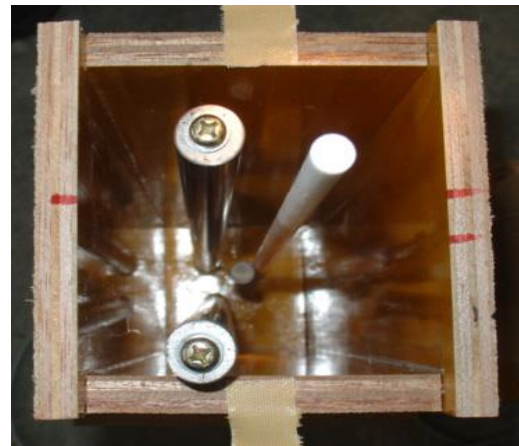
(a)



(b)



(c)



(d)

Figure 2.1: (a) Test specimen setup showing corrosion monitoring system, placement of rebars (UP and DO) and application zone of 10% NaCl solution (b) Cross section of test specimen showing the position of plain rebars and electrode (c) Embedded Reference Lead Electrode (d) Placement of electrode in formwork (units in mm)

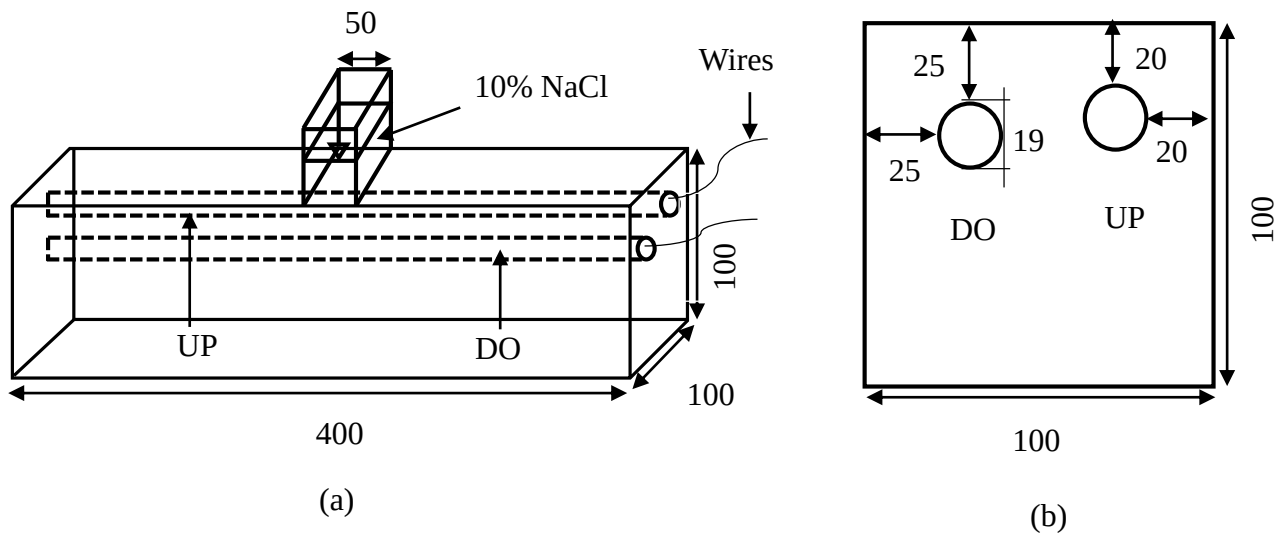


Figure 2.2: (a) Test specimen setup showing placement of rebars along with the application zone of 10% NaCl solution (b) Cross section of test specimen showing details of rebars (units in mm)

2.3 Embedded Reference Electrode

A commercially available Lead/Lead oxide electrode (Pb/PbO_2), was used as an embedded reference electrode for determining the onset of corrosion of rebars in fly ash concrete for the corrosion initiation specimens. The mean value of half-cell potential measured by the Pb/PbO_2 electrode in the saturated calcium hydroxide solution against Copper-Copper (II) Sulfate electrode was -800 ± 20 (mV vs CSE). The reliability of using the embedded lead electrode in the normal concrete (N50P) for measuring the half-cell potential has already been determined by Islam [20].

The embedded reference was placed in all the initiation series except N50D, which was monitored only by AC impedance spectroscopy. The details of reference electrode and its placement are shown in Figure 2.1 (c) and (d). The reference electrode was placed inside the formwork at a depth of 50 mm cover from the top surface before concrete casting. Also it was held in exact position during casting by means of an 8 mm diameter plastic rod.

Table 2.5 Configuration of Cracked Concrete Specimens

Specimen Series	Fly ash Replacement (%)	Exposure Type	Number of Specimens
N2C	0	Wet and Dry	4
F30C	30		4

The reference electrode is about 100 mm in length and 13 mm in diameter. Special care was taken during concrete placement and compaction to avoid the electrode displacement from its original position and any disturbance in electrical connection. The embedded reference electrode and rebars were connected to a computer operated automatic data logger.

2.4 Electrochemical Measurements

The continuous monitoring of the half-cell potential was done by using automatic data logger system for the corrosion initiation series. The data logger measured half-cell potential at regular interval of 8 hours with reference to Pb/PbO₂ electrode embedded in concrete specimens. The measurement of half-cell potential with respect to embedded reference electrode is on the same principle of ASTM C 876. An AC impedance spectroscopy (Corrosion meter), CM-V Type, was also used to measure the half-cell potential and impedance data at an interval of about one month. The measurement done by corrosion meter is shown in Figure 2.3 (a). This device allows measurement of impedance by using both Single Counter Electrode (SCE) and a Double Counter Electrode (DCE) method. However, to enhance the reliability of AC impedance data, DCE system is used in this study.

The entire electrode system consists of Guard Counter Electrode (GCE), Central Counter Electrode (CCE) and a silver/silver chloride (Ag/AgCl) reference electrode. The working principle of AC impedance measurement and distribution of current flowing lines using DCE is referred to [47]. In this research corrosion meter employed a two frequency method along with the conventional AC impedance measurement at wider range of frequencies, to minimize the measurement time. In the two frequency method, two frequencies i.e. a high frequency of 10 Hz and a low frequency of 0.01 Hz were used. The typical Randles Circuit model and Cole-Cole plot (Nyquist plot) was used to estimate the apparent polarization resistance and concrete resistance. The details of estimating the apparent polarization resistance (free of ohmic losses) by Cole-Cole plot for two frequency method is referred to Yokota et al., 1996 [48]. Corrosion meter converted the apparent polarization resistance ($k\Omega$) obtained by two frequency method to true polarization resistance ($k\Omega\text{-cm}^2$) by multiplying with the surface area of the rebar under CCE. The values of true polarization resistance, thereafter known as polarization resistance are discussed in this study. Likewise the concrete resistance ($k\Omega$) was converted to specific concrete resistance ($k\Omega\text{-cm}$) by multiplying with the surface area of rebar under CCE and dividing by the distance between the concrete surface and surface area of rebar. To obtain the electrochemical data by corrosion meter, the salt solution canister was removed and DCE was positioned at six different locations as shown in Figure 2.3 (b). UM, UC and U correspond to the measurement done at the middle portion, the electrical connection end and the end without connection for UP rebar respectively. Similar notations are used for the measurement done for DO rebar. Corrosion of reinforcement in concrete was detected either by automatic data logger/corrosion meter or combination of both methods.

The corrosion monitoring of all the propagation specimens was done by measuring the half-cell potential at regular intervals by using Lead-lead oxide electrode (Pb/PbO₂). The schematic diagram for the measurement of half-cell potential relative to reference electrode is shown in Figure 2.4 (a) and the measurement of half-cell potential relative to Pb/PbO₂ for F30Z (1) specimen is shown in Figure 2.4 (b). The corrosion meter was also used to obtain the impedance data (polarization resistance and concrete resistance) along with half-cell potential values after every two- week interval. Measurements were made at a location where the saline solution was applied on the top surface of the specimen. The corrosion current density, I_{corr} , is estimated by using Stern and Geary equation and using the recommended value of constant (B) as 26 mV, also the conversion of corrosion rate into attack penetration is done using a formula based on Faraday's law [34]:

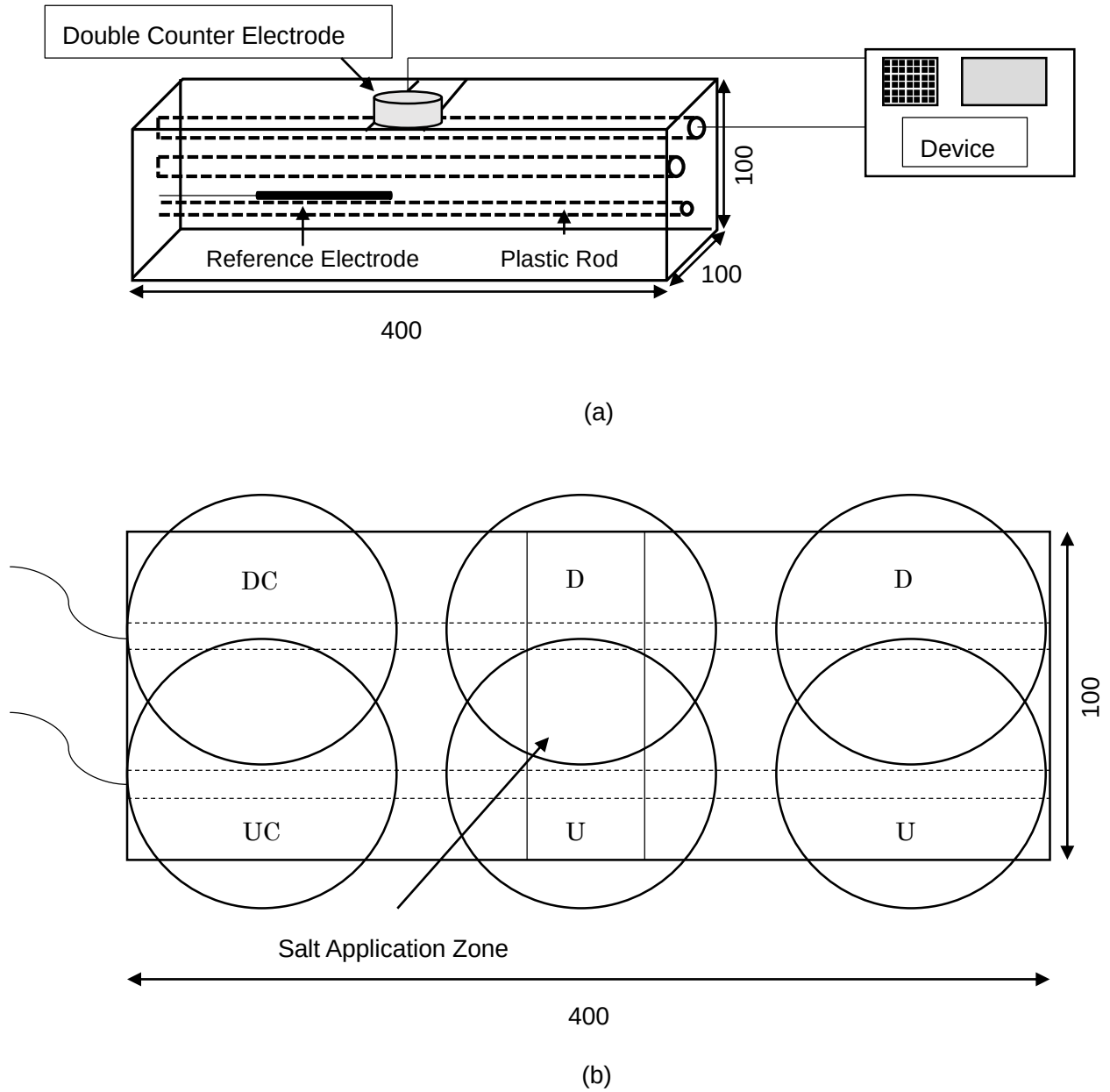
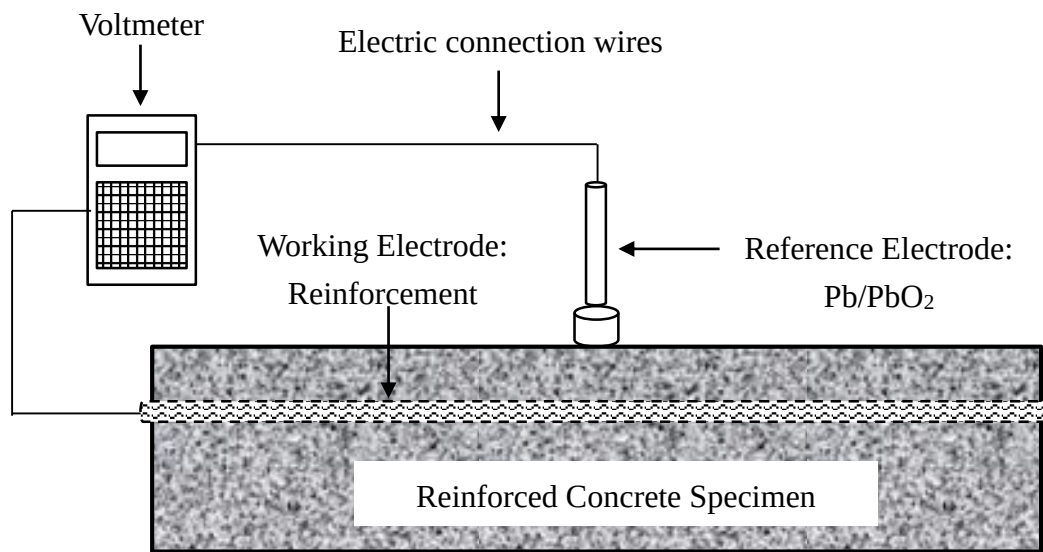


Figure 2.3: (a) Test specimen setup showing corrosion monitoring by corrosion meter (b) Schematic view for the measurement positions done by corrosion meter (All units in mm)

$$\Delta r = \alpha \times 0.0116 \times \int I_{corr} \times t \quad \text{-----} \quad (2.1)$$

Where Δr = attack penetration (mm), α = pitting factor = 10, 0.0116 = conversion factor ($\mu\text{A}/\text{cm}^2$ to $\mu\text{m}/\text{year}$), I_{corr} = corrosion current density in $\mu\text{A}/\text{cm}^2$ and t = propagation period in years.

The corrosion status of the cracked specimens was observed at the end of one complete cycle (wet and dry) for each series. The measurement of half-cell potential was done by using Lead-Lead oxide electrode (Pb/PbO_2). In addition the corrosion meter was also used to obtain the impedance data (apparent polarization resistance and apparent concrete resistance) along with half-cell potential (with reference to Ag/AgCl electrode) at the end of each cycle. The mean corrosion depth was estimated by using the equation (2.1).



(a)



(b)

Figure 2.4: (a) Schematic diagram for half-cell potential measurement relative to a reference electrode (b) Measurement of half-cell potential relative to Pb/PbO₂ for F30Z (1) specimen

2.5 Determination of Chloride Ion Concentration

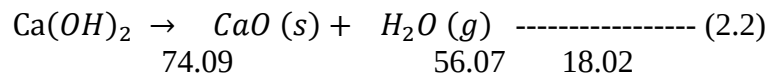
In case of initiation concrete specimens, after the confirmation of corrosion initiation, chloride analysis was conducted to estimate the total chloride ion concentration for all concrete specimens. The entire chloride application zone (50 mm × 100 mm) of concrete specimens was used for chloride analysis. Japanese Industrial Standard (JIS A1154) was used to determine the total chloride concentration in each sliced layer of the concrete. As per the standard, the minimum weight of each sliced layer (powdered) should be around 10 grams. So to obtain the required weight of concrete powder, the concrete was sliced to approximately 7 mm thick layers. A nonlinear regression analysis was done to fit the experimental chloride profile with the solution of the Fick's 2nd law of diffusion. Fick's second law of diffusion has been used under the assumption that concrete cover under the application zone was fully saturated because during the experiment the concrete surface was continuously subjected to the application of salt solution. The surface chloride ion concentration (C_s) and diffusion coefficient (D_o) were obtained from the fitting curve. The obtained values of C_s and D_o were then used to evaluate the chloride profiles at the estimated corrosion initiation time. In the last, for the determination of Chloride Threshold Level, the concentration of chloride ion corresponding to the cover depth (20 mm) was used.

After certain period of chloride application, when the propagation concrete specimens had reached the specified corrosion current limit, from moderate to high corrosion rate (0.5 - 1.0 $\mu\text{A}/\text{cm}^2$), the specimens were cut to visually observe the corrosion products and conduct the chloride analysis. The total chloride ion concentration was measured following the same procedure as described for initiation concrete specimens.

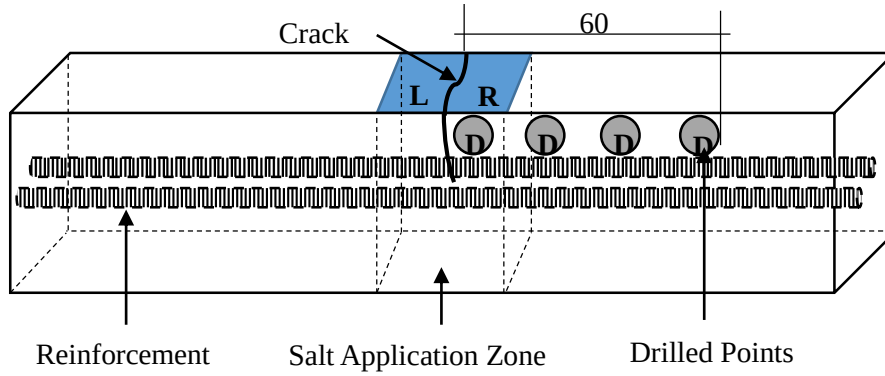
Chloride analysis for the cracked concrete specimens was conducted at the end of exposure period. In order to have a chloride ion distribution perpendicular and along the length of rebar, left (L) and right (R) side of the crack, were used for chloride analysis respectively. To obtain the chloride distribution along the length of rebar, R side of the concrete specimen was used to obtain the concrete powder by drilling. The location and diameter of drill points are shown in Figure 2.5 (a). While to have a chloride distribution along the depth, L side of the application zone was sliced in approximately 7 mm thick layers as shown in Figure 2.5 (b).

2.6 Calculation of Hydroxide Content

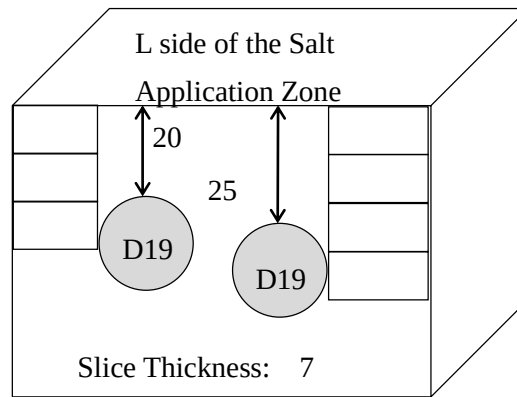
Hydroxide content was calculated for initiation specimens only. by the measurement of Portlandite [$\text{Ca}(\text{OH})_2$] quantity through Thermo-Gravimetry/Differential Thermal Analyzer (TG/DTA) technique. The concrete specimen used in chloride ion estimation was also used for this technique. The sliced specimen near the vicinity of reinforcement bars were selected for the analysis. The analysis was carried out with the temperature range of 20 to 1000 °C with an increment rate of 10 °C/min. Nitrogen (N_2) gas was used for the test with a flow rate of 200 ml/min. Alumina (Al_2O_3) was used as a reference weight for the concrete samples. It was assumed that the decomposition of $\text{Ca}(\text{OH})_2$ occurred in the temperature range of 400 to 450 °C as shown in Equation 2.2.



Amount of $\text{Ca}(\text{OH})_2$ present in test sample = Water loss in 400-450 °C x 74.09 / 18.02



(a)



(b)

Figure 2.5: (a) Schematic diagram showing the location of the point drilled (R side) for chloride analysis (b) Slicing of salt application zone (L side) (All units in mm)

2.7 Measurement of Surface Corroded Area

The Surface corroded area was measured for both propagation and cracked concrete specimens. For propagation concrete specimens, when the concrete specimens had reached the specified corrosion current limit i.e. $0.5 - 1.0 \mu\text{A}/\text{cm}^2$, the specimen were cut to visually observe the nature of corrosion products and quantify the corroded surface area of rebars. In case of cracked concrete specimens, the corroded surface area of rebar was measured after the completion of all cycles.

Corroded surface area was measured followed by the cutting and splitting of corrosion test specimens. A thick and transparent type scotch tape was used. This tape was wrapped carefully on the circumferential surface of corroded reinforcement. Then a permanent marker pen with a fine tip was used to carefully sketch the corrosion area. Allowing sufficient time to dry the drawing, the tape was detached from the reinforcement surface and associated carefully on a comparatively thicker and white paper. An image of this paper has been produced by scanning the paper. Computer image analysis software (Image J) has been used to quantify the corrosion area.

2.8 Crack Formation

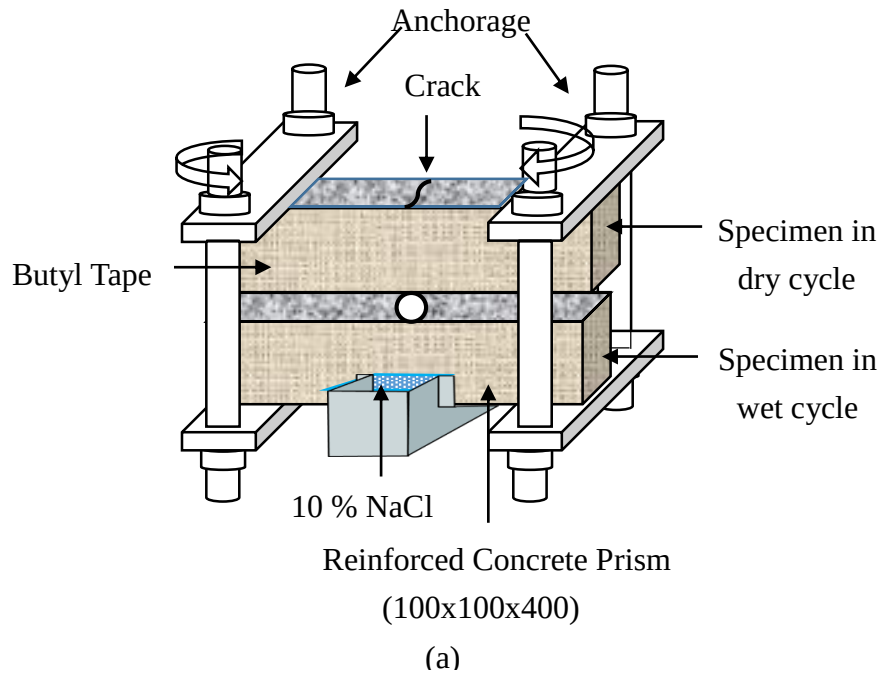


Figure 2.6: Apparatus showing the specimens in a three point bending mode along with the application of 10% NaCl solution during wet and dry cycle

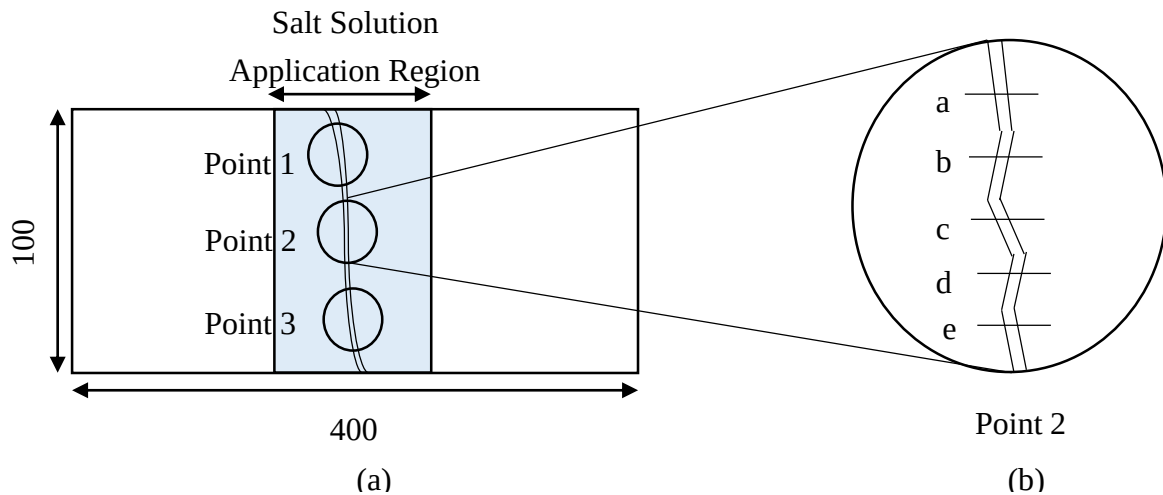


Figure 2.7: (a) Three measurement points on the surface of tension fiber along the length of crack (b) Five measurement locations for each measurement point (all units in mm)

The cracks were generated by using a specifically designed apparatus as shown in Figure 2.6. The apparatus was uniquely shaped to keep the specimens under constant bending moment along with the application of salt solution only in the limited region. This was intended to cover the limited area near the crack opening exposed to saline solution, so that maximum transport of the saline solution occurs through the crack which as a result will also limit the anodic area on the embedded rebars.

2.9 Crack Width Measurement

A portable digital microscope was used to observe the crack width at the end of one complete cycle (wet and dry) for each. The crack width in this study is defined as the distance between the two jaws of crack on the surface of concrete along its exposed side. The initial crack width, before the application of salt solution, for all the specimens was kept less than 0.1 mm. The crack width was not constant along the length of crack on the surface of concrete. It is common because concrete is not a homogenous material and response to same stress level can be different for different components of concrete. It was for the same reason that three points were selected along the length of crack and for each point the average of five measurement was taken. So the average crack width for each specimen refers to the average of fifteen points along the length of crack on the exposed surface of concrete as shown in Figure 2.7. The average initial crack width for all the specimen series is shown in Table 2.6.

Table 2.6 Average Initial Crack width for Cracking Specimens

Specimen No.	Initial Crack Width (μm)	
	N2C	F30C
1	47	59
2	61	64
3	76	50
4	65	85

2.10 Exposure Conditions

After the generation of cracks, all the specimen series were exposed to 10% NaCl solution through wet and dry cycle as shown in Figure 2.6. The duration of each wet and dry cycle was kept as 7 days for a period of 56 days and the duration of last wet and dry cycle was increased to 25 days each to observe the effect of increased duration of cycle. During the wet cycle the cracked specimens were exposed to 10% NaCl solution and during dry cycle the specimens were allowed to dry at room temperature. It was assumed that the transport of the salt solution in the crack was mainly governed by the capillary suction phenomenon during the wet cycle and then penetration into the non-cracked concrete through crack walls occurred under the diffusion mechanism.

2.11 Measurement of Attack Penetration

After the completion of all cycles, the specimens were cut to visually observe the rebar condition and measure the corroded surface area of rebar. After the measurement of surface corroded surface area the corrosion products were removed from the surface of the rebar as per Japanese Concrete Institute (JCI SC1). After cleaning of the rebar's surface, maximum pit depth, number of pits and mean corrosion depth were measured by using a computer operated three dimensional scanner. The automated scanner gives the change in the depth with reference to a certain datum with a least count of 1 micro meter. The scanner measures the depths at an interval of 10 micro meters in both the directions of the plane, forming a grid. The values obtained are then used to draw the surface profiles and calculate the maximum pit depth, number of pits and mean corrosion depth by using a commercially available software.

2.12 In-Service Reinforced Concrete Waste Water Outlet Structure

The corrosion monitoring of a reinforced concrete waste water outlet structure incorporating fly ash cement at Date Power Plant, which is in service for last 40 years was done. The Power plant is located near the sea shore to make use of the sea water for cooling down the steam. This structures takes the cooled water, through a water channel back to the adjoining sea. Figure 2.8 (a) shows the corrosion monitoring of reinforced concrete waste water outlet structure. The corrosion meter was employed to measure the half-cell potential (E_{corr}) and corrosion current (I_{corr}) of the rebars as shown in Figure 2.8 (b). The purpose of this measurement was to non-destructively evaluate the corrosion status of rebars embedded in the structure. The cover depth and diameter of the rebar was 80 mm and 13 mm respectively. The details of the waste water outlet structure is given in Table 2.7.

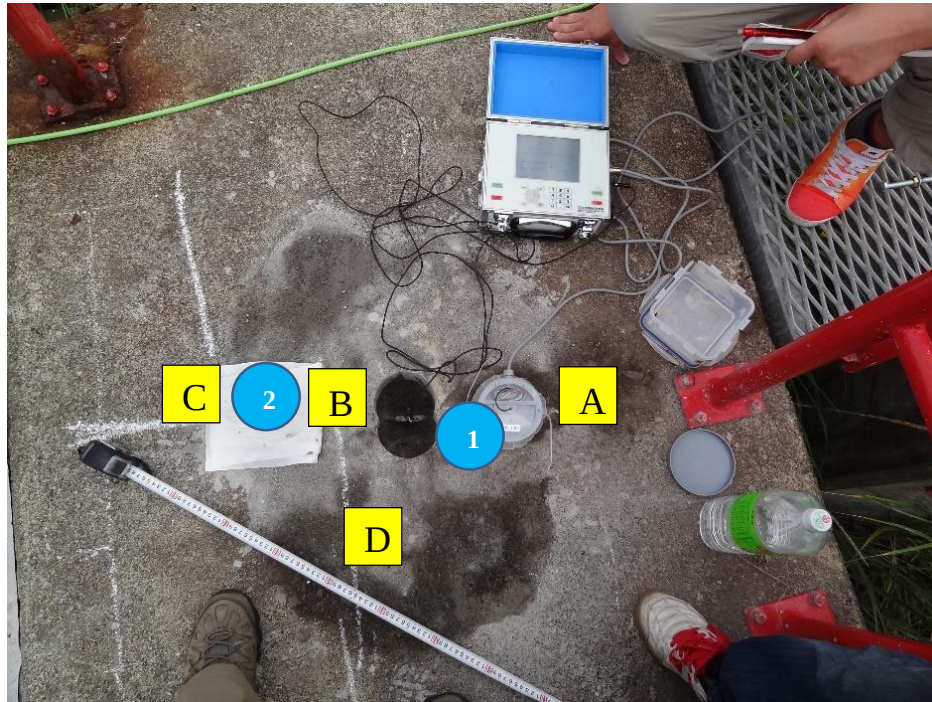
Table 2.7 Details of the waste water outlet structure

Year of Construction	Cement Type	Water to Cement ratio	Design Strength (kgf/cm ²)	In-Service
1974	Fly ash Cement Type B	55.5	210	yes

The cores were also drilled in order to estimate the apparent diffusion coefficient and chloride ion concentration near or at the reinforcement level. The drilled core section is represented by point 1 in Figure 2.8 (b). Cylindrical core specimens had a diameter and height of 100 mm and 80 mm respectively. The cores were cut in approximately 50 x 30 x 15 mm thick slices and then ground to get about 10 grams of powder for the chloride analysis. Japanese Industrial Standard (JIS A1154) was used to determine the total chloride ion concentration in each sample of the concrete.



(a)



(b)

Figure 2.8: (a) Corrosion monitoring of a RC waste water outlet structure (b) Location of electrochemical measurements (A to D) and drilled cores (1 to 2) for chloride analysis

CHAPTER 3

CORROSION INITIATION OF REBARS IN FLY ASH CONCRETE

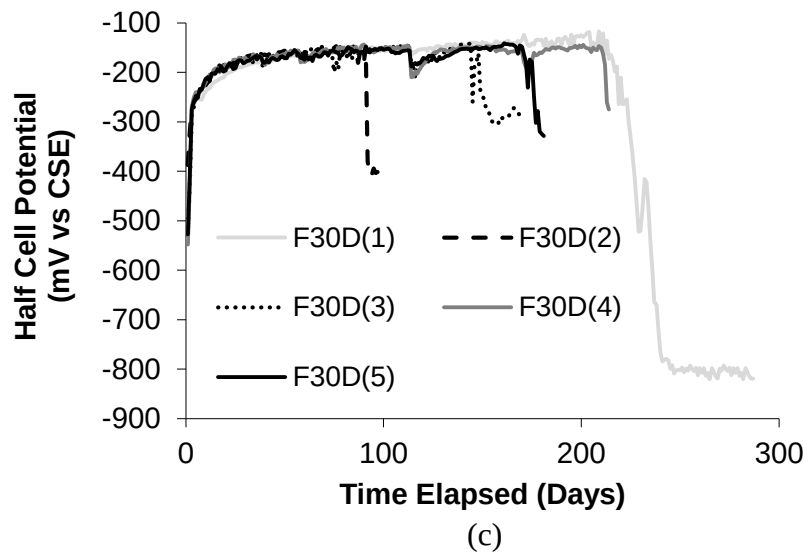
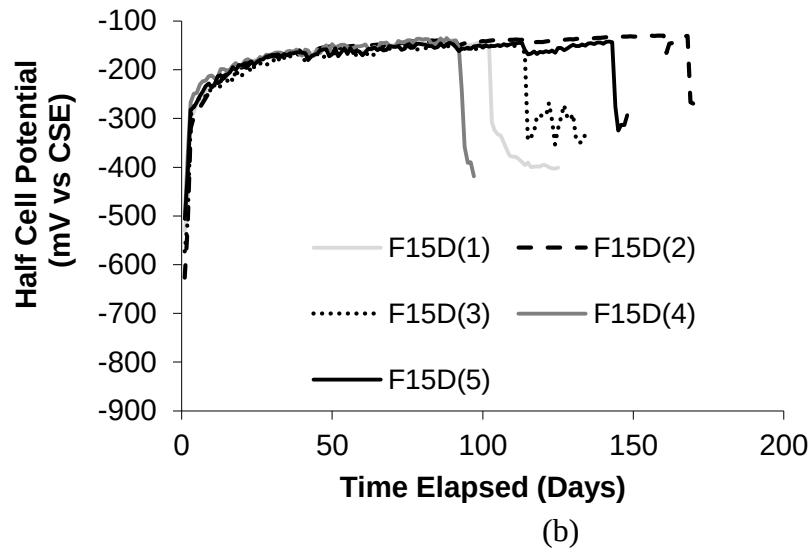
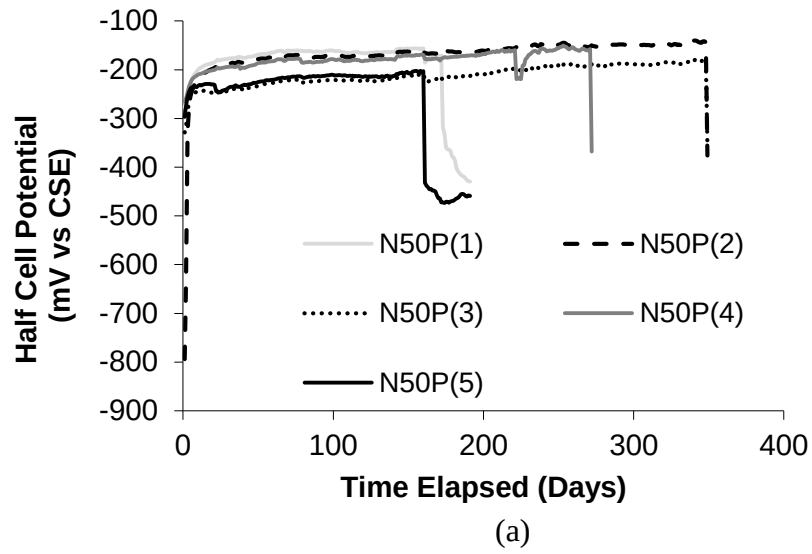
3.1. Performance of Embedded Reference Electrode

The trend of half-cell potential measured at regular interval by automatic data logger system using embedded reference electrode is shown in Figure 3.1. The onset of the corrosion was detected by a sudden drop in the half-cell potential value. It has been observed that embedded electrode can reliably detect the onset of corrosion of rebars in normal and fly ash concrete specimens with shorter curing periods. However, the increased curing period or cover depth for fly ash concrete has caused the values of half-cell potential, after a certain time period of salt application, to gradually drop towards more negative value and remain constant within a range of -815 ± 15 (mV vs CSE) as shown in Figure 3.1. The constant region in the graph i.e. -815 ± 15 (mV vs CSE) can be related to the half-cell potential values of reference electrode in saturated calcium hydroxide solution (-800 ± 20 mV vs CSE), as mentioned in the specifications of reference electrode.

On the contrary the values of half-cell potential measured by corrosion meter lie well within in the passive zone, indicating no corrosion activity at that particular time period of drop shown by embedded electrode. So, the embedded electrodes in fly ash concrete with long curing can sometimes give false indication of corrosion initiation. This was even verified by the visual observation of steel reinforcement of F30DL (2) specimen. The embedded reference electrode for F30DL (2) showed the value around -800 mV while the corrosion meter indicated the value of about -220 mV as shown in Figure 3.2 (a). So, the specimen was cut to verify the state of corrosion and it was found that no corrosion has initiated yet as shown in Figure 3.2 (b). On the other hand, F30DL (4) specimen was cut when the corrosion meter had shown a drop in the half-cell potential value regardless of the early gradual drop exhibited by embedded reference electrode as shown in Figure 3.2 (c). It was found that corrosion products were observed on the rebar confirming the onset of corrosion as shown in Figure 3.2 (d). In the current study, the specimens which showed this gradual drop trend, the initiation of corrosion was estimated by the half-cell potential values measured by corrosion meter.

The temporal gradual increase of half-cell potential drops towards more negativity is mainly because of reduced oxygen supply due to high degree of saturation around the embedded electrode region. The degree of saturation in the area under the application of salt solution where the embedded electrode is also located is dependent on the micro structure of concrete of each specimen. This is because the time period for acquiring the high degree of saturation and corresponding drops in half-cell potential values varied of every specimen as depicted in Figure 3.1. This behavior of exhibiting more negative values of half-cell potential is common in the submerged concrete structures because of the limited oxygen supply under the water [52].

In the current methodology, the corrosion test specimens were designed in such a way that the middle portion (UM, DM) under the application of salt solution will act as anode. In this way the area of corrosion on the rebar are intended to limit as compared to the experimental methodologies in which the test specimens are fully submerged in the salt solution. The advantage of this method is that the anodic area is highly likely to occur in a pre-determined area (UM) as compared to the submerged conditions in which the length of rebar acting as anode is not clear.



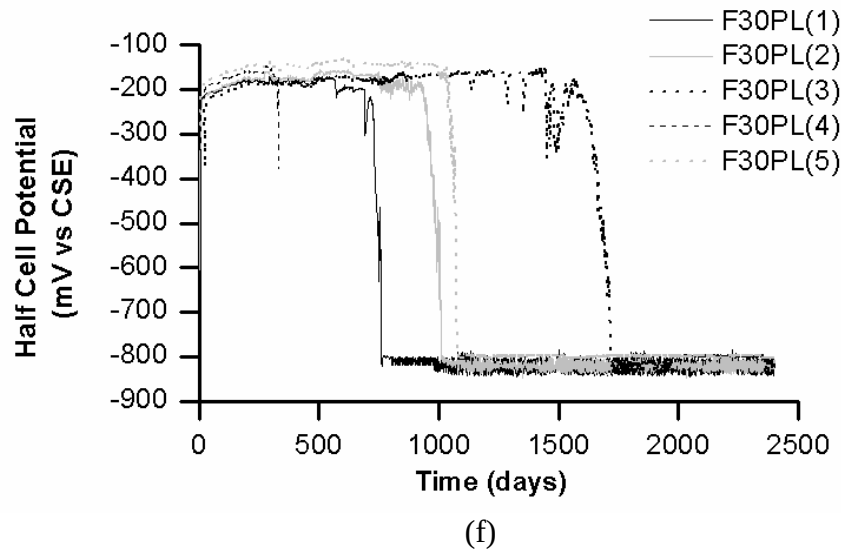
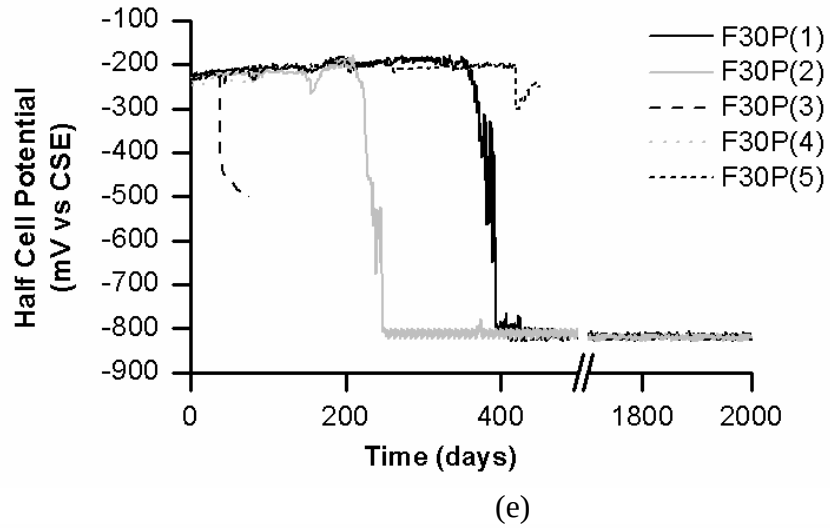
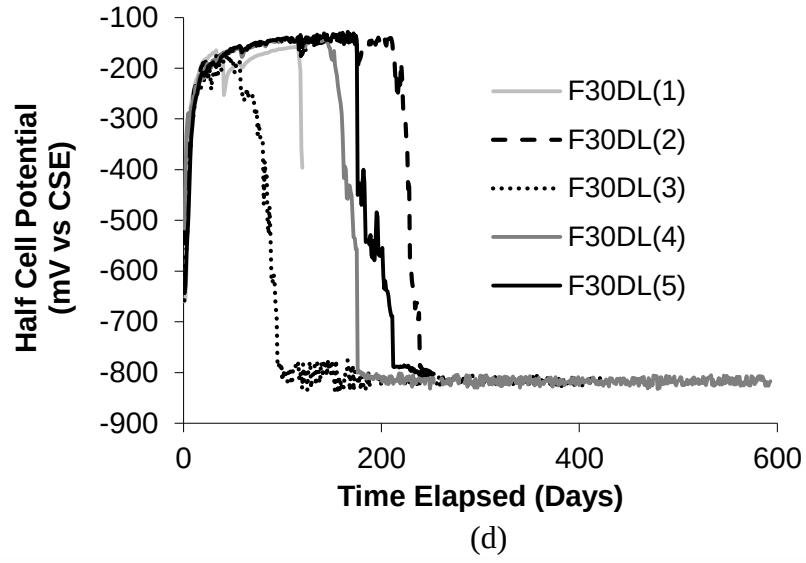
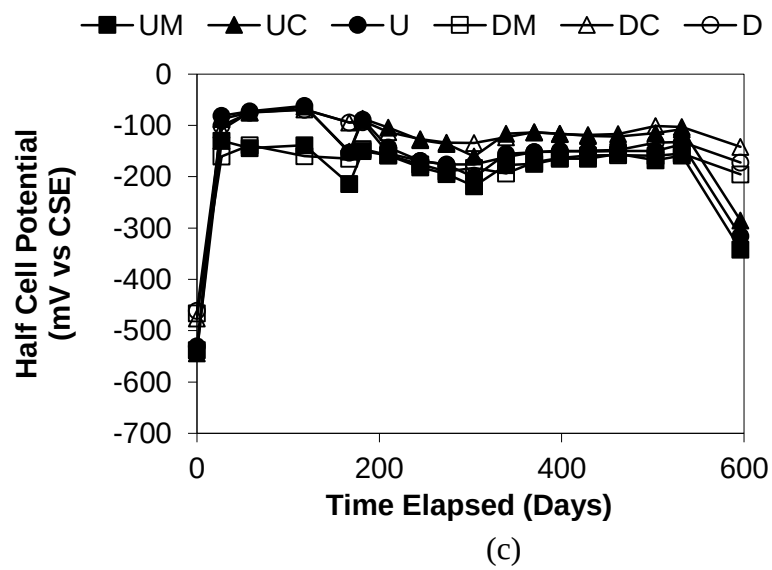
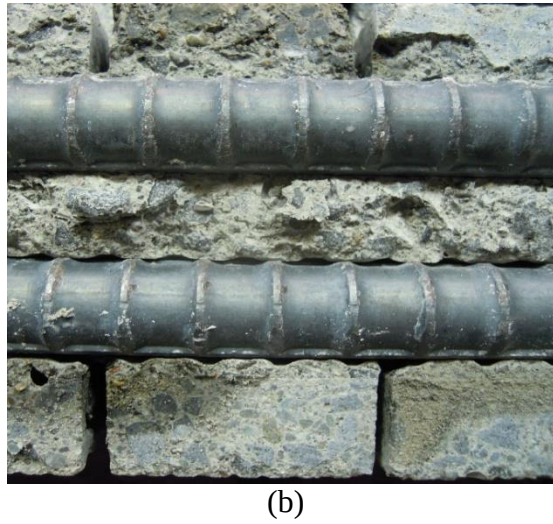
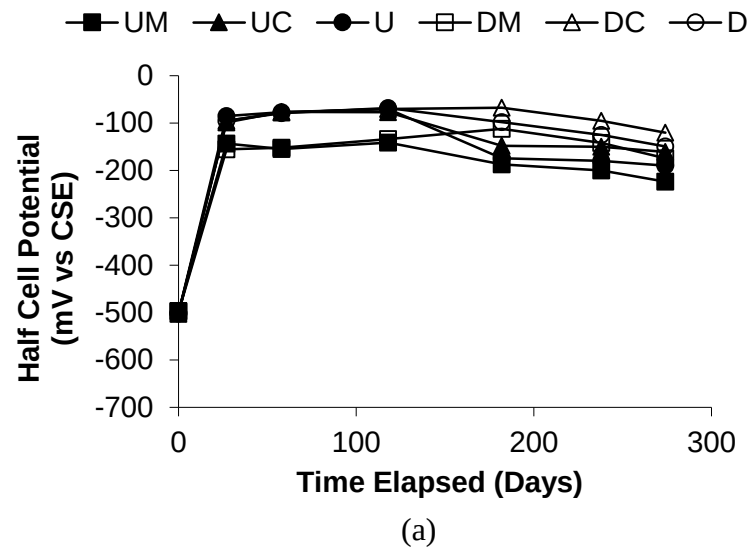
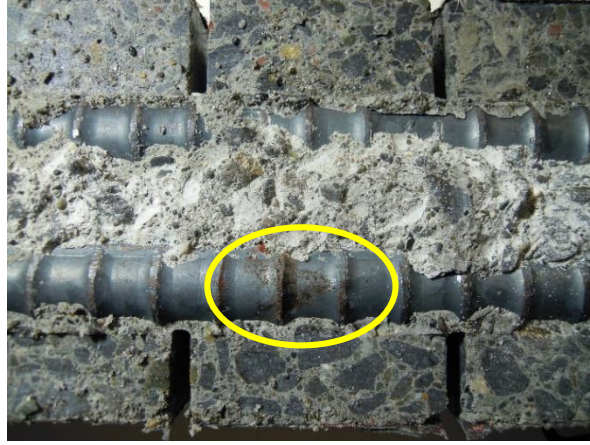


Figure 3.1: Measurement of Half-cell Potential values by Embedded Lead Electrode of (a) N50P, (b) F15D, (c) F30D, (d) F30DL, (e) F30P and (f) F30PL series





(d)

Figure 3.2: (a): Half-Cell Potential measured by Corrosion Meter of F30DL (2) Specimen and (b): No Visible Corrosion Products on the Reinforcement of F30DL (2) Specimen, (c): Half-Cell Potential measured by Corrosion Meter of F30DL (4) Specimen and (d): Visible Corrosion Products on the Reinforcement of F30DL (4) Specimen

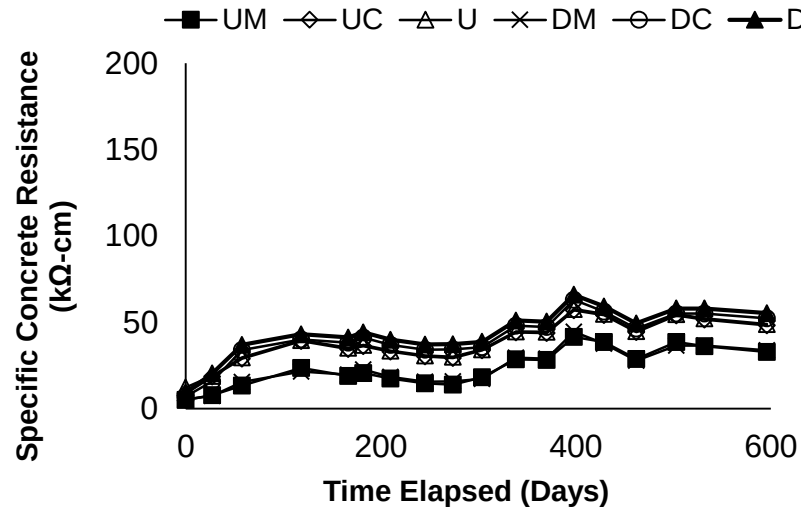
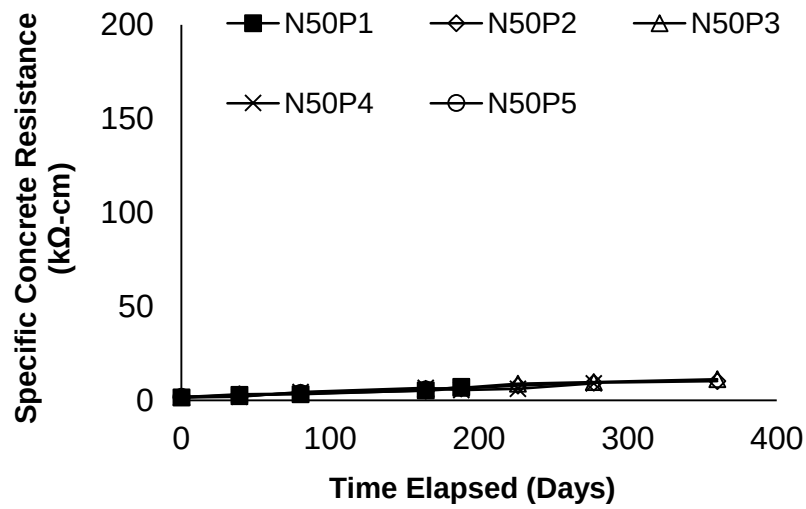


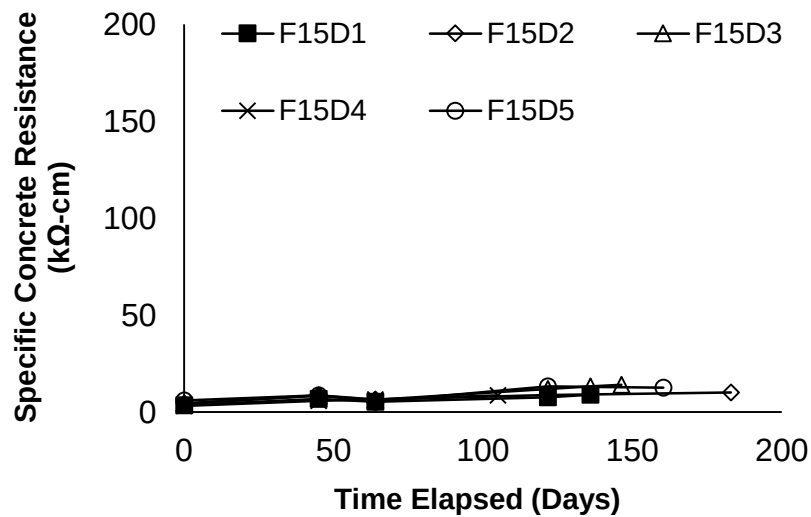
Figure 3.3: Measurement of Specific Concrete Resistance at different Locations for F30DL (4) Specimen

The results of specific resistance of concrete can also explain this decrease in the supply of oxygen. The specific resistance of concrete for F30DL (4) specimen is shown in Figure 3.3. It was found that the specific resistance of concrete measured at the middle portion (UM and DM) were low as compared to the values measured at either side (UC, U, DC, D) of specimen. Same trend was observed in all the specimen of each series. The decrease in the specific resistance of concrete in the middle portion is because of the higher degree of saturation as both of them are inversely related to each other [53]. The degree of saturation in this middle portion will increase with time to the deeper parts and ultimately high level of saturation will be observed in the embedded electrode region causing the reduction in the oxygen supply. On the other hand the specific concrete resistance (UM) is found to increase with time for the fly ash concrete specimens especially with increased curing and cover depth as shown in Figure 3.4. This increase is because of the pozzolanic reaction which continues even after one year [54] and the resulting products from pozzolanic reaction occupy the pore spaces. This results in more

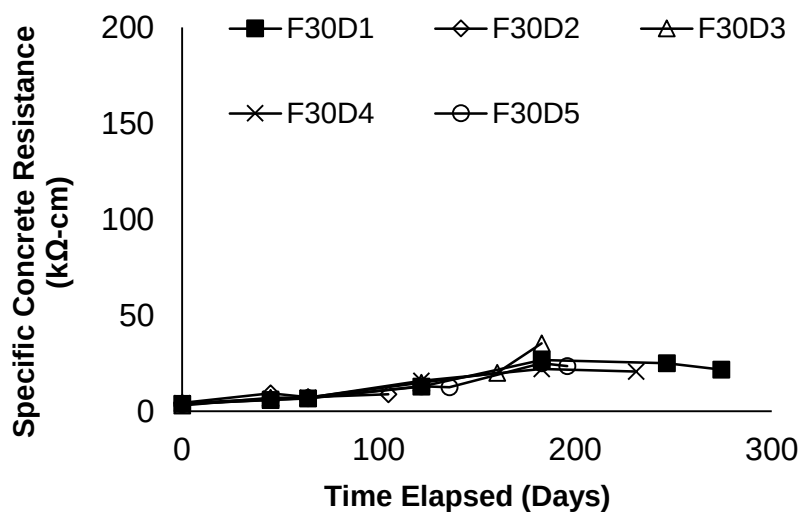
dense micro structure of concrete by reducing the pore size and total porosity which can cause a decrease in the oxygen supply.



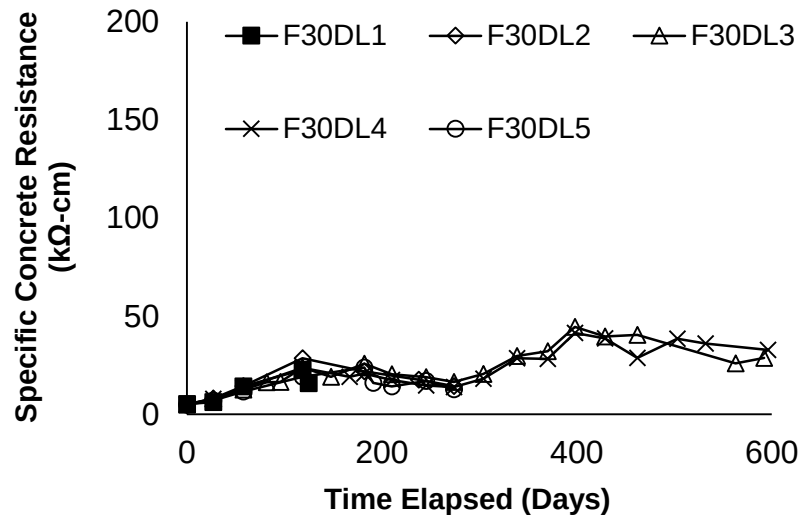
(a)



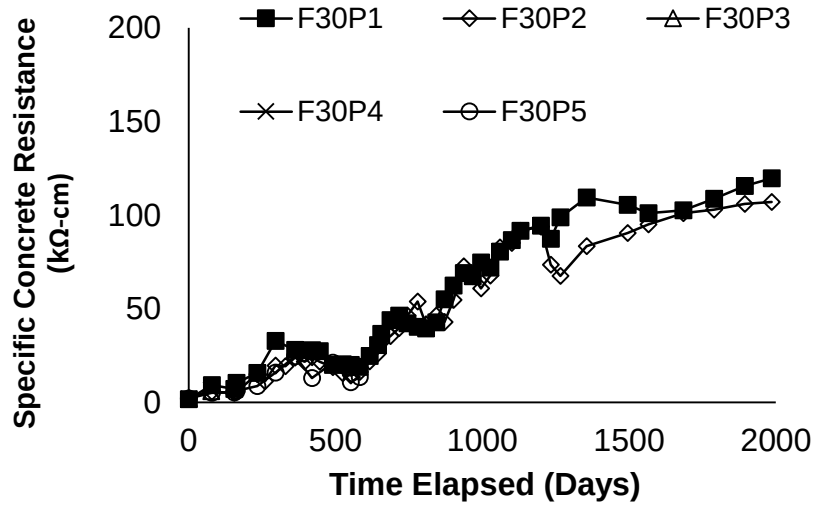
(b)



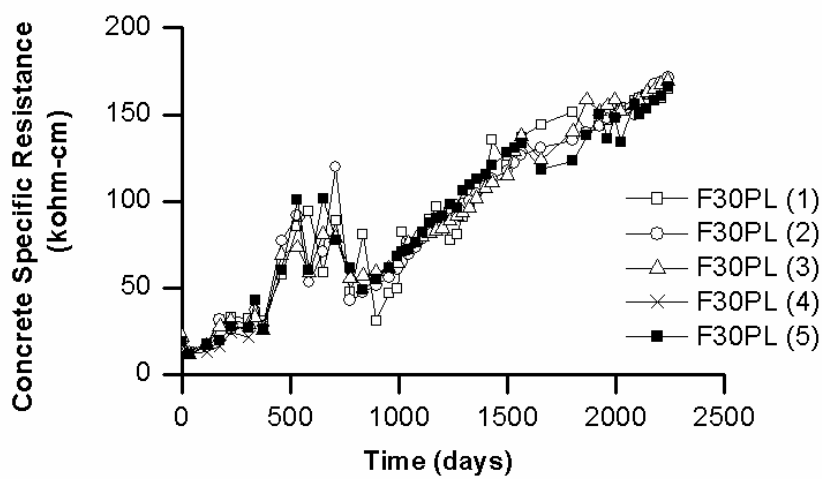
(c)



(d)



(e)



(f)

Figure 3.4: Measurement of Specific Concrete Resistance at UM for (a) N50P, (b) F15D, (c) F30D, (d) F30DL, (e) F30P and (f) F30PL Series

3.2. Time to Initiate Corrosion (T_i)

The average values of T_i for all the specimen series are shown in Table 3.1. It was noticed that the average corrosion initiation time for fly ash concrete prolonged as compared to the normal concrete specimens. It was also observed that increase in the replacement ratio of fly ash and curing period tend to have a positive effect in delaying the onset of corrosion. An average increase of 16%, 41% and 79% in T_i values was found for F15D, F30D and F30DL specimens as compared to N50D specimens respectively. The increase in the initiation period for fly ash concrete is mainly because of the reduced diffusion coefficient as shown in Table 3.1. The reduced diffusion coefficient relates to the less chloride penetration because of filler effect and pozzolanic reactions of fly ash in concrete. Especially F30DL series exhibited larger values of T_i because of the dense micro structure formed as a result of longer curing periods. This increase can also be explained from the activity coefficient of fly ash as shown in Table 2.1. The activity coefficient for fly ash used in this research at 28 days is 87 while for 91 days is 114, clearly showing the increase in the pozzolanic activity at later stages for fly ash.

In this study, an effort was made to find the critical polarization resistance for fly ash concrete, as an indicator of corrosion initiation along with half-cell potential values. It was observed that the specimens in the passive state showed higher polarization resistance and the values tend to decrease at the start of the corrosion activity. In this regard the polarization resistance can be assumed as a resistor, whose resistance drops as the corrosion instigates and as a result allows the current to pass through it. The polarization resistance of all the specimen series plotted against the half-cell potential values is shown in Figure 3.5. It was observed that polarization resistance decreased with the drop of half-cell potential values indicating the onset of corrosion. It was found that all the fly ash specimen series showed the corrosion initiation at values of polarization resistance and half-cell potential less than $1300 \text{ k}\Omega\text{-cm}^2$ and -250 mV respectively. The value of $1300 \text{ k}\Omega\text{-cm}^2$ relates to the corrosion current of $0.02 \text{ }\mu\text{A/cm}^2$ by using Stern and Geary constant as 26 mV . Admitting that $0.02 \text{ }\mu\text{A/cm}^2$ is quite low and normally considered as the passive current density, this study has shown that corrosion can initiate even at such lower values of corrosion current density. As shown in Figure 3.5 that few specimens are in the passive state at the corrosion density value of $0.02 \text{ }\mu\text{A/cm}^2$, while on the other hand at the similar values of corrosion current density few specimens have also shown the corrosion initiation, which was even verified upon cutting the specimen.

Table 3.1. Average values of T_i , D_o , C_s , CTL and CH for all specimen series

Specimen	T_i (days)	D_o (cm^2/year)	C_s (kg/m^3)	CTL (kg/m^3)	CH (kg/m^3)
N50D	119	3.10	22.4	2.3	24.3
N50P	268	2.10	22.5	5.0	25.8
F15D	138	1.71	15.8	1.1	20.6
F30D	170	1.30	12.6	1.2	14.8
F30DL	382	1.13	15.1	1.9	12.5

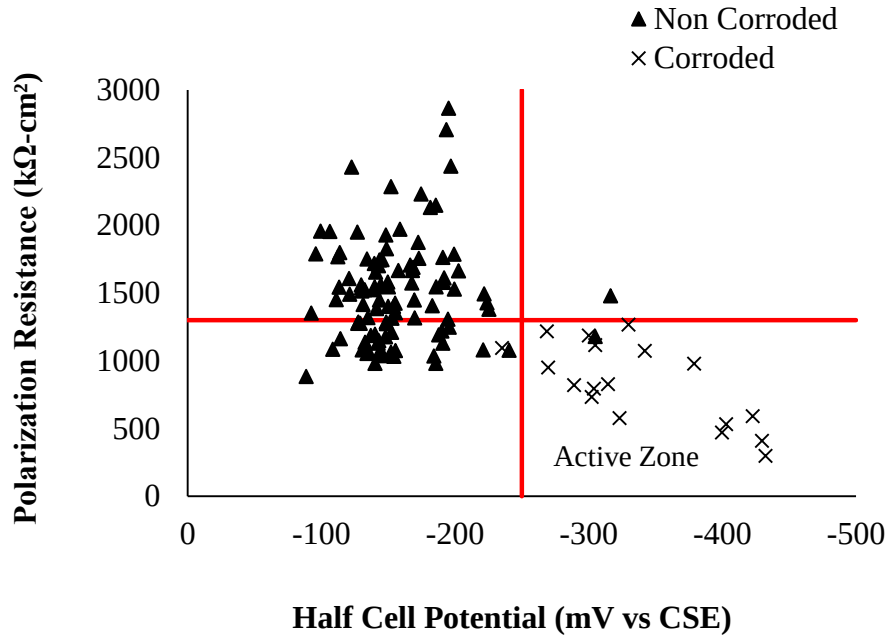


Figure 3.5: Threshold Values for Half Cell potential and Polarization resistance for Fly ash concrete

The rebar type was observed to have a significant effect on the corrosion initiation and this effect was more profound for fly ash concrete. Except few, all the specimens of fly ash concrete with plain bars (F30P and F30PL) are still under the corrosion monitoring and have not exhibited the onset of corrosion. The better performance of plain bars against the corrosion due to chloride attack is explained in terms of steel-concrete interface, which has been explicated in the later section.

It was also noted that for fly ash concrete the increase in the cover depth by 10 mm also delays the initiation period but with a lower degree of probability as equated to the small cover with long curing. It was found that three out of five specimens (F30P) have shown early corrosion as compared to the one specimen out of five specimens (F30PL). This means that for fly ash concrete the long curing results in better protection against corrosion as compared to the increase in the cover depth by 10 mm. However high cover depths can also provide sufficient internal curing for better resistance against chloride penetration.

3.3 Chloride Threshold Level (CTL)

In the present study, chloride threshold level is defined as the minimum amount of total chloride ions at the depth of reinforcement required to initiate corrosion. The discrete values of CTL for each corroded rebar along with the average values are shown in Figure 3.6. The average values of N50P, N50D, F15D, F30D and F30DL are found to be 1.54 %, 0.71 %, 0.38 %, 0.41 % and 0.66 % by mass of binder (C + FA) respectively. These average values for normal concrete with deformed bars are well in accordance with the previously reported values [17]. The discrete mean values of CTL for fly ash concrete vary from the previous research [23]. This is partially due to the different compositions of fly ash and exposure conditions. However the trend of decrease in CTL values against the increase in the replacement ratio of fly ash remained the same. The effect of the curing period on CTL values for fly ash concrete is quite clear from Figure 3.6.

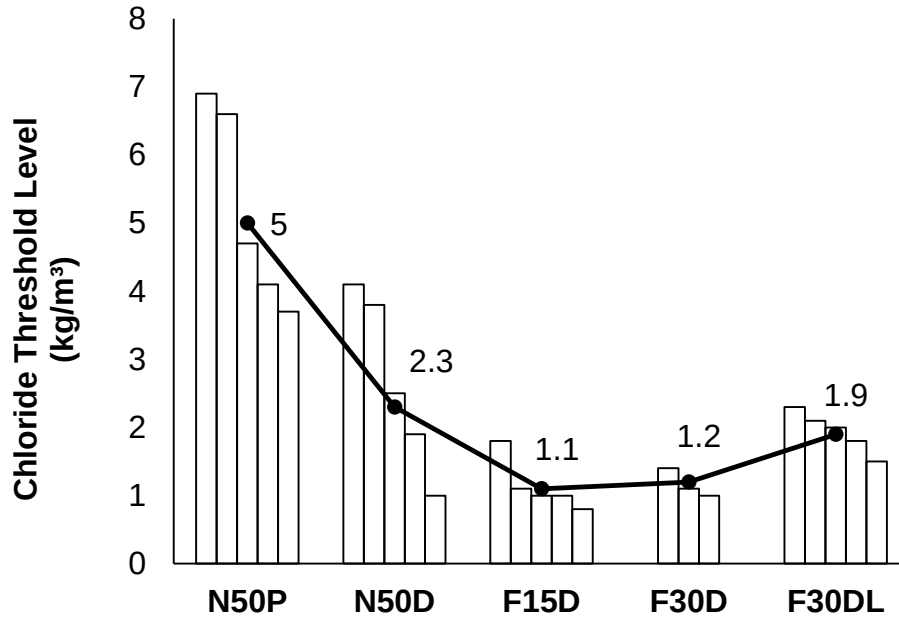


Figure 3.6: Chloride Threshold Values for all the specimen series

It was found that the average CTL values for fly ash concrete cured for 91 days (F30DL) are higher than the specimens cured for 28 days (F15D and F30D). In addition to that, the values of CTL for F30DL series are approaching to that of N50D series.

The reduction in CTL values with reference to Portland cement concrete (N50D) of about 50% and 40% by mass of binder (C + FA) for F15D and F30D respectively was observed. The decrease in the CTL values for fly ash concrete is mainly because of the reduction in the Calcium Hydroxide (CH) content. The CH present at the interface normally inhibit the corrosion initiation by the formation of passive film around the reinforcement [55]. The reduced CH content in fly ash concrete is due to the decreased cement content and utilization of CH in the pozzolanic reaction. The lowered CH content ultimately drops the pH of fly ash concrete creating favorable environment for corrosion initiation. The reduction in values of CH with increase in fly ash percentage is shown in Table 3.1.

The mean CTL value for prolonged curing of fly ash specimens was found to increase in spite of reduced CH content. In this regard the increased degree of pozzolanic reaction can result in lowering the corrosion risk. Recently it has been suggested that along with CH other hydrations products can also effectively act as a solid phase inhibitor to restrict the local fall in pH necessary to sustain the corrosion process [56]. This increase in CTL values for prolonged curing may be due to the dense microstructure, increased binding effects of chlorides and new constituents acting as an inhibitor generated by the reaction.

Accordingly CTL values are not dependent on a single variable, as numerous factors affect the pore solution chemistry and steel-concrete interface [57], so the mechanism by which the CTL values for fly ash concrete increase with long curing is still unclear and needs further detailed research for better understanding of the mechanism.

3.4 Steel-Concrete Interface

The steel- concrete interface is one of the major influential factor for determining the CTL for reinforced concrete specimens [58]. The steel-concrete interface typically contains a dense layer of hydration products with a major percentage of CH [55].



(a)



(b)

Figure 3.7: Corrosion Products attached to the concrete interface at (a) ribs for deformed bar and (b) air void for plain bar

This layer has an ability to buffer the pH of the concrete. The presence of defects (air voids, bleed-water zone and ribs) make the layer vulnerable to chloride attack.

The visual observation of the steel-concrete interface revealed that the percentage as well as the size of air voids for the fly ash concrete were quite less as compared to the normal concrete. The CTL is reported to be inversely proportional to the number of air voids at the steel-concrete interface [59]. In addition to that the bleed-water zone regardless of the direction of chloride ingress was found to trigger the corrosion [60]. In our case, the casting direction i.e. lengthwise, for all the specimen was same but the main difference among the specimen series is replacement of fly ash and curing period. The replacement of fly ash in concrete reduces the water demand which helps to minimize the bleeding water and as a result decreases the permeability of fly ash concrete.

It was observed that irrespective of the mix proportion and curing period, for deformed bars the corrosion always generated from the ribs while for plain bars the trigger for corrosion initiation was always an air void as shown in Figure 3.7. Moreover, plain steel bars were found to have longer initiation time than deformed bars. The cause of this nature may be due to the ribs of deformed bars which causes weaker and uneven interfacial zone between the concrete and steel that caused corrosion initiation in the specimens with deformed bars at early age with a relatively lower chloride concentration. For plain bars, due to smoothness of the bar it creates a very dense and smooth interfacial zone between the concrete and steel and this effect was intensified with the incorporation of fly ash in concrete. Also the interfacial zone is rich with sufficient CH content and other hydration products which inhabits corrosion initiation.

Therefore, the plain bar specimens without defects of air voids initiated corrosion at considerable longer time with higher estimated threshold chloride concentration than the deformed bar specimen although same mix proportion concrete was used for both the specimens.

3.5 Probabilistic Analysis for Corrosion Initiation

In the present study, it was noted that the values of T_i , D_o , C_s and CTL vary for the specimens even with same mix proportion, rebar type and exposure condition. Therefore these are treated as probabilistic parameters as suggested in a recent study as well [26]. The statistical tools were applied on the experimental results, to estimate the best fit probability distribution among normal, log-normal and Weibull distribution for each parameter. The R^2 values based on statistical tools for each parameter against each probability distribution was compared and highest among three distributions was selected for best fit. The results of the statistical analysis for all the specimen series indicated that for T_i and CTL parameters R^2 (Log-normal) > R^2 (Normal) > R^2 (Weibull) while for D_o and C_s there was not much difference between R^2 values of normal and log-normal distribution but the values of R^2 for Weibull distribution were quite low. So in the light of this it was found that T_i and CTL parameters best follow the log-normal probability distribution irrespective of the mix proportion and reinforcement type. In order to verify the estimated probability distributions of the parameters, Monte Carlo Simulation was applied to predict the values of T_i and compare with the experimental value. The input parameters for the simulation are shown in Table 3.2. Fick's second law of diffusion with Crank's error solution is normally used to estimate the time to initiate corrosion [61] as shown in Equation (3.1).

$$T_i = \frac{x^2}{4 * D_o * \left[\text{erf}^{-1} \left(1 - \frac{CTL}{C_s} \right) \right]^2} \quad \text{--- (3.1)}$$

The number of iterations for Monte Carlo Simulation was kept as 10000 to increase the precision of the simulation. The values of T_i obtained from the simulation are summarized in Table 3.3. Log normal probability distribution was selected to represent the results of T_i predicted from the simulation as the experimental values of T_i also followed the same probability distribution as mentioned earlier. So in order to compare the values with the experimental values, the natural log (LN) of the mean estimated T_i values was calculated. It was noticed that there was not much difference between LN of the mean estimated T_i values and the mean of experimental T_i values. However the coefficient of variation (COV) for the values of T_i predicted from simulation are quite different from the experimental values. This difference for the predicted value from simulation might be because of the dependency of T_i on the probability distribution of D_o , C_s and CTL as shown in equation 3.1. The probability of corrosion initiation for all the specimen series predicted from the model are shown in Figure 3.8. It was noticed that the slopes of the probability curves for N50D, F15D and F30D are quite steep as compared to those of F30DL and N50P series. The steep slopes of N50D, F15D and F30D series indicate a high probability of corrosion initiation whereas F30DL and N50P specimen series showed a gradual decrease from the steep slope indicating the effect of prolonged curing for fly ash concrete and plain bars for normal concrete in mitigating the onset of corrosion.

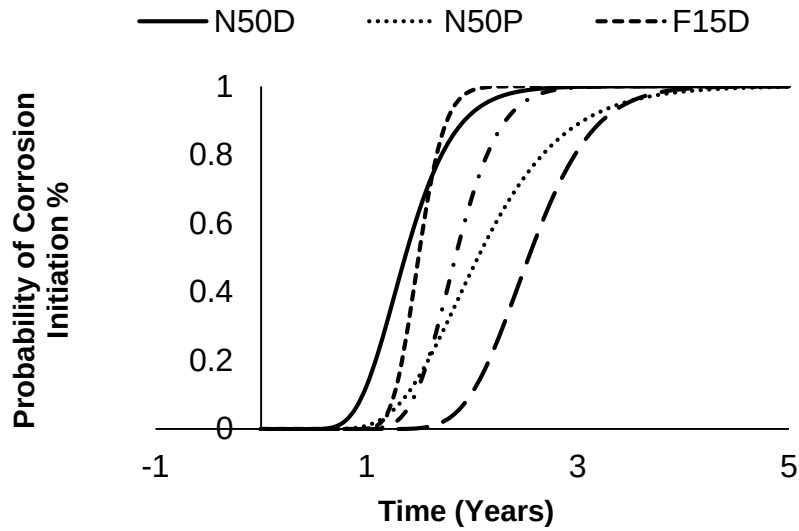


Figure 3.8: Probability of corrosion initiation estimated by Monte-Carlo simulation

Table 3.2. Input parameters for Monte Carlo Simulation in terms of Log-Normal Probability

Specimen	Do (cm ² /year)	Cs (kg/m ³)	CTL (kg/m ³)
N50D	(3.10 ^a ,0.56 ^b)	(22.4,1.05)	(2.3,1.30)
N50P	(2.10,0.50)	(22.5,1.10)	(5.0,1.25)
F15D	(1.71,0.34)	(15.8,4.34)	(1.1,0.38)
F30D	(1.30,0.28)	(12.6,4.10)	(1.2,0.20)
F30DL	(1.13,0.15)	(15.7,1.60)	(1.9,0.30)

a: first term in the parenthesis is the mean, b: Second term is the Standard Deviation.

Table 3.3. Comparison of Experimental and Predicted values of Ti

Specimen	Experimental values of Ti (years)		Estimated values of Ti (years)		
	Mean	COV ^a	Mean	LN ^b of Mean	COV ^a
N50D	0.33	0.05	1.36	0.31	0.60
N50P	0.74	0.20	2.05	0.72	0.43
F15D	0.38	0.15	1.50	0.40	0.32
F30D	0.47	0.30	1.84	0.61	0.30
F30DL	1.1	0.42	2.53	0.93	0.20

a: Coefficient of Variation, b: Natural Log

3.6 Summary

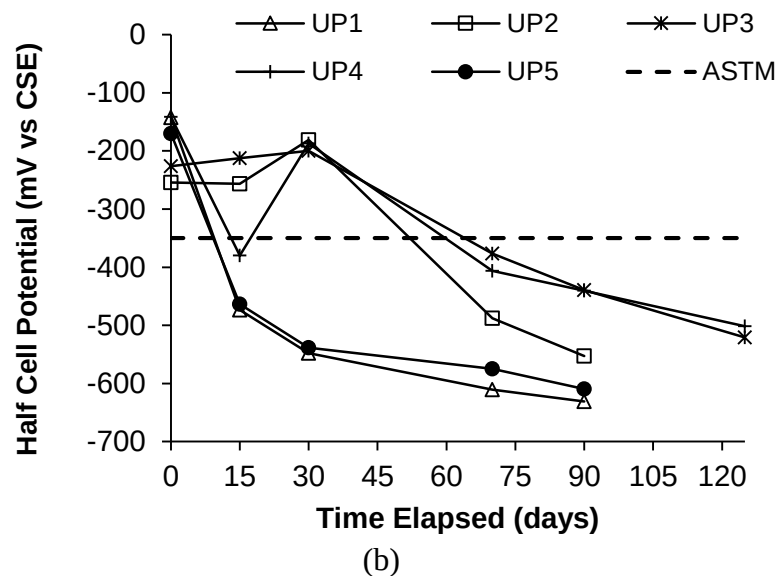
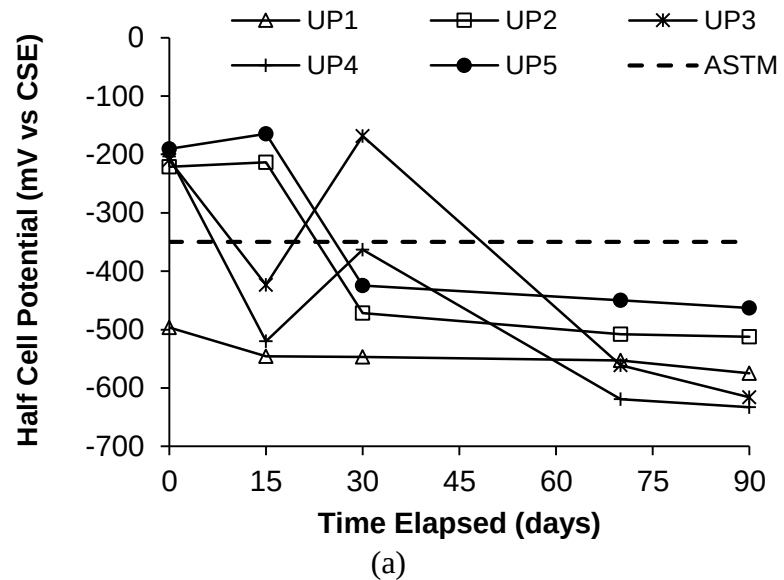
The effect of fly ash on the corrosion initiation of rebars in concrete using the embedded electrode and corrosion meter was investigated. It was found that the monitoring of half-cell potential through embedded lead electrode can reliably detect the onset of corrosion in fly ash concrete with 28 days curing. However, the probability of accurately determining the onset of corrosion by embedded lead electrode decreased for longer curing period irrespective of the reinforcement type. The use of corrosion meter resulted in the threshold values of half-cell potential and polarization resistance for fly ash concrete being -250 mV and 1300 k Ω -cm² respectively. In addition, the long curing period for fly ash concrete resulted in a dual beneficial effect of delaying the onset of corrosion due to lowered diffusion coefficient and pushing the CTL values of fly ash concrete close to that of normal concrete. After 28 days of curing, the CTL value for 30% replacement of fly ash was 0.41% by mass of binder (C+FA), compared to 0.71% for normal Portland cement concrete. The CTL value for fly ash concrete after 91 days of curing, however, was increased to 0.66% by mass of binder. Furthermore, the longer curing of fly ash concrete resulted in better protection against corrosion as compared to just increasing the cover depth. The probabilistic analysis of corrosion initiation revealed that log-normal distribution might be used for representing the time to initiate corrosion and chloride threshold level, irrespective of the mix proportion and reinforcement type.

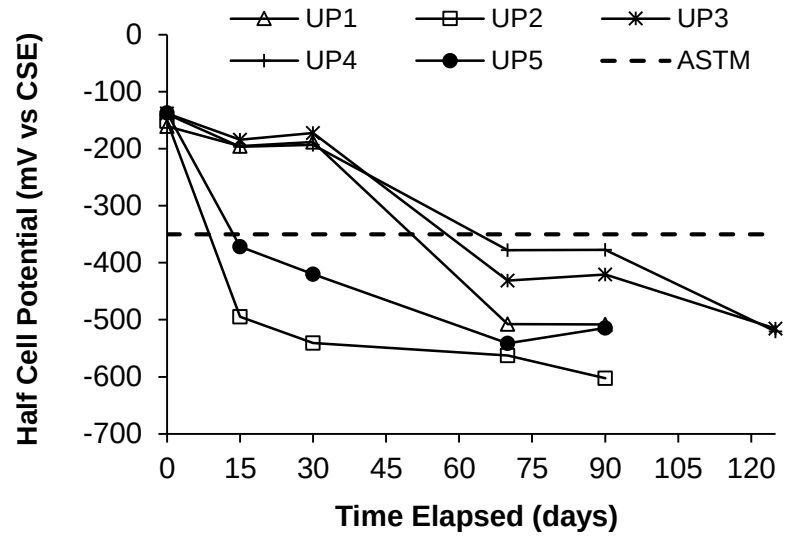
CHAPTER 4

CORROSION OF REBARS IN FLY ASH CONCRETE FROM MODERATE TO HIGH CORROSION RATE

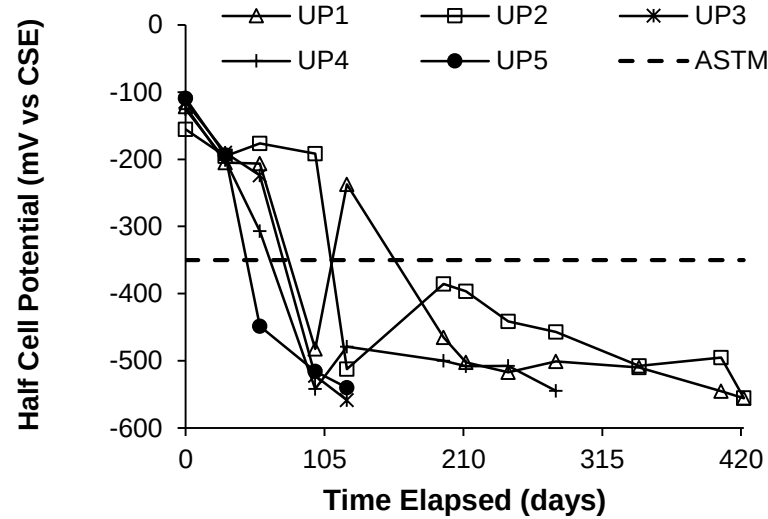
4.1. Half-Cell Potential Measurement

The difference in the values of the half-cell potential measured by Lead-Lead oxide electrode and corrosion meter were in the range of $\pm 20\text{mV}$. So the values measured by corrosion meter are presented here. The trend of half-cell potential values of UP rebars for all the series of reinforced concrete, measured by corrosion meter are shown in Figure 4.1. It was found that UP bars of all the specimens have shown the values of half-cell potential well below the ASTM criteria i.e. -350mV . As shown in Figure 4.2, the average time period of corrosion initiation for N2Z, F15Z and F30Z, varied from two to four weeks after the application of salt solution. F30ZL series took around 100 days to reach the threshold value, about three times better resistance than the other concrete specimens. The higher negative values of half-cell potential of all the specimens implied that specimens have started to corrode which was confirmed later by the visual observation. The DO rebars for majority of the specimens were in passive state due to the higher cover depth.





(c)



(d)

Figure 4.1: Trend of half-cell potential measurements for (a) N2Z, (b) F15Z, (c) F30Z and (d) F30ZL series

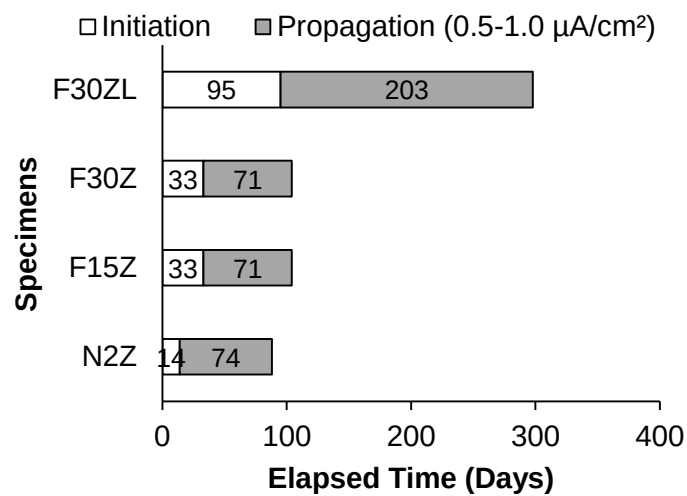
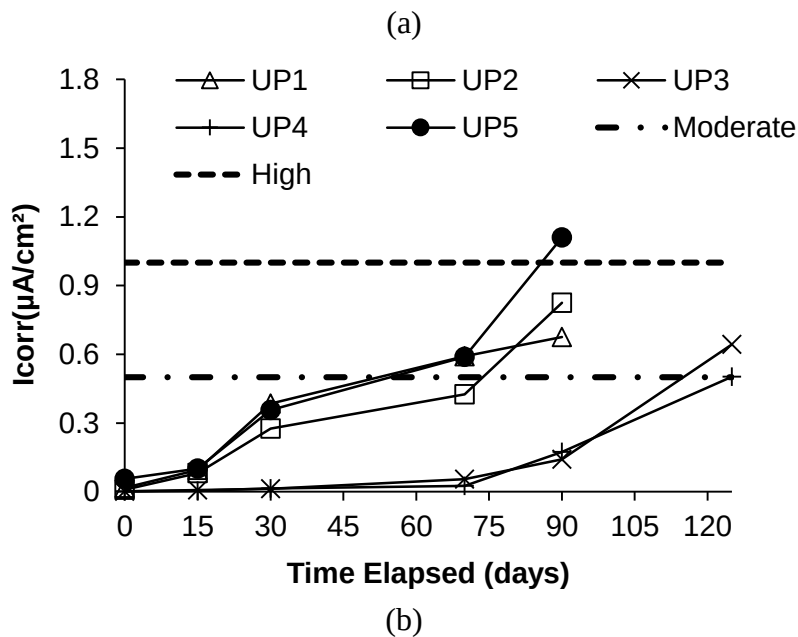
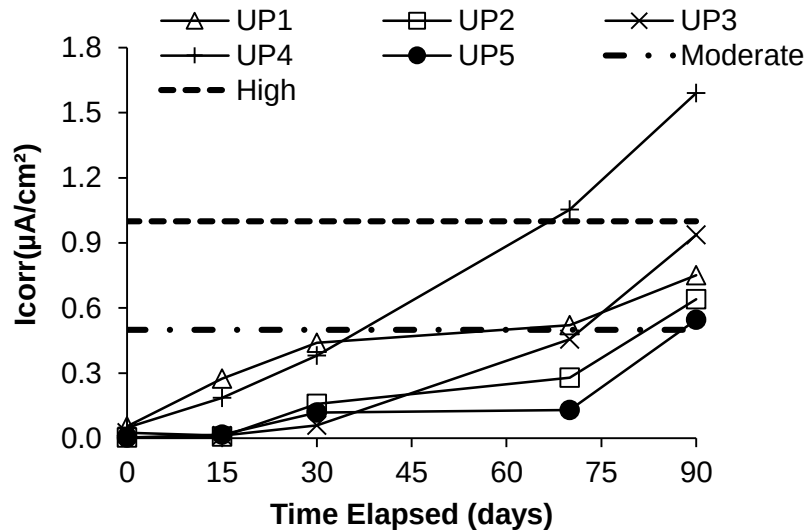
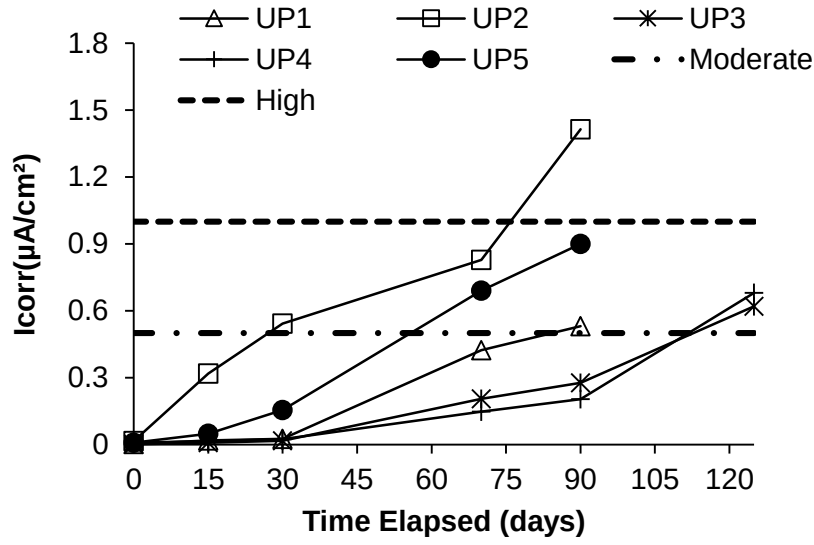


Figure 4.2: Time period for initiation and propagation period for N2Z, F15Z, F30Z and F30ZL series

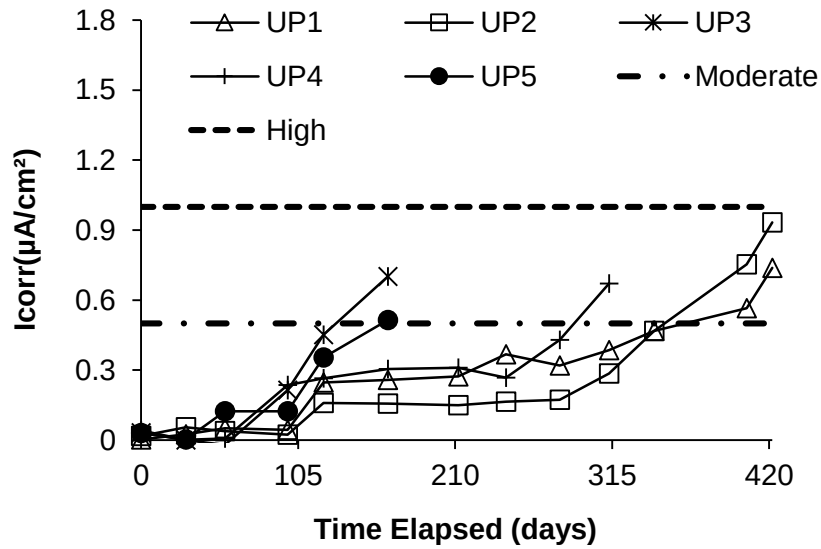
4.2. Corrosion Current Density Measurement

In this study the corrosion current density values were used as a criteria for estimating the corrosion level of rebars embedded in concrete specimens. For all the specimen series, $0.1 \mu\text{A}/\text{cm}^2$ was used as a benchmark for defining the start of active corrosion. The variation of corrosion current with time for all the four series is shown in Figure 4.3. It was observed that the slope of the I_{corr} -time graph for N2Z, F15Z and F30Z are quite steep as compared to F30ZL series. The average time period availed by each series of concrete specimens to reach the specified criteria of $0.5 - 1.0 \mu\text{A}/\text{cm}^2$ was found to be 88, 104, 104 and 298 days for N2Z, F15Z, F30Z and F30ZL series respectively. Although the initiation time for N2Z, F15Z and F30Z specimens was different but they showed almost the same time period to reach the limit criteria as shown in Figure 4.3. It implies that the 15% and 30% replacement of fly ash with shorter curing period showed the same behavior as that of normal concrete during the corrosion propagation stage. On contrary F30ZL series took the longest duration of time to initiate as well as reach the criteria of corrosion current density values compared to the other concrete specimens. It was mainly because in fly ash concrete with longer curing period the mobility of chloride ions is hindered as hydration of the cement matrix along with other pozzolanic reactions proceed, which slow down the anodic process[62].





(c)

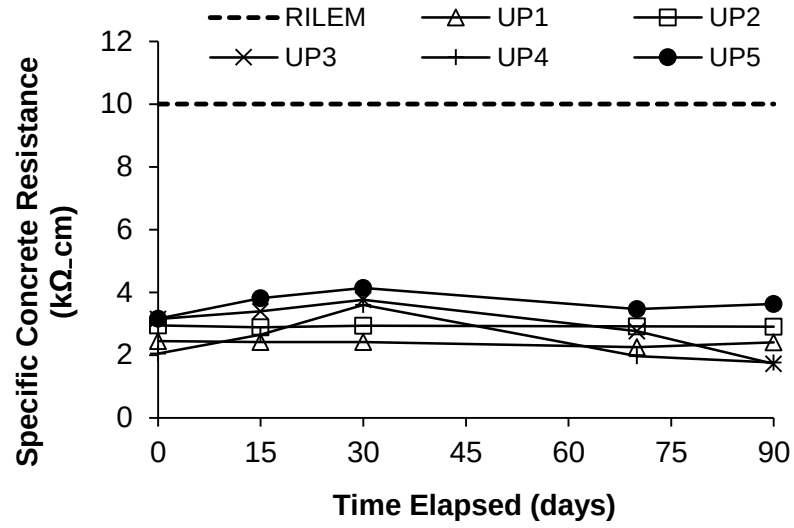


(d)

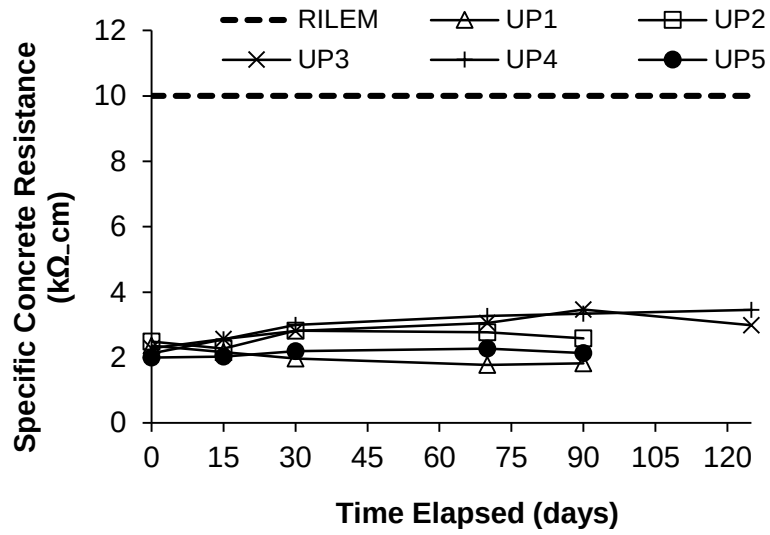
Figure 4.3: Trend of corrosion current density measurements for (a) N2Z, (b) F15Z, (c) F30Z and (d) F30ZL series

4.3. Specific Concrete Resistance Measurement

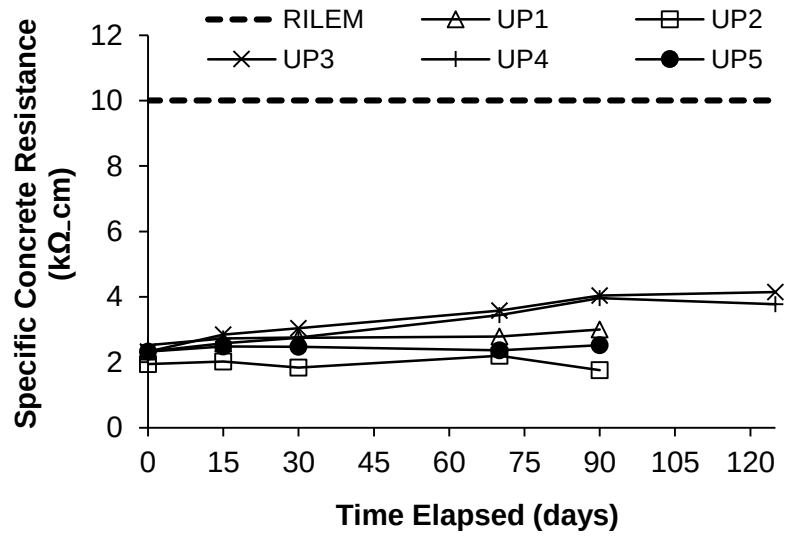
The values of specific resistance of concrete were measured along with half-cell potential and polarization resistance using corrosion meter. Figure 4.4 shows that the average values of concrete resistance for all the specimen series lie within the range of 2 KΩ-cm to 4 KΩ-cm except F30ZL series. The average values for F30ZL series was about 9 KΩ-cm. These values of concrete resistance are very small as compared to the normal values of concrete resistance. The small values of concrete resistivity are because of the small cover depth and high degree of saturation, as all the measurements are done on the salt application zone. On the other hand, F30ZL series has showed a little increase in the values because of the pozzolanic reactions which can continue even after one year [54] but still lie in the region of high corrosion risk. So, in our case for all the specimen series the resistivity of concrete is not the controlling parameter of the corrosion rate, as the values of concrete resistance for all the specimen series are less than 10 kΩ-cm [31].



(a)



(b)



(c)

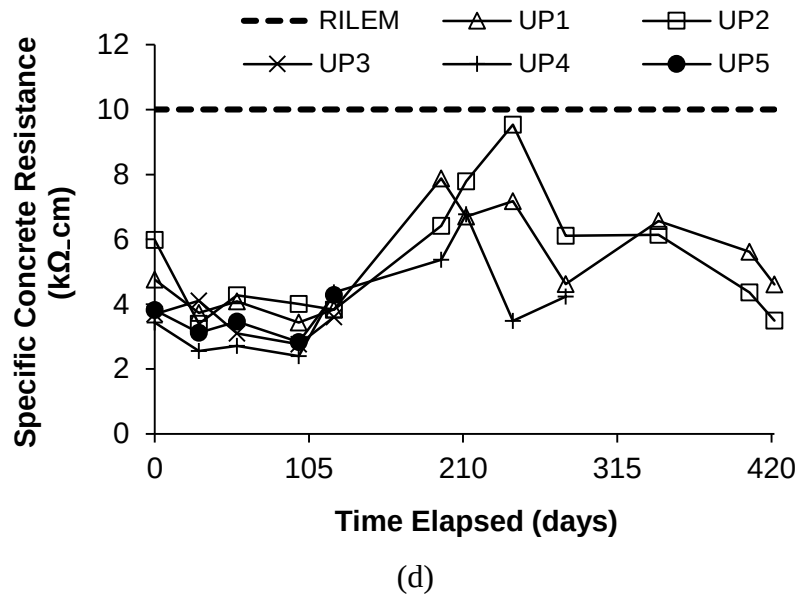
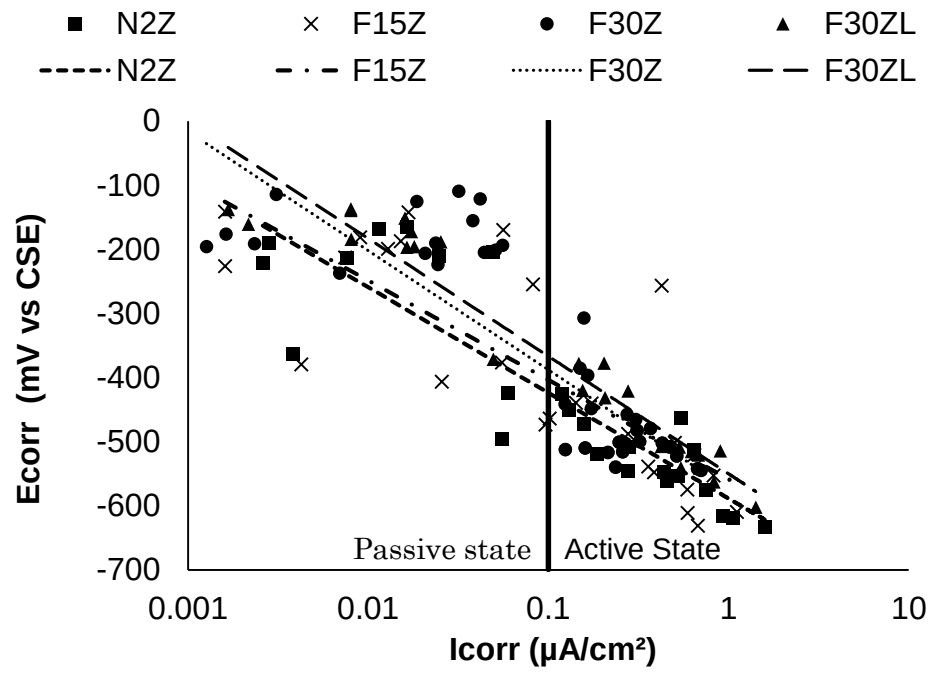


Figure 4.4: Trend of Specific concrete resistance for (a) N2Z, (b) F15Z, (c) F30Z and (d) F30ZL series

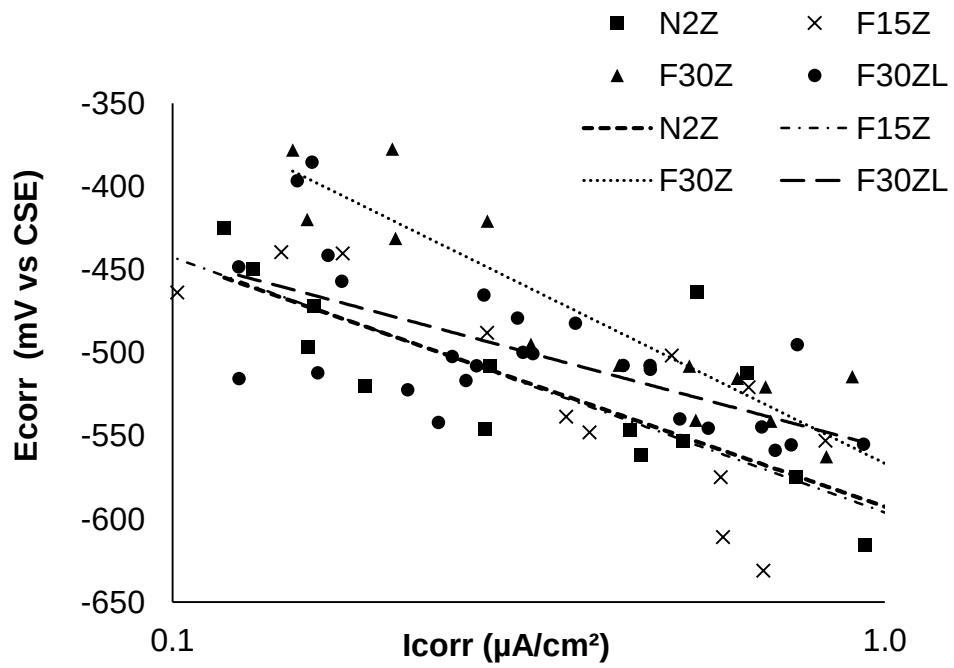
4.4. Relationship between Corrosion Potential and Corrosion Current Density

Figure 4.5(a) shows the logarithm relationship between E_{corr} and I_{corr} for the reinforcement within concrete exposed to chloride conditions. $0.1 \mu A/cm^2$ has been found to be the boundary between the active and passive corrosion state in terms of corrosion current density. It has clearly been depicted in Figure 4.5(a) that corrosion current density is independent of the corrosion potential until $0.1 \mu A/cm^2$ which refers to the passive state of rebar. After crossing the mark of $0.1 \mu A/cm^2$ the corrosion current is increasing as the potential is becoming more and more negative which shows that the reinforcement has started to corrode.

It was observed that the corrosion current is increasing as the potential is becoming more and more negative which shows that the reinforcement has started to corrode. The relation between E_{corr} and I_{corr} for active state, as shown in Figure 4.5(b) also gives an insight to the mechanism that an increase in the values of corrosion current corresponding to the decreased corrosion potential suggests to the fact that it is anodic dissolution of iron, rather than the cathodic reduction of oxygen, which establishes the rate determining step in corrosion process [63]. The absolute values of Tafel slopes for N2Z, F15Z, F30Z and F30ZL are found to be 149, 154, 180 and 85 mV/decade respectively. The absolute values of the slopes, in spite of the fly ash addition fall within or just above the normal range of Tafel slope which is the characteristics of activation controlled electrode processes [64]. These results imply that activation polarization is the governing mechanism for all the specimen series. It should be noted here that F30ZL has shown a slight decrease in the absolute value of the slopes which is because of the small values of corrosion current, indicating small corrosion activity and superior corrosion resistance behavior of fly ash concrete under long curing but might lead to pitting corrosion shown in a recent study that the local corrosion of steel reinforcement in concrete is strengthened with the decrease of the Tafel constants [65].



(a)



(b)

Figure 4.5: (a) Relationship between E_{corr} and I_{corr} for all the specimen series (b) Relationship between E_{corr} and I_{corr} during Active state of corrosion

4.5. Corroded Surface Area and Attack Penetration of Concrete Specimens

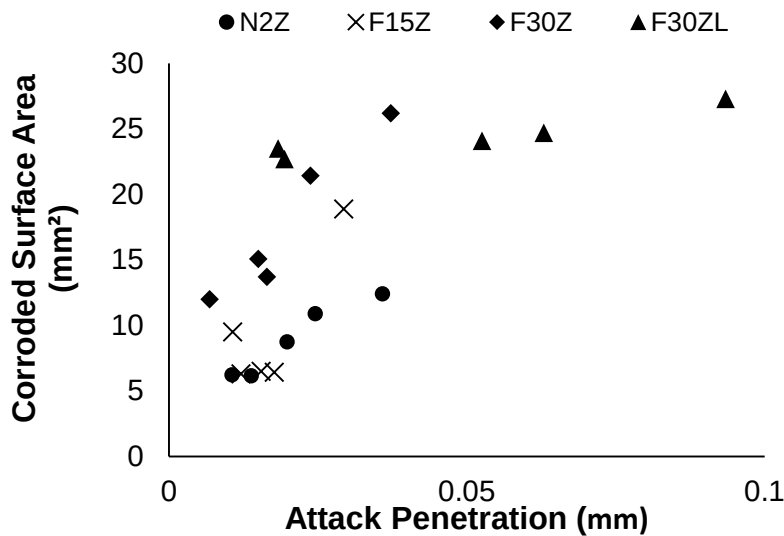


Figure 4.6: Relation between Corroded Surface Area and Attack Penetration

The relation between the corroded surface area and attack penetration has been shown in Figure 4.6. It has been observed that for N2Z, F15Z and F30Z the increase in the corroded surface area also relates to the increase in the attack penetration while for F30ZL series the increase in attack penetration is observed at a constant corroded surface area. The average values of corroded surface area and attack penetration of F30ZL series are the largest among all the specimen series. The increase in the attack penetration of F30ZL at constant corroded surface area is because of the increase in the pitting corrosion. It is known that in chloride contaminated environments the dissolution of iron proceeds by pitting. The high quality of concrete is considered to provide environment more favorable for pitting corrosion [66].

Based on the values of the average time period for initiation and propagation period F30ZL can be categorized as high quality concrete. The increase in the degree of pitting for F30ZL series as compared to other specimen series was even confirmed by the visual observation and color analysis of rebar corroded surface. Different corrosion products with different colors are formed depending upon the availability of oxygen and water [67]. It was suggested that in the lack of oxygen conditions black colored magnetite while areas with excess of oxygen supply, brownish yellow or green rust will be formed. Although detailed chemical analysis was not done in this study to verify the composition of corrosion product but the difference in the color of corrosion products as shown in Figure 4.7 also supported the formation of pits in F30ZL series. It can be seen that the percentage of black color in F30ZL (4) is more as compared to the N2ZBL (4). Figure 5c and d clearly show that as we move towards left side the intensity of black color is decreasing so does the pitting corrosion.

The average values of diffusion coefficient and chloride ion concentration are for all series are shown in Figure 4.8. It was found that the diffusion coefficient of N2Z, F15Z and F30Z are almost same. The increased diffusion coefficient of fly ash concrete is because of the short curing period. On the other hand F30ZL has the lowest diffusion coefficient. This is because of the longer curing period which increases the degree of hydration and the pozzolanic reactions resulting in a dense micro structure. While for other specimens the shorter curing period, especially for fly ash concrete, did not allow the concrete to achieve a certain degree of hydration and make itself permeable to the aggressive chloride ions.

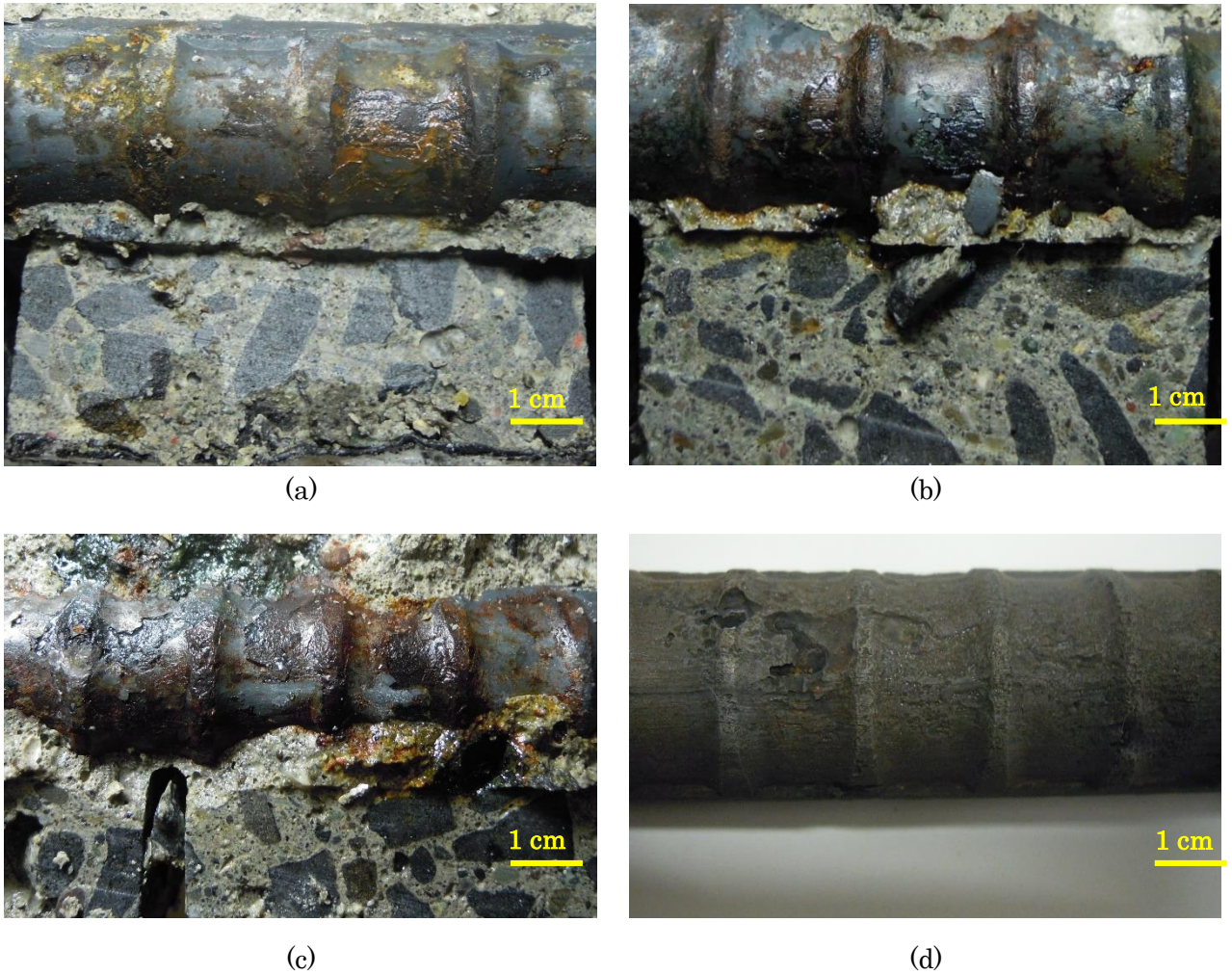


Figure 4.7: Corroded Surface of UP rebar: (a) N2Z (4), (b) F30ZL (4), UP rebar of F30ZL (1) specimen after cutting and removal of corrosion products in (c) and (d) respectively.

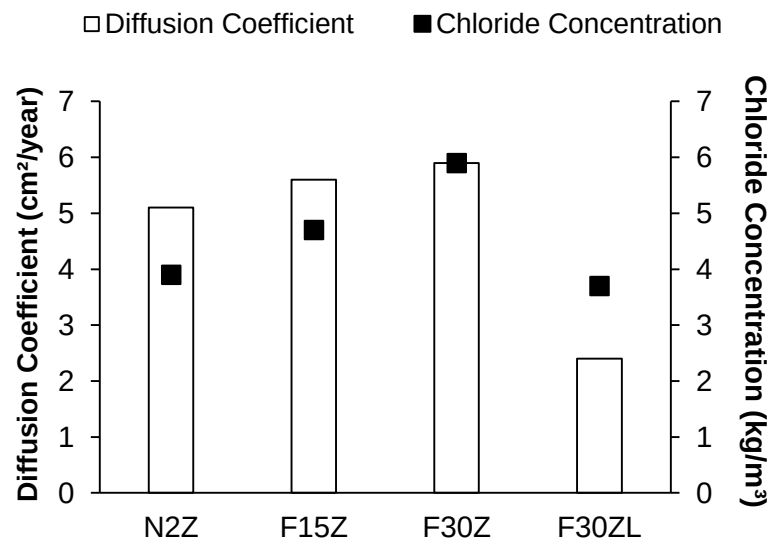


Figure 4.8: Histogram for the Diffusion Coefficient and Chloride Concentration

4.6. Summary

The corrosion resistance of the steel rebars embedded in fly ash concrete was evaluated in the range of moderate to high corrosion rate under different fly ash replacement ratios and curing period. It was observed that the increase in the percentage of fly ash replacement was found to have no effect on the reaction mechanism of corrosion which remained as activation polarization for all the specimen series. In addition, it was also noticed that the corrosion resistance behavior of fly ash concrete is sensitive to curing period. Furthermore, it was also observed that the value of the diffusion coefficient for fly ash concrete significantly reduced when the curing period was increased from 28 to 91 days. Moreover it was noted that, from moderate to high corrosion rate, the longer curing for fly ash concrete has increased the probability of pitting corrosion.

CHAPTER 5

CORROSION OF REBAR IN CRACKED FLY ASH CONCRETE

5.1 Crack Width Variation

The variation of the crack width, measured at the end of each cycle for N2C (2) and F30C (2) are shown in Figure 5.1 (a) and (b) respectively. It was observed that average crack width remained almost constant for all the series. It was observed that after the generation of flexural cracks, the closure of the crack occurred at some points due to the falling of loose concrete into the crack. The fallen concrete particles were observed to have either faced out during the exposure period or have moved in the deeper parts by breaking down into more small particles.

It was observed that the average crack width remained almost constant for both the series. However it noticed that the degree of closure of cracks was more for smaller crack widths i.e. around 50 microns than higher crack width. Furthermore as comparison with the normal concrete series the fly ash concrete had shown higher degree of self-healing. Although the exact composition of the product was not verified but Figure 5.1 (b) clearly depict the closure of crack mouth. The self-healing did not occur at the full length of crack rather was found at certain locations along the length of crack. The self -healing of the cracks in fly ash concrete might be because of the pozzolanic reaction as reported previously that fly ash at low water to cement ratio has a tendency to heal the micro cracks under the water supply because of the delayed pozzolanic reactions which ultimately can fill the crack space [68]. Sharman et al also reported the self-healing of engineered cementitious composites containing fly ash when exposed to 3 % NaCl solution [39]. Furthermore, the concentration of salt solution being used in this study is relatively high, causing the increase in the alkali content in the crack which might have triggered the activation of fly ash.

5.2 Electrochemical Measurements

The trend of the half-cell potential and corrosion current for N2C and F30C series are shown in Figure 5.2 (a), (b) and Figure 5.3 (a), (b) respectively. It was observed that almost all the specimens had shown corrosion initiation, based on ASTM C-876, within first two weeks of salt application period, irrespective of the fly ash addition.

For cracked concrete it is normally considered that macro cell corrosion activity will govern the corrosion mechanism and subsequently the corrosion rate will depend on the diffusion of oxygen through the un-cracked concrete to the cathodic sites or the electric resistance around the steel [69]. In cracked fly ash concrete, the high electrical resistance of concrete at the non-cracked region (acting as cathode), will restricts the flow of electrons from anode to cathode. In addition the restricted supply of oxygen at the cathodic sites due to dense internal structure of fly ash concrete, as compared to normal concrete, will push the corrosion rate values towards the lower side. Another factor which may also influence is the closure of the cracks in fly ash concrete as compared to the normal concrete as shown clearly in Figure 5.1, which will affect the corrosion activity inside the crack.

The semi log graph between the half-cell potential and corrosion current density for both N2C and F30C are shown in Figure 5.4. As a reference for non-cracked specimen, having almost same mix proportions (N2Z and F30ZL), are plotted in Figure 5.4 (Zafar et al. 2014b). The absolute values of the slopes for the best fit plots of half-cell potential and corrosion current density were found to be 149, 85, 211 and 291 mV/decade for N2Z, F30ZL N2C and F30C respectively. There is clear difference between the slopes of cracked and non-cracked specimens referring towards the difference in the corrosion mechanism of both. For non-cracked specimens the values of the slopes lie within the normal range of activation-controlled electrode process i.e. 50 to 150 mV/decade (Fontana et al. 1978), while for cracked specimens

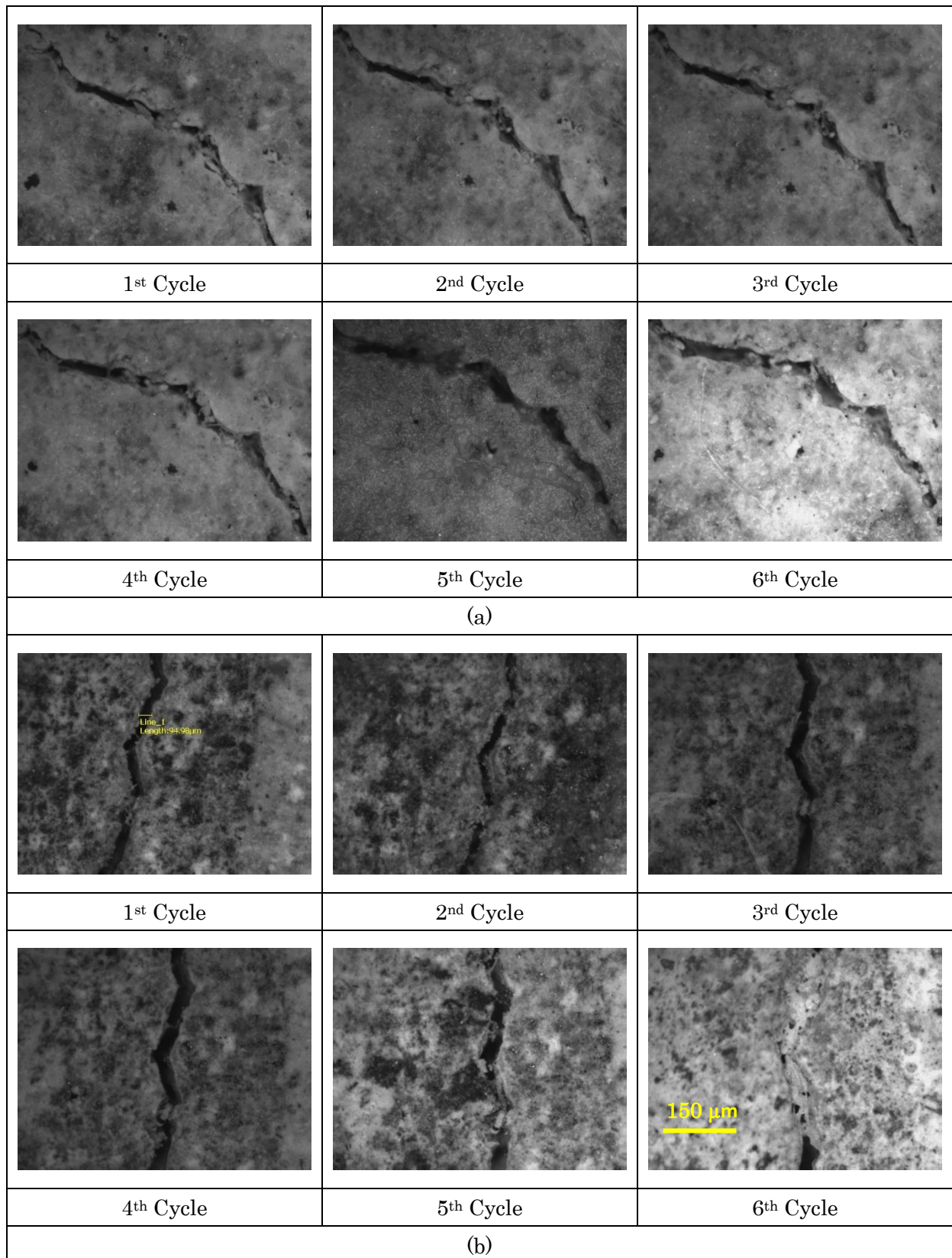


Figure 5.1: Crack width variation at the end of each cycles for (a) N2C2 and (b) F30C2 Specimen

the values of gradients lie well above than mentioned range. This suggests that for cracked concrete the cathodic process of oxygen reduction might be subjected to concentration-controlled electrode process because of the protective film of the corrosion products formed at the rebar surface.

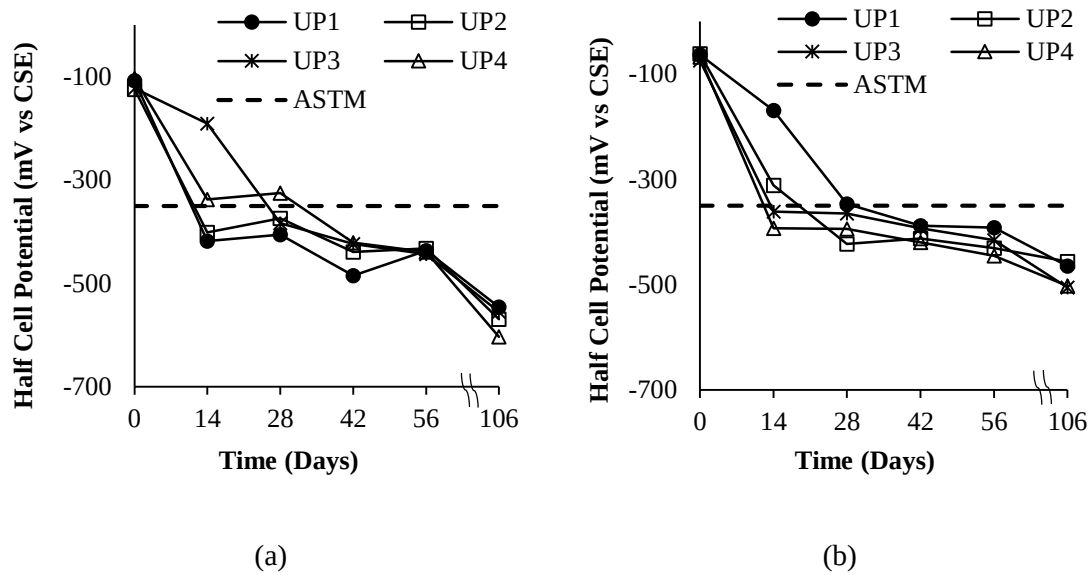


Figure 5.2: Trend of half-cell potential against time for (a) N2C and (b) F30C Series

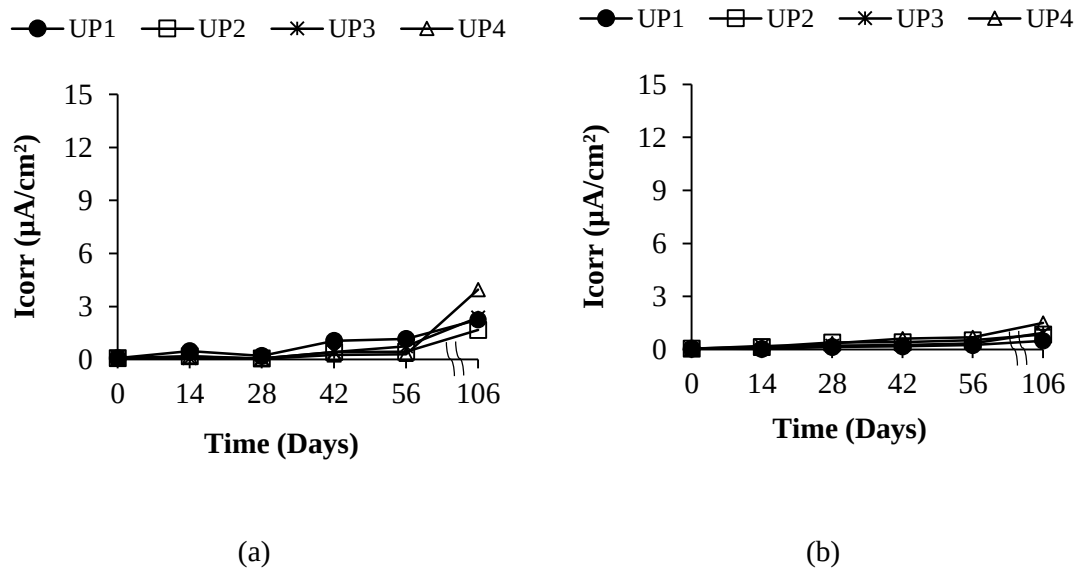


Figure 5.3: Trend of corrosion current density values against time for (a) N2C and (b) F30C Series

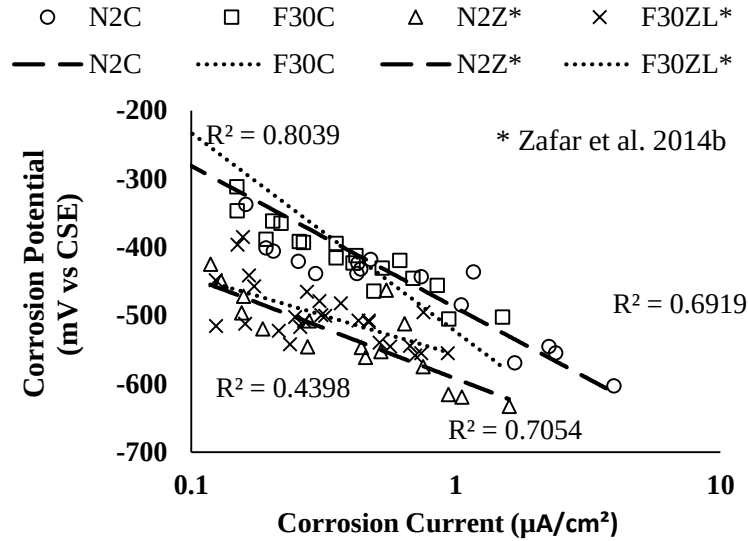


Figure 5.4: Semi-log plots of half-cell potential versus corrosion current for the steel embedded in N2C, F30C, N2Z and F30ZL series

5.3 Chloride ion Concentration

Figure 5.5 shows the variation of chloride ion concentration in the cover concrete for N2C series and F30C series respectively. It was found that although the surface chloride ion concentration was found to be more for normal Portland cement concrete but the chloride ion concentration at the rebar level was observed to be the same for both types of concrete. The average value of chloride ion concentration for N2C and F30C at a depth of 25 mm from the exposure surface was about 10 kg/m³. However it was observed that the corrosion rate for F30C series was on the lower side as compared to that of N2C series. Although the average value of total chloride ion is same for both types of cracked specimen the amount of free chloride ions, generally responsible for corrosion initiation, is less in fly ash concrete as compared to that of normal Portland cement concrete because of higher chloride binding for fly ash concrete [70].

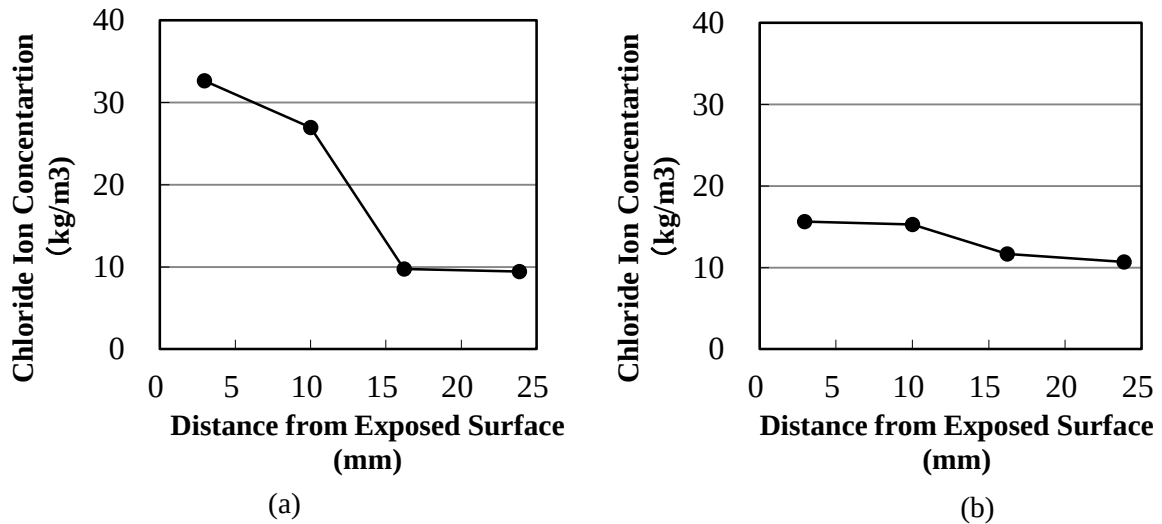


Figure 5.5: Distribution of chloride ion concentration: from exposed surface for (a) N2C2 and (b) F30C2 specimen

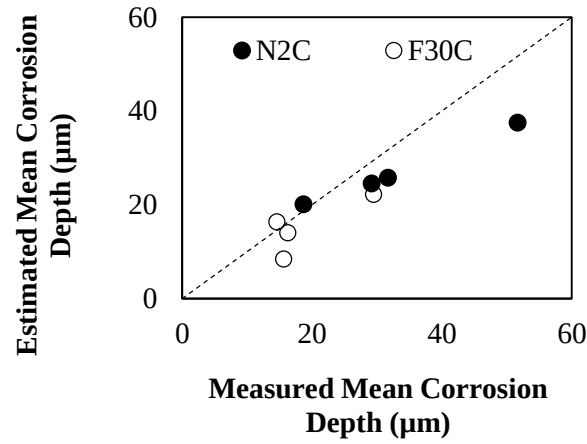


Figure 5.6: Plot between estimated mean corrosion depth and measured mean corrosion depth

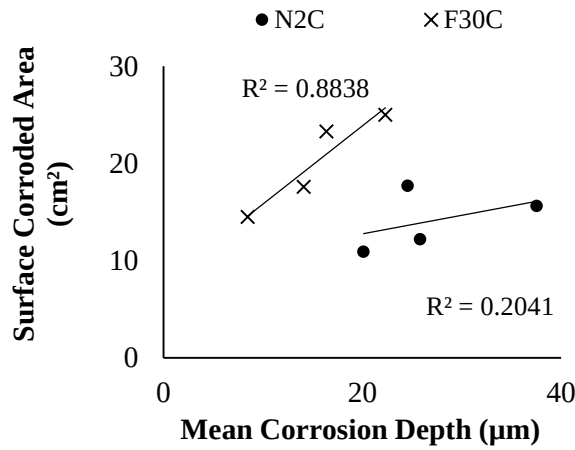


Figure 5.7: Plot between surface corroded area and mean corrosion depth

5.4 Surface Corroded Area and Attack Penetration

Figure 5.6 shows the plot between the measured and estimated mean corrosion depth. Although the measured values are on the lower side still a good co-relation between the estimated and measured mean corrosion depth was observed. The relation between surface corroded area and estimated mean corrosion depth for both the specimen series is shown in Figure 5.7. It was observed that the fly ash specimens have shown higher surface corroded areas as compared to the normal concrete specimens indicating to uniform corrosion. While the normal concrete specimen has shown high mean corrosion depth at relatively low values of surface corroded areas indicating to the more localized and severe corrosion. Tittarelli has also reported the corrosion attack to be more diffusive and less penetrating for the partial replacement of fly ash with ordinary Portland cement in recycled aggregate concrete when exposed to wet and dry cycles [71]. In addition the corrosion experiments on reinforced concrete beams have also showed the least steel loss percentage for the rebars embedded in fly ash concrete as compared to the ordinary Portland cement concrete, silica fume and slag concrete [72]. The reduced severity of corrosion damage in cracked fly ash concrete is mainly attributed to the high concrete resistance at non-cracked region. In addition the closure of the crack mouth

and chloride binding during the wet and dry cycle might also assist to suppress the corrosion penetration in fly ash concrete as compared to normal Portland cement concrete.

The corrosion products were removed from the surface of rebar to verify the extent of corrosion and measure the pit depths. The example of the cleaned rebar specimens for normal, N2C (4) and fly ash concrete, F30C (4) are shown in Figure 5.8 (a) and (b) respectively. It is evident from the Figure 11 that the pitting effect was more prominent in N2C specimen than F30C specimens. It was observed that for N2C series the number of pits were less but deep and larger in diameter while for fly ash concrete the number of pits were greater but shallow and small in diameter. It clearly shows the diminishing effect of localized corrosion in cracked fly ash concrete as compared to normal Portland cement concrete when exposed to wet and dry cycle. In addition to that, the rebar surface analysis revealed that number of pits are proportional to the surface corroded area while the depth of a pit is inversely proportional to the surface corroded area.



(a)



(b)

Figure 5.8: Rebar surface after removal of corrosion products for (a) N2C4 and (b) F30C4 specimen

5.5 Summary

The performance of fly ash concrete in the presence of flexural cracks against corrosion, under static loading conditions was examined. All the reinforced concrete specimens were subjected to 10% NaCl solution under wet and dry cycle. The results of half-cell potential indicated that the corrosion initiation period for cracked fly ash concrete occurred to be the same as that of cracked normal Portland cement concrete. It was also observed that fly ash concrete as compared to the normal concrete in cracked condition, subjected to salt solution under wet and dry cycle had shown suppressed values of corrosion current density. The better performance of fly ash concrete under cracked conditions is implied with considerations of high resistivity as well as the self-healing effect for fly ash concrete as compared to the normal concrete. Furthermore, it was also noticed that fly ash concrete had shown suppression of localized corrosion as compared to normal concrete under cracked conditions, when exposed to wet and dry cycle under static loading.

CHAPTER 6

CORROSION MONITORING OF REAL REINFORCED CONCRETE STRUCTURES

6.1. In-Service Reinforced Concrete Waste Water Outlet Structure

6.1.1 Electrochemical Measurements

Figure 6.1 is the scanning electron microscope image of the concrete core taken from the RC waste water outlet structure (courtesy by Hokkaido Electric Power Co. Inc.). It clearly shows the presence of fly ash particles in the concrete.

The results of the half-cell potential (E_{corr}) and corrosion current density (I_{corr}) measurements for the RC structure are shown in Figure 6.2. It was observed that almost all the measured points have shown the values of half-cell potential less than -350 mV vs CSE except point C, whose value is also not very high i.e. -371mV vs CSE. According to ASTM C 876, the steel reinforcement is still in the passive state for A, B and D points while there is a likely hood of corrosion initiation at point C. On the other hand the values of corrosion current density for all the points are less than $0.1 \mu\text{A}/\text{cm}^2$ which is also suggesting the passive state of rebars embedded in fly ash concrete. The electrochemical results of rebars have clearly suggested that the corrosion has yet to initiate for the rebars and is mainly because of the high durability of fly ash concrete against aggressive agents even after the exposure of 40 years.



Figure 6.1: The presence of fly ash particle by Scanning Electron Microscope (Courtesy by Hokkaido Electric Power Co. Inc.)

6.1.2 Chloride ion Concentration Analysis

Figure 6.3 shows the distribution of chloride ion concentration along the depth for the

cores specimens. It was noticed that the value of chloride ion concentration is approaching the zero mark at a depth of 60 mm from the exposure surface which relates that the chloride ion have not yet reached the level of rebar i.e. 80 mm. The dense microstructure of concrete incorporating fly ash has restricted the chloride ion from reaching the rebar level and initiate corrosion. The average value of surface chloride ion concentration and apparent diffusion coefficient for the cores was found to be 13.2 kg/m³ and 0.101 cm²/year respectively.

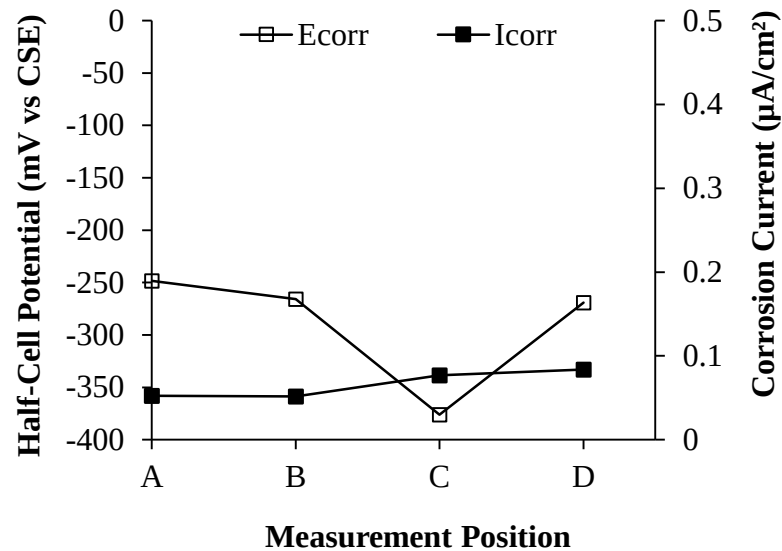


Figure 6.2: Half-Cell Potential (Ecorr) and Corrosion Current (Icorr)

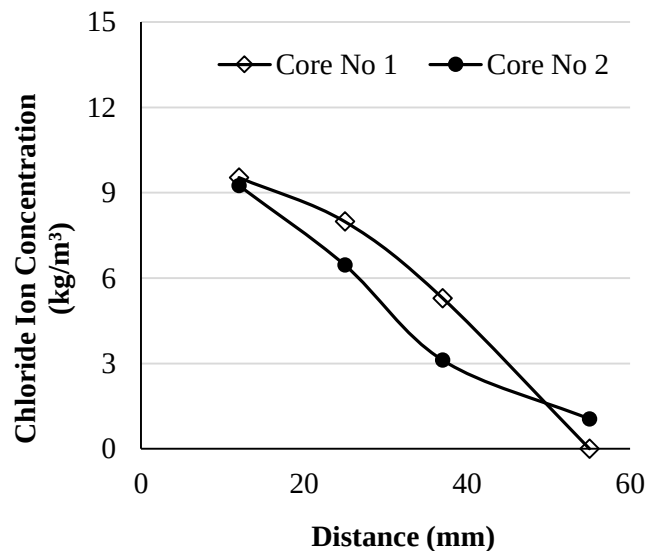


Figure 6.3: The profiles of chloride ion concentration for core specimens

6.1.3 Verification for Corrosion Reinforcement with regard to Service life

The performance of concrete structures be different over time due to environmental and loading conditions. The inspection on whether such change brought to concrete structures by

the various factors is in the permissible range is necessary. In order to conduct these inspections various standards like JSCE, ACI and RILEM are followed. In this study JSCE Standard Specifications for Concrete Structures-2012 are used to obtain the values of chloride threshold level and apparent diffusion coefficient for the current fly ash concrete structure and compared with the already obtained experimental values in the previous section. In addition the amount of chloride ion concentration and apparent diffusion coefficient will be predicted after 50, 100 and 125 years of service life. Furthermore for the comparison purpose, the chloride ion concentration and apparent diffusion coefficient will also be calculated for normal Portland cement concrete with same W/C ratio and service life. According to JSCE, the critical chloride ion concentration required to initiate the corrosion can be estimated using following equations:

For Normal Portland cement Concrete:

$$C_{lim} = -3.0 \left(\frac{W}{C} \right) + 3.4 \text{ ----- (6.1)}$$

For Fly ash Concrete:

$$C_{lim} = -2.6 \left(\frac{W}{C} \right) + 3.1 \text{ ----- (6.2)}$$

Where

C_{lim} : Critical chloride concentration for initiation of steel corrosion embedded in concrete.

W/C is the water to cement ratio, in case of fly ash concrete, C is the blended cement i.e. fly ash cement. As described in Table 2.7, Type B fly ash cement was used in the current structure and W/C for this structure is 0.55.

From equation 6.1 and 6.2, the critical chloride concentration for normal Portland cement concrete and fly ash concrete at W/C of 0.55 are found to be 1.75 kg/m³ and 1.67 kg/m³ respectively.

According to JSCE Standard Specifications for Concrete Structures-2012, the apparent diffusion coefficient can be estimated by using the following equations:

For Normal Portland cement Concrete:

$$\log D_{ap} = 3.0 \left(\frac{W}{C} \right) - 1.8 \text{ ----- (6.3)}$$

For Fly ash Concrete:

$$\log D_{ap} = 3.0 \left(\frac{W}{C} \right) - 1.9 \text{ ----- (6.4)}$$

Where

D_{ap} : Apparent diffusion coefficient of chloride ions into concrete (cm² /year)

W/C is the same as described above for equation 6.1 and 6.2.

From equation 6.3 and 6.4, the values of apparent diffusion coefficient for normal Portland cement concrete and fly ash concrete at W/C of 0.55 are found to be 0.71 cm²/year and 0.56 cm²/year respectively. The following order of the apparent diffusion coefficient was observed:

$$D_{ap}\text{-OPC-est} (0.71 \text{ cm}^2/\text{year}) > D_{ap}\text{-FA-est} (0.56 \text{ cm}^2/\text{year}) > D_{ap}\text{-FA-exp} (0.101 \text{ cm}^2/\text{year})$$

Where

$D_{ap}\text{-OPC-est}$ is the apparent diffusion coefficient of normal Portland cement concrete estimated by using JSCE specifications

$D_{ap}\text{-FA-est}$ is the apparent diffusion coefficient of fly ash concrete estimated by using JSCE specifications

$D_{ap}\text{-FA-exp}$ is the apparent diffusion coefficient of fly ash concrete, experimentally obtained by chloride ion analysis of the cores taken from the reinforced structure.

It was noticed that the apparent diffusion coefficient estimated using the JSCE specifications, especially for fly ash concrete are on the higher side as compared to the experimental values. This may be because the equations 6.3 and 6.4 provide the apparent diffusion coefficient for the design purpose incorporating safety factors to be on the safe side.

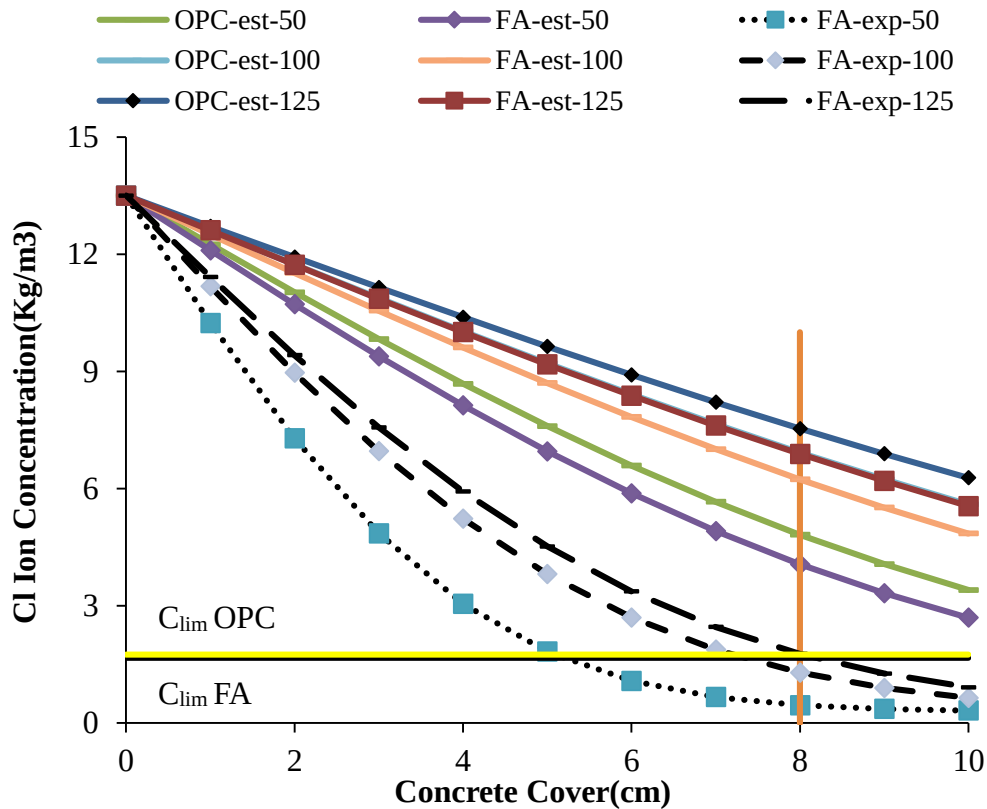


Figure 6.4: The predicted profiles of chloride ion concentration after a service life of 50, 100 and 125 years for normal concrete and fly ash concrete {Legend: [Type of cement] - [Estimated(est) or Experimental (exp) diffusion coefficient was used to predict the chloride ion values] - [service life in years]}.

The estimated chloride ion concentration for the normal concrete and fly ash concrete after a service life of 50, 100 and 125 years is shown in figure 6.4. The surface chloride ion concentration value was taken as 13.2 kg/m³, experimentally obtained from the core specimens. OPC-est stands for normal Portland cement concrete and estimated diffusion coefficient was used for predicting the chloride ion concentration values while FA-exp stands for fly ash concrete and experimentally obtained diffusion coefficient was used for predicting the chloride

ion concentration values. It was observed that at any time period of service life fly ash concrete had shown low chloride ion concentration as compared to the normal Portland cement concrete. The values of chloride ion concentration further dropped when experimental diffusion coefficient was used as shown in Table 6.1. The service life of the fly ash concrete with regard to corrosion initiation, using the critical chloride ion concentration as 1.67 kg/m^3 (estimated by equation 6.2), was found to be around 125 years. While the service life with regard to corrosion initiation using 'D_{ap}-FA-est' as the apparent diffusion coefficient, was found to be around 25 years. It was noticed that the service life of the reinforced structure incorporating fly ash occurred to be five times less when the apparent diffusion coefficient estimated by JSCE specifications instead of experimental apparent diffusion coefficient was used. This difference in the predicted service life is mainly because difference in the apparent diffusion coefficients. The estimated apparent diffusion coefficient, D_{ap}-FA-est, is used for the design purpose with an aim to be on the safe side and ultimately push the predicted service life values on the lower side.

Table 6.1: Predicted chloride ion concentration values at cover depth after certain period of service life

Service Life after 1974 (years)	Chloride ion Concentration (kg/m ³) at cover depth		
	OPC-Est	FA-Est	FA-Exp
50	4.82	4.06	0.46
100	6.93	6.24	1.29
125	7.54	6.89	1.77

6.2 Summary

The corrosion monitoring of an in-service reinforced waste water outlet structure incorporating fly ash was done. The structure had been in service for last 40 years. The scanning electron microscope image of the concrete core has clearly shown the presence of fly ash particles in the structure. The results of electrochemical measurement and chloride ion analysis had shown that the rebars embedded in the reinforced structure are still in the passive state. From the visual observation it was found that the virgin skin of the rebars are still in contact clearly representing the high durability of fly ash concrete even in real structures exposed to harsh environments. The results of simulation have shown that the service life of the reinforced structure incorporating fly ash was underestimated by using the apparent diffusion coefficient, estimated by JSCE specifications.

CHAPTER 7

CONCLUSIONS AND FUTURE WORKS

7.1 Conclusions

The conclusion drawn in the light of experimental results presented in this study are as follows:

1. The effect of fly ash on the corrosion initiation of rebars in concrete was investigated using the embedded electrode and corrosion meter. It was observed that the monitoring of half-cell potential through embedded lead electrode can reliably detect the onset of corrosion in fly ash concrete with 28 days curing. However, the probability of accurately determining the onset of corrosion by embedded lead electrode decreased for longer curing period irrespective of the reinforcement type. The use of corrosion meter resulted in the threshold values of half-cell potential and polarization resistance for fly ash concrete being -250 mV and 1300 k Ω -cm² respectively.
2. The long curing period for fly ash concrete resulted in a dual beneficial effect of delaying the onset of corrosion due to lowered diffusion coefficient and pushing the CTL values of fly ash concrete close to that of normal concrete. After 28 days of curing, the CTL value for 30% replacement of fly ash was 0.41% by mass of binder (C+FA), compared to 0.71% for normal Portland cement concrete. The CTL value for fly ash concrete after 91 days of curing, however, was increased to 0.66% by mass of binder. Furthermore, the longer curing of fly ash concrete resulted in better protection against corrosion as compared to just increasing the cover depth.
3. The corrosion resistance of the steel rebars embedded in fly ash concrete was evaluated in the range of moderate to high corrosion rate under different fly ash replacement ratios and curing period. It was noticed that the increase in the percentage of fly ash replacement was found to have no effect on the reaction mechanism of corrosion which remained as activation polarization for all the specimen series. The results of corrosion initiation and corrosion propagation stages have clearly depicted that the corrosion resistance behavior of fly ash concrete during both the stages is sensitive to curing period. Moreover it was noted that, although the fly ash specimens cured for 91 days had shown better corrosion resistance in terms of corrosion initiation time and time to reach the specified degree of corrosion, it had also shown larger surface corroded area.
4. The performance of fly ash concrete in the presence of flexural cracks against corrosion, when exposed to wet and dry cycle under static loading conditions was examined. The results of half-cell potential indicated that the corrosion initiation period for cracked fly ash concrete occurred to be the same as that of cracked normal Portland cement concrete. It was also observed that fly ash concrete as compared to the normal concrete in cracked condition had shown suppressed values of corrosion current density. The better performance of fly ash concrete under cracked conditions is implied with considerations of high resistivity as well as the self-healing effect for fly ash concrete as compared to the normal concrete. Furthermore, it was also noticed that fly ash concrete had shown suppression of localized corrosion as compared to normal concrete under cracked conditions, when exposed to wet and dry cycle under static loading.

5. The corrosion monitoring of an in-service reinforced waste water outlet structure incorporating fly ash was done. The structure had been in service for last 40 years. The Scanning electron microscope image of the concrete core has clearly shown the presence of fly ash particles in the waste water outlet structure. The results of electrochemical measurement and chloride ion analysis had shown that the rebars embedded in the reinforced structure are still in the passive state. From the visual observation it was found that the virgin skin of the rebars are still in contact clearly representing the high durability of fly ash concrete even in real structures exposed to harsh environments.
6. In this research the durability of the fly ash concrete with regard to corrosion resistance of reinforcement had been presented. The testing was done on the laboratory scale specimens as well as real structures which enabled to understand the performance of fly ash concrete against corrosion. It is inferred that the inclusion of fly ash as a partial replacement of ordinary Portland cement has shown high durability with regard to corrosion resistance of rebars and the increase in the use of fly ash in reinforced structures should be encouraged.

7.2 Future Works

1. The long curing has showed an increase in the CTL values for fly ash concrete but it is also known that CTL values are not dependent on a single variable, as numerous factors affect the pore solution chemistry and steel-concrete interface, so the mechanism by which the CTL values for fly ash concrete increase with long curing is still unclear and needs further detailed research for better understanding of the mechanism.
2. Steel-Concrete interface is an important factor with regard to corrosion of steel rebars in concrete. Further investigation is suggested to examine the effect of air voids, casting direction and rebar surface treatments on corrosion resistance of rebar in concrete at long exposure time to saline solution. Quantification of the hydration products with the passage of time at steel-concrete interface should also be investigated.
3. The chloride diffusion in cracked concrete has a significant influence on the time to initiate corrosion as well as the corrosion-propagation phase, as presented in this study. Experimental observations on chloride transport in cracked concrete with regard to corrosion damage to steel rebars in normal and fly ash concrete considering various exposure conditions (wet/dry or fully submerged) and various concrete parameters (binder composition, w/c ratio, etc.) are therefore recommended. In particular, knowledge on the transport properties through crack, non-cracked and de-bonded area along the reinforcement is lacking.

REFERENCES

1. Mehta PK (1997) Durability- critical issues for the future. *Concrete International* 19(7): 27-33.
2. Cabrera JG and Ghoddoussi P (1994) Influence of fly ash on the resistivity and rate of corrosion of reinforced concrete. *American Concrete Institute SP 145*: 229-244.
3. Sugiyama T, Tsuji Y, Bremner TW (2001) Relationship between coulomb and migration coefficient of chloride ions for concrete in a steady-state chloride migration test. *Magazine of Concrete Research* 53(1): 13-24.
4. Promentilla MAB, Sugiyama T, Hitomi T et al (2009) Quantification of tortuosity in hardened cement paste using synchrotron-based X-ray computed micro tomography. *Cement and Concrete Research* 39(6): 548:557.
5. Darma IS, Sugiyama T and Promentilla MAB (2013) Application of X-ray CT to study diffusivity in cracked concrete through the observation of tracer transport. *Journal of Advanced Concrete Technology* 11: 266-281.
6. Japanese Industrial Standards (1999) JIS A 6201 Use of fly ash in concrete, Japan. (In Japanese).
7. Pourbaix M (1974) Atlas of Electrochemical Equilibria in Aqueous Solutions. *National Association of Corrosion Engineers (NACE), Houston, Texas, USA*.
8. Foley RT (1975) Complex ions and corrosion. *Journal of the Electrochemical Society*, 122(11), 1493-1549.
9. Sandberg P (1995) Critical evaluation of factors affecting chloride initiated reinforcement corrosion in concrete. *Report TVBM-3068, Lund University (LTH), Lund, Sweden*.
10. Strehblow HH (2002) Mechanisms of Pitting Corrosion. *Corrosion Mechanisms in Theory and Practice, 2nd edition (P. Marcus), Marcel Dekker Inc., New York, USA*.
11. Page CL and Treadaway KWJ (1982) Aspects of electrochemistry of steel in concrete. *Nature*, 297 (5862):109-115.
12. DuraCrete (2000), Probabilistic performance based durability design of concrete structures, The European Union - Brite EuRam III.
13. Marcotte TD (2001) Characterization of chloride-induced corrosion products that form in steel-reinforced cementitious materials. *Ph.D. Thesis, University of Waterloo: Waterloo, Canada*.
14. Schiessl P and Raupach M (1990) Influence of concrete composition and microclimate on the critical chloride content in concrete. in *Page CL, Treadaway KWJ and Bamforth PB (Eds.), Corrosion of Reinforcement in Concrete, Elsevier Applied Science, London UK*, 49-58.
15. Gouda VK (1970) Corrosion and corrosion inhibition of reinforcing steel. *British Corrosion Journal* 5(2): 198-202.
16. Hausmann DA (1967) Steel corrosion in concrete; How does it occur? *Materials and Protection* 6(11): 19-23.

17. Alonso C, Andrade C, Castellote M et al. (2000) Chloride threshold values to depassivate reinforcing bars embedded in a standardized OPC mortar. *Cement and Concrete Research* 30: 1047-1055.
18. Horiguchi K, Maruya T and Takewaka K (2006) Estimation of initiation stage for corrosion by half-cell potential and chloride threshold value. *Proceedings of JCI* 28:1007-1012 (In Japanese).
19. Horiguchi K, Maruya T and Takewaka K (2007) An effect of mix proportion on chloride threshold value. *Proceedings of JCI*, 29: 1377-1382 (In Japanese).
20. Islam GMS, Sugiyama T (2010) Corrosion initiation state of rebars in concrete subjected to chloride penetration. In proceedings of the 6th International Conference on Concrete under severe conditions, Environment and loading. CRC Press, Merida, Mexico, pp. 453-460.
21. Furumura J, Islam GMS, Sugiyama T et al. (2010). Investigation of threshold chloride concentration of steel in concrete using an embedded lead electrode. In *proceedings of 2nd International Conference on Durability of Concrete Structures*. Hokkaido University Press, Sapporo, Japan, pp. 353-360.
22. Andrade C, Page CL (1986) Pore solution chemistry and corrosion in hydrated cement systems containing chloride salts. A study on specific effects. *Cement and Concrete Research* 21: 49-53.
23. Thomas M (1996) Chloride threshold in marine concrete. *Cement and Concrete Research* 26(4): 513-519.
24. Xu J, Jiang L, Wang W et al. (2011) Chloride threshold value for reinforcement corrosion in concrete with additions of silica fume and fly ash. *Magazine of Concrete Research* 63(12): 905-913.
25. Shi X, Xie N, Fortune K et al. (2012) Durability of steel reinforced concrete in chloride environments: An overview. *Construction and Building Materials* 30: 125-138.
26. Hartt WH, Nam J (2008) Effect of cement alkalinity on chloride threshold and time to corrosion of reinforcing steel in concrete. *Corrosion* 64(8): 671-680.
27. Ferreira M, Jalali S, and Gjorv OE (2004) Software for probability based durability analysis. In proceedings of the International Conference on Concrete under severe conditions, CONSEC' 04 (B.H. Oh et al. (eds)). Seoul, Korea, pp. 1015-1024.
28. Mullard A and Stewart M (2011) Corrosion-Induced Cover Cracking: New Test Data and Predictive Models. *ACI Structural Journal* 108 (1): 71 – 79.
29. Tuutti K (1982) Corrosion of steel in concrete. Swedish Cement and Concrete Research Institute, Sweden: 17-21.
30. Vu K, Stewart M and Mullard J (2005) Corrosion-Induced Cracking: Experimental Data and Predictive Models. *ACI Structural Journal* 102 (5):719 – 726.
31. Andrade C and Alonso C (2001) On-site measurement of corrosion rate of reinforcement. *Construction and Building Materials* 15:141-145.
32. YuanY, Ji Y and Shah SP (2007) Comparison of two accelerated corrosion techniques for concrete structures. *ACI Structural Journal* 104 (3):344–347.
33. Austin SA, Lyons R and Ing MJ (2004) Electrochemical behavior of steel-reinforced concrete during accelerated corrosion testing. *Corrosion* 60 (2): 203–212.

34. RILEM TC 154-EMC. 2004. Electrochemical Technique for Measuring Metallic Corrosion. Recommendations. Test method for on-site corrosion rate measurement of steel reinforcement in concrete by means of the polarization resistance method. *Materials and Structures* 37: 623-643.
35. Japan Society of Civil Engineers (JSCE), (2012) Standard specifications for concrete structures.
36. American Concrete Institute ACI 224R-01., (2001) Control of cracking in concrete structures.
37. Mehta PK (2004) High performance, high volume fly ash concrete for sustainable development. In Wand, K., Eds. International Workshop on Sustainable Development and Concrete Technology, 20-21 May, Beijing, China. Iowa: Iowa State University, 3-14.
38. Zafar I and Sugiyama T (2014a) Laboratory Investigation to study the corrosion initiation of rebars in fly ash concrete. *Magazine of Concrete Research*, 66(20): 1051-1064.
39. Sahmaran M, Keskin BS, Ozerkan G and Yaman IO (2008) Self-healing of mechanically- loaded self-consolidating concretes with high volumes of fly ash. *Cement and Concrete Composites*, 30: 872-879.
40. Na HS, Hama Y, Taniguchi M, Sagawa T and Zakaria M (2012) Experimental investigation on reaction rate and self-healing ability in fly ash blended cement mixtures. *Journal of Advanced Concrete Technology* 10: 240-253.
41. Aldea CM, Shah SP and Karr A (1999) Effect of cracking on water and chloride permeability of concrete. *Journal of Materials and Civil Engineering*, 181-197.
42. Djerbi A, Bonnet S, Khelidj A and Baroghel V (2008) Influence of traversing crack on chloride diffusion into concrete. *Cement and Concrete Research*, 38: 877-883.
43. Kato E, Kato Y and Uomoto T (2005) Development of simulation model of chloride ion transportation in crack concrete. *Journal of Advanced Concrete Technology*, 3(1): 85-94.
44. Scott A and Alexander M (2007) The influence of binder type, cracking and cover on corrosion rates of steel in chloride-contaminated concrete. *Magazine of Concrete Research*, 59(7): 495-505.
45. Miyazato S and Otsuki N (2010) Steel corrosion induced by chloride or carbonation in mortar with bending cracks or joints. *Journal of Advanced Concrete Technology* 8(2): 133-144.
46. Blaaoievic A, Fennis S and Walraven J (2012) Impact of cracks on chloride-induced corrosion and durability of reinforced concrete structures - a literature review. *Proceeding of V International PhD Student Workshop on Durability of Reinforced Concrete, 9-10 February Espoo, Finland. Finland: VTT Technical Research Centre of Finland Publishers*, 80-91.
47. Yokota M (1998) Study on corrosion monitoring of reinforcing steel bars in 36-year old actual concrete structures, Translation from proceedings of JCI 20, Concrete library of JSCE (1999) 33: 155-164.

48. Yokota M, Yoshida M, Miyuki H et al. (1996) Corrosion monitoring of steel rebars in concrete structures by AC impedance method. *Sumitomo Metal*, 48(2): 30-38 (In Japanese).
49. Japanese Industrial Standards (2003) JIS A 1154:472-482 Methods of test for chloride ion content in hardened concrete, Japan. (In Japanese).
50. Japanese Concrete Institute JCI SC1. (2004) "Corrosion evaluation method of steel in concrete." (In Japanese).
51. Promentilla MAB and Sugiyama T (2010) X-ray micro tomography of mortars exposed to freezing-thawing action. *Journal of Advanced Concrete Technology*, 8(2): 97-111.
52. Bamforth PB, Price WF, Emerson M (1997) An international review of chloride ingress into structural concrete. *Taywood Engineering Limited*, 1-162.
53. Glass GK, Page CL, Short NR (1991) Factors affecting the corrosion rate of steel in carbonated mortars. *Corrosion Science* 32 (12): 1283-1294.
54. Poulsen SL (2009) Methodologies for measuring the degree of reaction in Portland cement blends with supplementary cementitious materials by ²⁹Si and ²⁷Al MAS NMR spectroscopy. *PhD Thesis, Aarhus University*, pp. 1-147.
55. Page CL (1975) Mechanism of corrosion protection in reinforced concrete marine structures. *Nature* 258 (5535): 514-515.
56. Glass GK (2006) Engineering the chemistry at the steel –concrete interface to enhance concrete durability. *Magazine of Concrete Research* 58 (10): 645-646.
57. Angst U (2009) Critical chloride content in reinforced concrete – A review. *Cement and Concrete Research* 39: 1122-1138.
58. Page CL (2009) Initiation of chloride-induced corrosion of steel in concrete: role of the interfacial zone. *Materials and Corrosion* 60, No: 9999.
59. Glass GK, Reddy B, Clark LA (2007) Making reinforced concrete immune from chloride corrosion. *Proceeding of ICE- Construction Materials* 160 (4): 155-164.
60. Mohammad TU, Otsuki N, Hamada H et al. (1999) Chloride-induced corrosion of steel bars in concrete with presence of gap at steel-concrete interface. *ACI material Journal* 99 (2): 1270-1276.
61. Ryan PC, O' Connor AJ (2011) Probabilistic modelling of marine bridge deterioration. *World Academy of Science, Engineering and Technology* 60: 876-882.
62. Page CL & Havdahl J (1985) Electrochemical monitoring of corrosion of steel in micro silica cement pastes. *Materials and Structures* 18(1): 41-47.
63. Evans UR (1960) *The corrosion and oxidation of metals*: 875-876. London: Edward Arnold Ltd.
64. Fontana M. & Greene ND (2nd edition, 1978) *Corrosion Engineering*: 309. Tokyo: McGraw- Hill International Book Company.
65. Xu J, Jiang L & Wang Q (2009) Finite element model of reinforcement corrosion in concrete. *Water Science and Engineering* 2(2): 71-78.
66. Busba E & Sagüés AA (2013) Critical Localized Corrosion Penetration of Steel Reinforcement for Concrete Cover Cracking. *NACE conference and Expo 2013*, Paper No.2747 (access online).

<http://www.eng.usf.edu/~sagues/Documents/Nace%2013%202747%20Critical%20Local%20Corr%20Penetr%20Crack.pdf>

67. Herholdt AD & Justesen, CFP (1985) *Beton-Bogen (The Concrete Book - in Danish)*. Denmark: Aalborg Portland Co.
68. Japan Concrete Institute, JCI. (2009) Technical committee reports on autogenous healing in cementitious materials. Tokyo (in Japanese).
69. Bentur A, Berke N and Diamond S (1997) *Steel Corrosion in Concrete: Fundamentals and civil engineering practice*. London: E and F.N. Spon.
70. Otsuki N, Odchimar A and Saito T (2012) Influence of the ions in pore solution and around the steel bar on corrosion of steel in BFS and FA mortars. *Journal of the Society of Materials Science, Japan*, 61(8): 736-741.
71. Tittarelli F and Moriconi G (2002) The effect of fly ash and recycle aggregate on the corrosion resistance of steel in cracked reinforced concrete. *Proceeding of 9th International Conference on Durability of Building Materials and Components (9DBMC), 17-21 Mar, Brisbane, Australia. In-house publishing Rotterdam, Netherlands, Paper 70*.
72. Ahmed SFU, Maalej M., Paramasivam P and Mihashi H (2006) Assessment of corrosion-induced damage and its effect on the structural behaviour of RC beams containing supplementary cementitious materials. *Progress in the Structural Engineering and Materials*, 8 (1): 69-77.