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Effect of Some Synergic Corrosion Inhibitors on Reinforced Concrete and Their Activity

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By

*Mohammed Salah Nasr
Al-Ammar*

Under Supervision of

Asst.Prof.Dr. Mahdi S. Essa Asst.Prof.Dr. Falah K. Matlob

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من قبل
محمد صلاح نصر العمار

بإشراف
أ.م.د. مهدي صالح عيسى أ.م.د. فلاح كفي مطلوب

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ
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أَنْ تَنْفُذُوا مِنْ أَقْطَارِ السَّمَوَاتِ
وَالْأَرْضِ فَأَنْفُذُوا لَا تُنْفِذُونَ إِلَّا بِسُلْطَانٍ
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أولاً: المعلومات الشخصية

الاسم الثلاثي واللقب: محمد صلاح نصر العمار

محل وتاريخ الولادة: بابل - 1984

عنوان السكن: حلة - حي شبر

الحالة الاجتماعية: اعزب

الجنسية: عراقي

الايمل: msn_alar@yaho.com

ثانياً: الشهادات العلمية

1- بكالوريوس هندسة مدنية/ كلية الهندسة/ جامعة بابل - 2006.

2- ماجستير هندسة مدنية- تخصص: هندسة مواد إنشائية/ كلية الهندسة/ جامعة بابل - 2009.

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"Effect of Some Synergic Corrosion Inhibitors on Reinforced Concrete and Their Activity"

أسماء المشرفين:

1- أ. م. د. مهدي صالح عيسى/ كلية الهندسة/ جامعة بابل.

2- أ. م. د. فلاح كفي مطلوب/ كلية الهندسة/ جامعة بابل.

تاريخ المناقشة: 8 / 10 / 2009.

اعضاء لجنة المناقشة:

1- أ. م. د. محمد مصلح سلمان/ كلية الهندسة /الجامعة المستنصرية - رئيساً.

2- أ. م. د. غالب محسن حبيب/ كلية الهندسة/ جامعة بابل - عضواً.

3- أ. م. د. سامر عبد الامير المشهدي/ كلية الهندسة/ جامعة بابل - عضواً.

4- أ. م. د. مهدي صالح عيسى/ كلية الهندسة/ جامعة بابل - عضواً ومشرفاً.

5- أ. م. د. فلاح كفي مطلوب/ كلية الهندسة/ جامعة بابل - عضواً ومشرفاً.

CERTIFICATE OF THE EXAMINING COMMITTEE

We certify as an Examining Committee that we have read this thesis titled “*Effect of Some Synergic Corrosion Inhibitors on Reinforced Concrete and Their Activity*” and examined the student “*Mohammed Salah Nasr Al-Ammar*” in its content and what related to it, and found it meets the standard of thesis for the degree of Master of science in Civil Engineering (Construction Materials).

Signature:

Name: **Asst.Prof. Dr. Mahdi S. Essa**

(Supervisor)

Date: / /2009

Signature:

Name: **Asst.Prof. Dr. Falah K. Matloub**

(Supervisor)

Date: / /2009

Signature:

Name: **Asst.Prof. Dr. Ghalib M. Habeeb**

(Member)

Date: / /2009

Signature:

Name: **Asst.Prof. Samir A. Al-Mashhadi**

(Member)

Date: / /2009

Signature:

Name: **Prof. Dr. Mohammed M. Salman**

(Chairman)

Date: / /2009

Approved by the Head of the Civil Engineering Department

Signature:

Name: **Prof. Dr. Ammar Y. Ali**

(The Head of the Civil Engineering Department)

Date: / /2009

Approved by the Dean of the College of Engineering

Signature:

Name: **Asst.Prof. Dr. Salah T. Al-Bazzaz**

(The Dean of the College of Engineering)

Date: / /2009

الخلاصة

تم في هذه الدراسة استخدام طريقة الاستقطاب الخطي ثلاثية الاقطاب لبيان كفاءة ثلاث مضافات ثنائية على عملية تآكل حديد التسليح في الخرسانة من خلال قياس تيار التآكل والمقاومة الكهربائية. كذلك تم اجراء فحص مقاومة الانضغاط، فحص مقاومة الشد، فحص تركيز الكلوريدات وفحص الامتصاص لمعرفة تأثير تلك المضافات المثبطة على بعض خصائص الخرسانة.

تم صب 99 مكعب (150) ملم لفحص مقاومة الانضغاط وفحصت عند 60, 28 و 90 يوم. وتم صب 33 اسطوانة (200×100) ملم لفحص مقاومة الشد. تم صب 33 مكعب (100) ملم لفحص الامتصاص. كما تم صب 33 موشور (200×150×140) ملم للفحوصات الكهرو كيميائية. تم صب تلك العينات بنسب خلط (1:1.8:2.5) ونسبة ماء/اسمنت تساوي 0.5. تم انضاج جميع العينات في ماء الاسالة.

تم صب احدى عشرة خلطة لهذه الدراسة: خلطتان مرجعيتان وثلاث خلطات لكل مجموعة ثنائية. الثنائي الاول هو (نترات الكالسيوم + ايثانول امين) وتم استخدامه بثلاث تراكيز: $(0.2B_{CN} + 0.8B_{EA})$, $(0.5B_{CN} + 0.5B_{EA})$ و $(0.8B_{CN} + 0.2B_{EA})$. الثنائي الثاني هو (بنزوات الصوديوم + سليكات الصوديوم) وتم استخدامه بثلاثة تراكيز: $(0.8B_{SB} + 0.2B_{SS})$, $(0.5B_{SB} + 0.5B_{SS})$ و $(0.2B_{SB} + 0.8B_{SS})$. الثنائي الثالث هو (دايكرومات البوتاسيوم + ستايرين-بيوتادين-مطاط) وتم استخدامه بثلاث تراكيز: $(0.2B_{PD} + 0.8B_{SBR})$, $(0.5B_{SBR} + 0.5B_{PD})$ و $(0.8B_{PD} + 0.2B_{SBR})$. حيث ان الحرف "B" يمثل التركيز الافضل لاضافة كل مثبط.

تم غمر النماذج جزئياً في محلول 3.5% كلوريد الصوديوم لمدة ثلاثة اشهر وتم فحصها كل اسبوعين خلال تلك المدة. بعد ستة اسابيع من التعرض تبين حصول تآكل قليل في النماذج وذلك بسبب التطور البطيء لعملية التآكل. لذا، تم عمل شقوق دقيقة في النماذج المسلحة لتسريع عملية التآكل وذلك بتحميل اثنان من الثلاث نماذج المسلحة لكل خلطة 10% من حمل مقاومة الانضغاط.

اظهرت نتائج فحص الانضغاط بأن جميع الخلطات التي تحتوي على المضافات المثبطة قد قللت مقاومة الانضغاط مقارنة بالخلطة المرجعية. وقد كانت للخلطة $(0.5B_{SBR} + 0.5B_{PD})$ اقل مقاومة بتقليل مقداره 30%، 33.3% و 34.3% في الاعمار 28, 60 و 90 يوم

على التوالي. لكن، تم الحصول على اقل تقليل بالمقاومة في الخلطة ($0.2B_{SBR} + 0.8B_{PD}$) بتقليل مقداره 11.3%، 15% و 16.4% في 28، 60 و 90 يوم على التوالي.

اظهرت نتائج فحص مقاومة الشد نقصاناً واضحاً في مقاومة الشد في جميع الخلطات التي تحتوي على مضافات مثبطة مقارنةً بالخلطة المرجعية. كما اظهرت نتائج فحص الامتصاص زيادةً في الامتصاص في جميع الخلطات الحاوية على مثبطات ماعدا خلطة ($0.8B_{EA} + 0.2B_{CN}$)، حيث اعطت اقل امتصاص، مساوياً للخلطة المرجعية.

بينت نتائج نسبة التاكل للخلطات التي تحتوي على شقوق دقيقة، بعد ثلاثة اشهر من التعرض، بوجود كبح جيد للتاكل في كل مجموعة ثنائية. حيث ان كفاءة ($0.5B_{EA} + 0.5B_{CN}$) حوالي 82%، كفاءة الخلطة ($0.5B_{SB} + 0.5B_{SS}$) حوالي 84% و كفاءة الخلطة ($0.2B_{SBR} + 0.8B_{PD}$) حوالي 85%. بينما اظهرت النماذج التي لا تحتوي على شقوق دقيقة تاثير عكسي على عملية التاكل (زادت من نسبة التاكل). اظهرت نتائج فحص المقاومة الكهربائية للخرسانة بان المقاومة الكهربائية قد قلت لاغلب الخلطات مع استمرار زمن التعرض لمحلول كلوريد الصوديوم.

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Abstract

Three Electrodes Linear Polarization method is used in this investigation to show the effectiveness of three synergic admixtures on the corrosion process of steel in concrete by measuring the corrosion current and electrical resistivity. Compressive strength test, splitting tensile strength test, chloride concentration test and absorption test have also performed to know the influence of these inhibiting admixtures on some properties of concrete.

For compressive strength test, 99 cubes (150) mm were cast and tested at 28, 60 and 90 ages. And 33 cylinders (200*100) mm were cast for splitting tensile strength test. 33 cubes (100) mm were cast for absorption test. For electrochemical tests 33 reinforced concrete prisms (140*150*200) mm were cast. These samples were cast with mix proportions (by weight) 1:1.8:2.5 (cement: sand: gravel) and w/c ratio equal to 0.5. All specimens were cured in tap water.

Eleven mixes have been cast for the study: two reference mixes and three mixes for each synergic group. The first synergic is (Calcium Nitrate + Ethanolamine) and used in three percentages: $(0.2B_{CN} + 0.8B_{EA})$, $(0.5B_{CN} + 0.5B_{EA})$ and $(0.8B_{CN} + 0.2B_{EA})$. The second synergic is (Sodium Benzoate + Sodium Silicate) and also used in three percentages: $(0.8B_{SB} + 0.2B_{SS})$, $(0.5B_{SB} + 0.5B_{SS})$ and $(0.2B_{SB} + 0.8B_{SS})$. The third synergic is (Potassium Dichromate + Styrene Butadiene Rubber) and used in the same three percentages: $(0.2B_{PD} + 0.8B_{SBR})$, $(0.5B_{PD} + 0.5B_{SBR})$, $(0.8B_{PD} + 0.2B_{SBR})$. Where, the letter "B" represents the best concentration of adding each admixture.

The reinforced concrete specimens were partially immersed in 3.5% NaCl solution for three months and tested within this period every two weeks. After six weeks of exposure, it is demonstrated that low corrosion

was recorded in the specimens because of the slowly development of corrosion process. Hence, microcracks were initiated in the reinforced concrete specimens to accelerate the corrosion process by loading two of the three reinforced specimens for each mix with 10% of the concrete compressive strength.

Compressive strength results showed that the mixes which contained inhibiting admixtures have an obvious reduction in compressive strength in comparison with reference mix. Lowest compressive strength is obtained in $(0.5B_{SBR} + 0.5B_{PD})$ mix with minimizing about 30%, 33.3% and 34.3% at ages 28, 60 and 90 days respectively. However, lower decrease in compressive strength has occurred in $(0.2B_{SBR} + 0.8B_{PD})$ mix with reduction about 11.3%, 15% and 16.4% at 28, 60 and 90 days sequently.

Results of splitting tensile strength test showed a clear reduction in the mixes which contain corrosion inhibiting admixtures relative to the control mix. Absorption test results showed an increase in the mixes which contain inhibitors except $(0.8B_{EA} + 0.2B_{CN})$ mix which has lower absorption, that's equal to the reference mix.

Corrosion rate results indicated that, after three months of exposure, for precracked specimens, there is a good corrosion inhibition in each synergic group. Where, the efficiency of $(0.5B_{EA} + 0.5B_{CN})$, $(0.5B_{SB} + 0.5B_{SS})$ and $(0.2B_{SBR} + 0.8B_{PD})$ mixes are about 82%, 84% and 85% respectively. While, non-precracked samples showed opposite action on corrosion process (increased corrosion rate). Concrete electrical resistance results showed that most mixes exhibit a decrease in electrical resistance with time of exposure to sodium chloride solution.

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NOTATIONS AND ABBREVIATIONS

Symbol	Definition
AAP	4-aminoantipyrine
AC	Alternative current
Amp.	Ampere (current unit)
B _{CN}	The best concentration of adding Calcium Nitrate = 2% by weight of cement.
B _{EA}	The best concentration of adding Ethanolamine = 2% by weight of cement
B _{PD}	The best concentration of adding Potassium Dichromate = 2% by weight of cement.
B _{SB}	The best concentration of adding Sodium Benzoate = 2% by weight of cement.
B _{SBR}	The best concentration of adding Styrene Butadiene Rubber = 25% by volume of water.
B _{SS}	The best concentration of adding Sodium Silicate = 1% by weight of cement.
CI	Commercial inhibitor
CN	Calcium Nitrate (corrosion inhibitor)
Conc.	Concentration
C.R	Corrosion rate
CW1	Ethylene copolymer
CW2	Acrylic resin
C1	Sodium silicate
C2	Resin
C3	Wax emulsion
C4	White resin
D.C	Direct Current
EA	Ethanolamine (corrosion inhibitor)
ECE	Electrochemical chloride extraction
EIS	Electrochemical impedance spectroscopy
E _{pit}	Pitting potential
E, ΔE, V	Potential (voltage)
FM	Fineness modulus
GGBS	Ground granulate blast-furnace slag
HPC	High performance concrete
HRWA	High Range Water – Reducing Admixture

$I_{\text{corr.}}$	Corrosion current
$I_{\text{corr. av.}}$	The average of corrosion current
Δi	Current
k. Ohm	Kilo ohm (resistance unit)
LPR	Linear polarization technique
M	Mole
MCI	Migrating Corrosion Inhibitor
MFP	Monofluorophosphate
OCI, CNI	Organic corrosion inhibitor
OPC	Ordinary Portland cement
PD	Potassium Dichromate (corrosion inhibitor)
PFA	Pulverized fuel ash
RCPT	Rapid chloride penetration test
Ref.	Reference
RHA	Rice husk ash
R_p , RP, PR	Polarization resistance
SB	Sodium Benzoate (corrosion inhibitor)
SBR	Styrene –Butadiene-Rubber
SCC	self-compacting concrete
SEM	Scanning electron microscope
SPABS	4-(phenylamino) benzenesulfonate
SS	Sodium Silicate (corrosion inhibitor)
$w_{\text{IE}} \%$	Inhibition efficiency
w/c	Water / cement Ratio

Chapter One

Introduction

Chapter Two

Literature Review

Chapter Three

Experimental Work

Chapter Four

Results and Discussions

Chapter Five

Conclusions and Recommendations

Appendix 1

Appendix 2

References

**Corrosion rate values * 10^{-9} (kg/sec. m²) of non-precracked specimens
before and within three months of exposure to 3.5% NaCl solution.**

Mix \ age	0-week	2-weeks	4-weeks	6-weeks	8-weeks	10-weeks	12-weeks
Reference	5.224	58.923	157.695	766.687	333.051	49.506	1048.529
0.2B_{PD} + 0.8B_{SBR}	150.110	119.037	529.593	4721.118	2431.206	704.710	639.367
0.5B_{PD} + 0.5B_{SBR}	2.484	317.401	12529.015	2228.126	3725.594	4273.518	651.409
0.8B_{PD} + 0.2B_{SBR}	37.101	52.448	1805.947	1800.232	421.114	960.089	704.249
0.8B_{CN} + 0.2B_{EA}	373.176	2452.870	1253.973	1217.798	984.869	1736	1694.193
0.5B_{CN} + 0.5B_{EA}	70.147	1664.983	1373.705	2196.758	2112.532	546.670	2466.790
0.2B_{CN} + 0.8B_{EA}	107.794	122.385	49.753	2015.463	835.178	2860.286	1861.705
0.8B_{SB} + 0.2B_{SS}	8.492	17.978	10.402	2284.876	380.327	4455.522	3924.540
0.5B_{SB} + 0.5B_{SS}	6.806	73.827	252.784	307.002	167.098	1167.714	1557.328
0.2B_{SB} + 0.8B_{SS}	12.198	739.005	909.151	719.014	1217.741	1358.698	2705.038

**Corrosion rate values * 10^{-9} (kg/sec. m²) of precracked specimens before
and within three months of exposure to 3.5% NaCl solution.**

Mix \ age	0-week	2-weeks	4-weeks	6-weeks	8-weeks	10-weeks	12-weeks
Reference	49.150	1780.061	1417.806	676.815	5554.663	6843.098	8079.833
0.2B_{PD} + 0.8B_{SBR}	49.505	337.963	1192.357	1354.157	2219.126	2776.990	2487.026
0.5B_{PD} + 0.5B_{SBR}	14.4190	277.295	1314.468	500.362	1886.317	5073.765	4680.101
0.8B_{PD} + 0.2B_{SBR}	154.815	628.793	1318.715	262.890	519.048	1368.877	1244.131
0.8B_{CN} + 0.2B_{EA}	31.424	506.915	2119.467	1520.313	1007.442	4116.040	1922.852
0.5B_{CN} + 0.5B_{EA}	141.473	389.421	347.646	606.274	718.350	1071.707	1424.354
0.2B_{CN} + 0.8B_{EA}	286.280	320.787	723.608	416.698	545.830	1112.923	2149.381
0.8B_{SB} + 0.2B_{SS}	55.108	19.0241	1831.906	1039.420	1641.942	1874.725	1622.907
0.5B_{SB} + 0.5B_{SS}	7.384	263.814	217.5114	2231.589	924.614	1921.694	1291.406
0.2B_{SB} + 0.8B_{SS}	120.520	364.438	498.716	2833.605	2097.568	1873.342	2352.912

**Resistivity values (k.Ohm) of non-precracked specimens for three months
of exposure to 3.5% NaCl solution.**

Mix \ age	2-weeks	4-weeks	6-weeks	8-weeks	10-weeks	12-weeks
Reference	81.2	62.2	112.7	49.2	109.4	86.1
0.2B_{PD} + 0.8B_{SBR}	92.7	44.2	22.4	10.2	16.3	9.6
0.5B_{PD} + 0.5B_{SBR}	10.7	131.6	7.9	45.3	2.5	33.4
0.8B_{PD} + 0.2B_{SBR}	146.8	43	95.5	32.8	20.3	31.2
0.8B_{CN} + 0.2B_{EA}	40.2	71.8	12.5	56.2	25.7	38.1
0.5B_{CN} + 0.5B_{EA}	3.5	32.1	25	8.2	10.3	19.9
0.2B_{CN} + 0.8B_{EA}	205.5	72.5	41	8.8	57.5	50
0.8B_{SB} + 0.2B_{SS}	113.4	115.9	68.3	22.3	76.6	120.6
0.5B_{SB} + 0.5B_{SS}	94.8	12.1	13	13	37.9	68.9
0.2B_{SB} + 0.8B_{SS}	26.1	20.4	122.4	56.9	40.7	112.9

**Resistivity values (k.Ohm) of precracked specimens for three months of
exposure to 3.5% NaCl solution.**

Mix \ age	2-weeks	4-weeks	6-weeks	8-weeks	10-weeks	12-weeks
Reference	134.3	251.45	281.85	46.55	69	72.9
0.2B_{PD} + 0.8B_{SBR}	172.3	18.35	24.1	9.1	34.4	28.6
0.5B_{PD} + 0.5B_{SBR}	123.75	15.1	29.1	32.95	65.75	75.5
0.8B_{PD} + 0.2B_{SBR}	91	75.65	86.85	92.55	86.6	77.35
0.8B_{CN} + 0.2B_{EA}	42.95	22.05	14.8	24.05	20.65	72.55
0.5B_{CN} + 0.5B_{EA}	155.4	172.25	54.85	40.25	29.85	15.2
0.2B_{CN} + 0.8B_{EA}	140.3	42.6	104.4	59.75	51.85	28.1
0.8B_{SB} + 0.2B_{SS}	79.35	357.45	31.1	37.45	27.2	43.75
0.5B_{SB} + 0.5B_{SS}	86.5	45.05	108.15	56.5	40.8	37.85
0.2B_{SB} + 0.8B_{SS}	138.85	90.35	127.05	74.8	113.9	95.35

Corrosion program

This program is made by Visual Basic Language to Calculate Corrosion Current, Corrosion Rate and Polarization Resistance.

```
Private Sub Command1_Click()
```

```
Dim controlmixwithoutcrack (6, 5), controlmixwithcrack (6, 5),  
mixsixwithoutcrack (6, 5), mixesixwithcrack (6, 5), mixfivewithoutcrack  
(6, 5), mixfivewithcrack (6, 5), mixfourwithoutcrack (6, 5),  
mixfourwithcrack (6, 5), mixthreewithoutcrack (6, 5), mixthreewithcrack  
(6, 5), mixsevenwithoutcrack (6, 5), mixsevenwithcrack (6, 5),  
mixeightwithoutcrack (6, 5), mixeightwithcrack (6, 5),  
mixninewithoutcrack (6, 5), mixninewithcrack (6, 5), mixtenwithoutcrack  
(6, 5), mixtenwithcrack (6, 5), mixelevenwithoutcrack (6, 5),  
mixelevenwithcrack (6, 5)
```

```
If Option2.Value = True Then
```

```
Open "control mix without crack.dat" For Input As 1
```

```
Open "mix three without crack.dat" For Input As 2
```

```
Open "mix four without crack.dat" For Input As 3
```

```
Open "mix eleven without crack.dat" For Input As 4
```

```
Open "mix seven without crack.dat" For Input As 5
```

```
Open "mix six without crack.dat" For Input As 6
```

```
Open "mix five without crack.dat" For Input As 7
```

```
Open "mix eight without crack.dat" For Input As 8
```

```
Open "mix nine without crack.dat" For Input As 9
```

```
Open "mix ten without crack.dat" For Input As 10
```

```
For i = 0 To 6
```

```
For j = 0 To 5
```

```
Input #1, controlmixwithoutcrack(i, j)
```

```
Input #2, mixthreewithoutcrack(i, j)
```

```

Input #3, mixfourwithoutcrack(i, j)
Input #4, mixelevenwithoutcrack(i, j)
Input #5, mixsevenwithoutcrack(i, j)
Input #6, mixsixwithoutcrack(i, j)
Input #7, mixfivewithoutcrack(i, j)
Input #8, mixeightwithoutcrack(i, j)
Input #9, mixninemwithoutcrack(i, j)
Input #10, mixtenwithoutcrack(i, j)
Next j
Next i
End If
If Option3.Value = True Then
Open "control mix with crack.dat" For Input As 1
Open "mix three with crack.dat" For Input As 2
Open "mix four with crack.dat" For Input As 3
Open "mix eleven with crack.dat" For Input As 4
Open "mix seven with crack.dat" For Input As 5
Open "mix six with crack.dat" For Input As 6
Open "mix five with crack.dat" For Input As 7
Open "mix eight with crack.dat" For Input As 8
Open "mix nine with crack.dat" For Input As 9
Open "mix ten with crack.dat" For Input As 10
For i = 0 To 6
For j = 0 To 5
Input #1, controlmixwithcrack(i, j)
Input #2, mixthreewithcrack(i, j)
Input #3, mixfourwithcrack(i, j)
Input #4, mixelevenwithcrack(i, j)
Input #5, mixsevenwithcrack(i, j)

```

```

Input #6, mixsixwithcrack(i, j)
Input #7, mixfivewithcrack(i, j)
Input #8, mixeightwithcrack(i, j)
Input #9, mixninewithcrack(i, j)
Input #10, mixtenwithcrack(i, j)
Next j
Next i
End If
For i = 0 To 6
For j = 0 To 5
If Option2.Value = True Then
If Option1(0).Value = True Then mixtype = controlmixwithoutcrack(i, j)
If Option1(1).Value = True Then mixtype = mixthreewithoutcrack(i, j)
If Option1(2).Value = True Then mixtype = mixfourwithoutcrack(i, j)
If Option1(3).Value = True Then mixtype = mixelevenwithoutcrack(i, j)
If Option1(4).Value = True Then mixtype = mixsevenwithoutcrack(i, j)
If Option1(5).Value = True Then mixtype = mixsixwithoutcrack(i, j)
If Option1(6).Value = True Then mixtype = mixfivewithoutcrack(i, j)
If Option1(7).Value = True Then mixtype = mixeightwithoutcrack(i, j)
If Option1(8).Value = True Then mixtype = mixninewithoutcrack(i, j)
If Option1(9).Value = True Then mixtype = mixtenwithoutcrack(i, j)
End If
If Option3.Value = True Then
If Option1(0).Value = True Then mixtype = controlmixwithcrack(i, j)
If Option1(1).Value = True Then mixtype = mixthreewithcrack(i, j)
If Option1(2).Value = True Then mixtype = mixfourwithcrack(i, j)
If Option1(3).Value = True Then mixtype = mixelevenwithcrack(i, j)
If Option1(4).Value = True Then mixtype = mixsevenwithcrack(i, j)
If Option1(5).Value = True Then mixtype = mixsixwithcrack(i, j)

```

```

If Option1(6).Value = True Then mixtype = mixfivewithcrack(i, j)
If Option1(7).Value = True Then mixtype = mixeightwithcrack(i, j)
If Option1(8).Value = True Then mixtype = mixninewithcrack(i, j)
If Option1(9).Value = True Then mixtype = mixtenwithcrack(i, j)
End If

If j = 0 Then I6 = mixtype
If j = 2 Then I4 = mixtype
If j = 1 Then I5 = mixtype
If j = 3 Then I1 = mixtype
If j = 4 Then I2 = mixtype
If j = 5 Then I3 = mixtype
Next j

r1 = I3 / I1
r2 = I1 / I4
r3 = I1 / I4
r4 = I6 / I4

Icorr1 = I1 / (r1 + 4 * r2) ^ 0.5
Icorr2 = I1 / ((r4 * r3) ^ 2 + 4 * r3) ^ 0.5
Icorravg = (Icorr1 + Icorr2) / 2
Icorr = Icorravg / 1000
Text1(i) = Icorr

V1 = 60
V3 = 120
V2 = 90
M1 = V3 / V1
M2 = V2 / V1

PR1 = (2 * M1 * (M1 ^ 2 - 1) * V1) / (2 * M1 ^ 2 * (I1 + I4) - (I3 + I6))
PR2 = (2 * M2 * (M2 ^ 2 - 1) * V1) / (2 * M2 ^ 2 * (I1 + I4) - (I2 + I5))
Text2(i) = Abs(PR1)

```

Text3(i) = Abs(PR2)

CR = Icorr * 0.11455

Text4(i) = CR

Next i

Close #10

Close #9

Close #8

Close #7

Close #6

Close #5

Close #4

Close #3

Close #2

Close #1

End Sub

Note:

Rows of the data below represent the ages of test (for three months, every two weeks). And the columns represent the voltage (in miliVolt.) at which the corrosion current (in mili Amp.) is measured.

Data in files:

- Data in "control mix without crack.dat" file → Reference without crack

	-120	-90	-60	60	90	120
0 weeks	0.009	0.0006	0.0002	0.0004	0.0015	0.0053
2 weeks	0.0116	0.0032	0.0028	0.0009	0.0005	0.0016
4 weeks	0.0199	0.0064	0.0077	0.0015	0.0004	0.0009
6 weeks	0.021	0.0148	0.0107	0.0334	0.054	0.0794
8 weeks	0.0199	0.0113	0.0053	0.0171	0.0203	0.0305
10 weeks	0.0142	0.0066	0.0001	0.0299	0.0471	0.0758
12 weeks	0.0687	0.0475	0.0337	0.0182	0.0331	0.0462

- Data in "control mix with crack.dat" file → Reference with crack

0.00615	0.00385	0.00225	0.00085	0.00225	0.0044
0.0258	0.02245	0.0243	0.05385	0.0685	0.07015
0.0187	0.0111	0.01525	0.0644	0.04805	0.09715
0.0377	0.0175	0.0099	0.03775	0.044	0.04535
0.16695	0.12045	0.10525	0.1299	0.1223	0.1356
0.2077	0.1548	0.14445	0.13335	0.11045	0.11695
0.2438	0.19735	0.1598	0.17325	0.12855	0.15075

- Data in "mix three without crack.dat" file → $0.2B_{PD}+0.8B_{SBR}$ without crack

0.0066	0.0011	0.0095	0.0016	0.0006	0.0075
0.0081	0.0052	0.0027	0.0032	0.0025	0.0039
0.0253	0.0226	0.0233	0.0039	0.0028	0.0002
0.0057	0.0221	0.0392	0.1818	0.263	0.2499
0.0053	0.0054	0.0178	0.111	0.1485	0.1582
0.0216	0.0061	0.0044	0.1199	0.1337	0.1699
0.0384	0.017	0.0079	0.0492	0.0455	0.0776

- Data in "mix three with crack.dat" file → $0.2B_{PD}+0.8B_{SBR}$ with crack

0.00615	0.00415	0.0018	0.0013	0.0042	0.0081
0.01985	0.012	0.00665	0.01185	0.0146	0.0244
0.0262	0.0191	0.0149	0.05475	0.07535	0.0917
0.1103	0.06955	0.04825	0.0226	0.0312	0.05965
0.12435	0.08085	0.05595	0.0443	0.04345	0.056
0.13835	0.08755	0.04775	0.10625	0.09135	0.1213
0.146	0.08675	0.0501	0.08125	0.117	0.1432

- Data in "mix four without crack.dat" file → $0.5B_{PD}+0.5B_{SBR}$ without crack

0.0035	0.0017	0.0002	0.0002	0.0025	0.007
0.0007	0.0011	0.0022	0.0156	0.0225	0.0267
0.3554	0.2906	0.2849	0.2083	0.1631	0.1207
0.1826	0.165	0.151	0.0207	0.0194	0.0543
0.1944	0.1394	0.1001	0.0618	0.0544	0.0542
0.2029	0.1801	0.119	0.0743	0.1115	0.1377
0.2637	0.2345	0.1743	0.0027	0.0428	0.0595

- Data in "mix four with crack.dat" file $\rightarrow 0.5B_{PD}+0.5B_{SBR}$ with crack

0.00455	0.00185	0.0007	0.0006	0.0029	0.0076
0.0052	0.0042	0.0048	0.0073	0.01895	0.02425
0.06565	0.04315	0.03015	0.0295	0.02835	0.04115
0.05835	0.0392	0.0283	0.006	0.00665	0.0215
0.1052	0.0988	0.08365	0.0182	0.0175	0.014
0.2526	0.15225	0.1339	0.0894	0.06885	0.1101
0.20205	0.1225	0.1151	0.08965	0.10355	0.13785

- Data in "mix five without crack.dat" file $\rightarrow 0.8B_{CN}+0.2B_{EA}$ without crack

0.015	0.009	0.0079	0.0091	0.012	0.018
0.127	0.0753	0.0487	0.0741	0.0913	0.1085
0.1162	0.0668	0.011	0.1616	0.2066	0.2078
0.061	0.0337	0.0186	0.0593	0.0696	0.0691
0.161	0.1382	0.1132	0.0072	0.0047	0.0359
0.2111	0.1476	0.1118	0.0206	0.0644	0.119
0.1406	0.1181	0.0878	0.0207	0.0174	0.0745

- Data in "mix five with crack.dat" file $\rightarrow 0.8B_{CN}+0.2B_{EA}$ with crack

0.01005	0.00625	0.00165	0.0012	0.0104	0.01625
0.0398	0.03085	0.0263	0.00465	0.0008	0.00455
0.1124	0.0826	0.06705	0.0274	0.0184	0.0179
0.0608	0.03975	0.0303	0.04105	0.04725	0.08195
0.07395	0.0479	0.03325	0.0204	0.0436	0.09055
0.17945	0.15025	0.11945	0.0602	0.0368	0.06245
0.2373	0.16715	0.12195	0.02185	0.0531	0.09505

- Data in " mix six without crack.dat" file $\rightarrow 0.5B_{CN}+0.5B_{EA}$ without crack

0.0167	0.0105	0.0046	0.0013	0.0115	0.017
0.0629	0.0561	0.0501	0.0184	0.0083	0.0011
0.0831	0.0536	0.0337	0.029	0.0056	0.0302
0.1378	0.0888	0.061	0.043	0.0411	0.0821
0.1202	0.0837	0.0527	0.0453	0.0596	0.0744
0.1337	0.0838	0.0628	0.0049	0.0688	0.0894
0.1281	0.0778	0.0529	0.0624	0.0524	0.074

- Data in "mix six with crack.dat" file $\rightarrow 0.5B_{CN}+0.5B_{EA}$ with crack

0.00535	0.00325	0.00205	0.007	0.01225	0.0171
0.00905	0.0035	0.00365	0.03335	0.052	0.06415
0.0247	0.01295	0.0029	0.04635	0.0504	0.0697
0.0222	0.01075	0.0078	0.03585	0.04125	0.06425
0.0348	0.02225	0.0137	0.02365	0.0373	0.0478
0.0453	0.02905	0.0156	0.05445	0.07275	0.10355
0.0949	0.0687	0.05765	0.02085	0.05015	0.0739

- Data in "mix seven without crack.dat" file $\rightarrow 0.2B_{CN}+0.8B_{EA}$ without crack

0.0001	0.0009	0.0019	0.0025	0.0077	0.0117
0.0024	0	0.002	0.0033	0.0055	0.0069
0.0027	0.0004	0.0004	0.0067	0.0072	0.01
0.0035	0.0066	0.0155	0.0858	0.1391	0.1471
0.0777	0.0514	0.0425	0.0096	0.0206	0.0226
0.1932	0.1755	0.1165	0.024	0.0114	0.002
0.0937	0.0599	0.032	0.073	0.0673	0.0991

- Data in "mix seven with crack.dat" file $\rightarrow 0.2B_{CN}+0.8B_{EA}$ with crack

0.0091	0.00625	0.0052	0.0087	0.02015	0.0275
0.004	0.00245	0.00365	0.01325	0.02375	0.0354
0.06955	0.0275	0.01605	0.02365	0.0159	0.01785
0.02855	0.0137	0.0062	0.02495	0.0317	0.0357
0.0354	0.02145	0.0136	0.01265	0.0145	0.02125
0.087	0.04755	0.0319	0.02355	0.03	0.04815
0.12125	0.0799	0.05155	0.0468	0.03705	0.05865

- Data in "mix eight without crack.dat" file $\rightarrow 0.8B_{SB}+0.2B_{SS}$ without crack

0.0039	0.0022	0.001	0.0001	0.0018	0.0053
0.0032	0.0002	0.0002	0.0019	0.0028	0.0033
0.0029	0.001	0.0001	0.0013	0.0015	0.0016
0.0886	0.0672	0.0609	0.0333	0.0261	0.0189
0.0199	0.0166	0.0133	0.0036	0.0022	0.0001
0.1654	0.1317	0.1149	0.0676	0.0537	0.0418
0.1184	0.0978	0.1243	0.048	0.0381	0.0374

- Data in "mix eight with crack.dat" file $\rightarrow 0.8B_{SB}+0.2B_{SS}$ with crack

0.0131	0.00895	0.00515	0.00065	0.0042	0.0163
0.0053	0.00235	0.0002	0.00225	0.00405	0.00685
0.0029	0.0034	0.01535	0.0724	0.1423	0.18235
0.02785	0.0144	0.0112	0.07355	0.0959	0.14205
0.0989	0.0461	0.02795	0.07525	0.09775	0.13775
0.0938	0.0552	0.03485	0.0639	0.0709	0.1021
0.0609	0.031	0.0197	0.10655	0.109	0.1502

- Data in "mix nine without crack.dat" file $\rightarrow 0.5B_{SB}+0.5B_{SS}$ without crack

0.0047	0.0015	0.0004	0.0004	0.0021	0.0072
0.0045	0.0017	0.0008	0.0069	0.0066	0.0113
0.0033	0.0024	0.0024	0.0153	0.0233	0.0354
0.0204	0.0088	0.0057	0.0137	0.0202	0.0407
0.0447	0.0293	0.0214	0.0015	0.0121	0.096
0.0494	0.0306	0.0189	0.0466	0.0373	0.0651
0.0865	0.0557	0.0288	0.0566	0.0672	0.0832

- Data in "mix nine with crack.dat" file $\rightarrow 0.5B_{SB}+0.5B_{SS}$ with crack

0.0074	0.0041	0.00045	0.00045	0.0035	0.007
0.03455	0.01115	0.00285	0.028	0.03405	0.04845
0.02515	0.00685	0.00445	0.0103	0.0154	0.0236
0.04865	0.03985	0.02865	0.09565	0.10365	0.1476
0.0342	0.02745	0.0221	0.023785	0.037945	0.1569
0.0917	0.0568	0.0351	0.0664	0.10325	0.11285
0.1019	0.0454	0.0184	0.08645	0.0913	0.1152

- Data in "mix ten without crack.dat" file $\rightarrow 0.2B_{SB}+0.8B_{SS}$ without crack

0.0073	0.0046	0.0013	0.0002	0.0017	0.0045
0.022	0.0198	0.0191	0.0103	0.008	0.0041
0.0325	0.0279	0.0245	0.0137	0.0122	0.0131
0.0385	0.0181	0.0184	0.0114	0.0069	0.0023
0.0478	0.0414	0.0367	0.0146	0.0118	0.0047
0.0706	0.0494	0.0379	0.0185	0.0013	0.0036
0.0942	0.0826	0.0806	0.0346	0.0451	0.0219

- Data in "mix ten with crack.dat" file $\rightarrow 0.2B_{SB}+0.8B_{SS}$ with crack

0.00865	0.0056	0.00225	0.0054	0.01075	0.01375
0.0141	0.01235	0.00465	0.0235	0.0428	0.06735
0.03635	0.0068	0.0077	0.0295	0.0404	0.0553
0.0885	0.0744	0.06015	0.05595	0.0421	0.0546
0.0816	0.06385	0.0448	0.04295	0.0356	0.02845
0.14115	0.061	0.06885	0.02955	0.04675	0.0812
0.1335	0.0509	0.0331	0.1383	0.1088	0.1022

- Data in "mix eleven without crack.dat" file $\rightarrow 0.8B_{PD}+0.8B_{SBR}$ without crack

0.0066	0.004	0.0011	0.0015	0.0039	0.007
0.0038	0.0003	0.0004	0.0077	0.0065	0.0052
0.0831	0.0662	0.0579	0.0212	0.0179	0.0088
0.0905	0.069	0.0494	0.0253	0.0058	0.0066
0.0782	0.0409	0.0241	0.0061	0.0272	0.026
0.0647	0.0313	0.0155	0.0496	0.0499	0.068
0.1125	0.0562	0.0142	0.0372	0.0468	0.0749

- Data in "mix eleven with crack.dat" file $\rightarrow 0.8B_{PD}+0.2B_{SBR}$ with crack

0.00945	0.006	0.00265	0.0065	0.0062	0.00465
0.0577	0.02905	0.01485	0.01825	0.0166	0.018
0.0738	0.05045	0.035	0.0234	0.0257	0.0237
0.04605	0.03405	0.0227	0.00315	0.0194	0.0758
0.0486	0.01835	0.01295	0.0169	0.03375	0.0488
0.09935	0.0453	0.02405	0.06195	0.06905	0.0696
0.1286	0.0872	0.0469	0.0152	0.0128	0.0083

Program for Determining Corrosion Current "I_{corr}", Corrosion Rate "CR", and Polarization Resistance "PR1 & PR2"

Mix Type

☒ Reference ☐ 0.5B CN + 0.5B EA
☐ 0.2B PD + 0.8B SBR ☐ 0.8B CN + 0.2B EA
☐ 0.5B PD + 0.5B SBR ☐ 0.8B SB + 0.2B SS
☐ 0.8B PD + 0.2B SBR ☐ 0.5B SB + 0.5B SS
☐ 0.2B CN + 0.8B EA ☐ 0.2B SB + 0.8B SS

Cracking State

☒ Non-Precracked State
☐ Precracked State

Corrosion Rate

C.R. before immersed	5.22430673077309E-09	Kg/(sec.m ²)
C.R. after 2 weeks	5.89236986981672E-08	Kg/(sec.m ²)
C.R. after 4 weeks	1.57695998980636E-07	Kg/(sec.m ²)
C.R. after 6 weeks	7.66687540504884E-07	Kg/(sec.m ²)
C.R. after 8 weeks	3.33051802806922E-07	Kg/(sec.m ²)
C.R. after 10 weeks	4.95068027780645E-08	Kg/(sec.m ²)
C.R. after 12 weeks	1.04852982892866E-06	Kg/(sec.m ²)

Corrosion Current

I _{corr} before immersed	4.56072172044792E-08	Amp.
I _{corr} after 2 weeks	5.1439283018915E-07	Amp.
I _{corr} after 4 weeks	1.37665654545418E-06	Amp.
I _{corr} after 6 weeks	6.69303832828358E-06	Amp.
I _{corr} after 8 weeks	2.90747972768155E-06	Amp.
I _{corr} after 10 weeks	4.32185096255473E-07	Amp.
I _{corr} after 12 weeks	9.15346947995334E-06	Amp.

Polarization Resistance

PR1 before immersed	75789.4736842105	volt./Amp.
PR1 after 2 weeks	43902.4390243902	volt./Amp.
PR1 after 4 weeks	13636.3636363636	volt./Amp.
PR1 after 6 weeks	2852.61489698891	volt./Amp.
PR1 after 8 weeks	5590.0621180124	volt./Amp.
PR1 after 10 weeks	4800	volt./Amp.
PR1 after 12 weeks	2397.6023976024	volt./Amp.

Polarization Resistance

PR2 before immersed	375000	volt./Amp.
PR2 after 2 weeks	17307.6923076923	volt./Amp.
PR2 after 4 weeks	6502.8901734104	volt./Amp.
PR2 after 6 weeks	1736.11111111111	volt./Amp.
PR2 after 8 weeks	3251.4450867052	volt./Amp.
PR2 after 10 weeks	2767.52767527675	volt./Amp.
PR2 after 12 weeks	1470.58823529412	volt./Amp.

RUN **EXIT**

Picture shows the face of the program

Chapter One

Introduction

1.1 General

Reinforced concrete is a versatile, economical, and proven construction material. Able to be placed to a variety of shapes and finishes, it is durable and strong, performing well throughout its service life [1].

However, Corrosion of steel may occur if the concrete is not of adequate quality, the structure was not properly designed for the service environment, or the environment was not as anticipated or changes during the service life of the concrete [2].

High-quality reinforced concrete is obtained under the following conditions: correct cure times, correct positioning of the steel reinforcement, an appropriate water/cement ratio and the correct use of aggregate. If these conditions are met then corrosion of the reinforcing steel is generally negligible because the high pH value (12.5-13) in concrete renders the steel passive [3].

Corrosion of a metal (reinforcement) can be defined as a spontaneous process of returning metals to their natural state by oxidation reduction reactions [4]. In other words, corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment [5].

For corrosion to occur four basic elements are required:

1. Anode – site where corrosion occurs and current flows from.
2. Cathode – site where no corrosion occurs and current flows to.

3. Electrolyte – a medium capable of conducting electric current by ionic current flow (i.e. soil, water or concrete).
4. Metallic Path – connection between the anode and cathode, which allows current return and completes the circuit [6].

Corrosion of reinforcement has been established as the predominant factor causing widespread premature deterioration of concrete construction worldwide, especially of the structures located in the coastal marine environment [7]. Corrosion of reinforcing steel in concrete is one of the major causes for deterioration of bridges, buildings and other concrete structures [8].

The economic loss and damage caused by the corrosion of steel in concrete is arguably the largest single infrastructure problem facing industrialized countries. One American estimate was that \$150 billion worth of corrosion damage on their interstate highway bridges is due to deicing and sea salt induced corrosion. In a recent Transportation Research Board Report on the costs of deicing, the annual cost of bridge deck repairs was estimated to be \$50 to \$200 million, with substructures and other components requiring \$100 million a year and a further \$50 to 150 million a year on multistory car parks [9].

The damage to concrete resulting from the corrosion of embedded steel manifests itself in the form of expansion, cracking, and eventual spalling of the cover as shown in Plate (1-1). In addition to loss of cover, a reinforced-concrete member may suffer structural damage due to loss of bond between steel and concrete and loss of rebar cross-sectional area sometimes to the extent that structural failure becomes inevitable [10].

Embedded steel in concrete should not corrode. It is protected against corrosion because of the passivating film of γ -ferric oxide, which is formed and maintained in the alkaline environment produced by cement hydration. Hydration products, mainly calcium hydroxide and

small proportions of sodium and potassium hydroxides, give the pore solution of concrete a pH of around 13 [11].

However, some aggressive agents can destroy this passivating film. Once destroyed, corrosion proceeds with the formation of electrochemical cells on the steel surface. It changes the concrete properties and the reinforcement. Finally, the corrosion product causes cracking and spalling of the concrete cover [11].

This passivating film can be attacked in two ways. On one hand a reduction of the pH due to carbonation process (reaction of carbon dioxide present in the atmosphere with the cement paste through formation of calcium carbonate) and on the other hand the introduction of chlorides which penetrate the protective oxides layer [12].

Since the mid 1960's, several methods have been investigated to extend the time to corrosion damage in structures. Efforts have included tighter quality control on materials and construction practices, design modifications, such as increased concrete cover over reinforcing steel, and the use of specialized systems for corrosion prevention. Such systems include epoxy and galvanized coatings of reinforcing steel, active and passive cathodic protection systems, and use of corrosion inhibiting admixtures (corrosion inhibitors) in concrete [13].

Corrosion inhibitor is a chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agent [14].

The use of corrosion inhibitors is of increasing interest as they are claimed to be useful in reinforced concrete not only as preventative measure for new structures (as addition to the mixing water) but also as surface-applied inhibitors for preventative and restorative purpose. Application on the concrete surface could be a promising technique to

protect existing structures from corrosion or increase the lifetime of structures that already show corrosion attack [15].

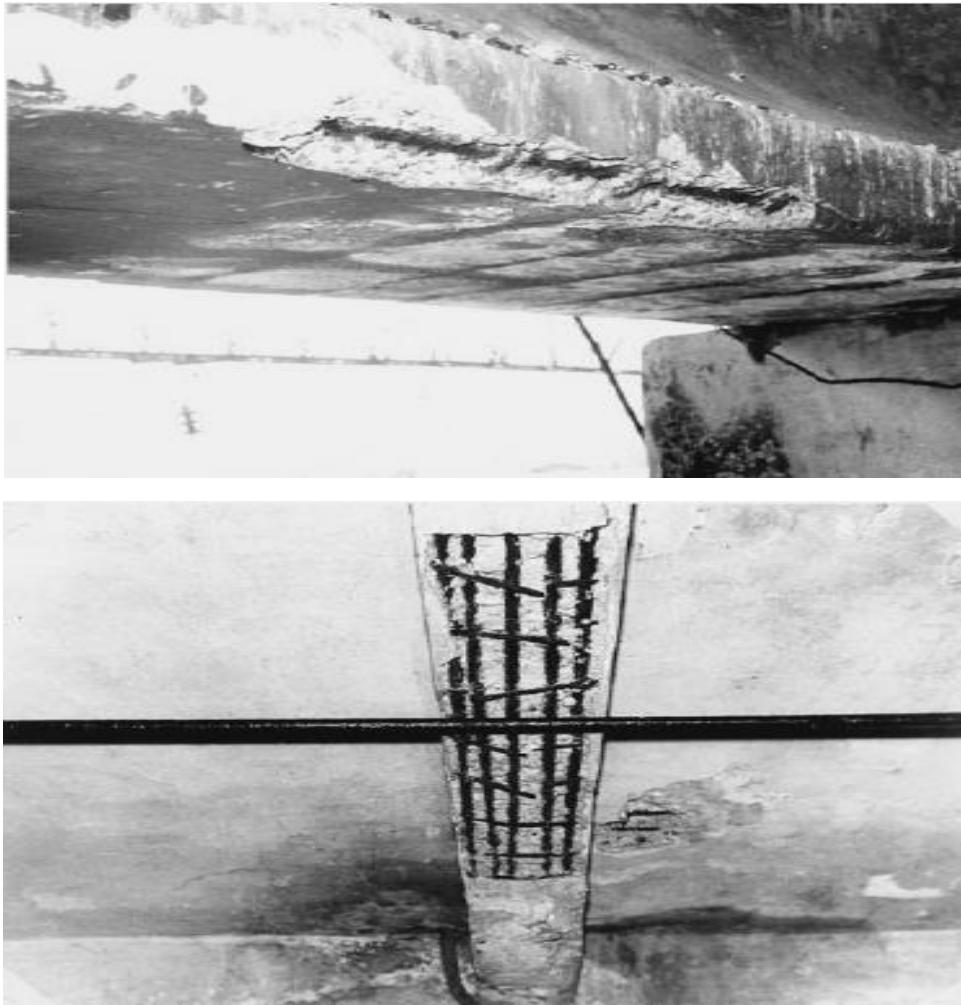
The Plates (1-1, 1-2 and 1-3) show the risk of corrosion on reinforced concrete structures:



Plate (1-1) delaminating of cover due to corrosion



Plate (1-2) Damage to reinforced concrete structures due to corrosion of steel [16].



Plate(1-3) Bridge reinforced concrete girder (top) and floor beam of industrial building (bottom) in service with corroding reinforcement [17].

In Iraq, structural problems due to corrosion have not yet received adequate appreciation. The engineers, who are concerned with durability problems of reinforced concrete, are conscious of the alarming situation. Extraneous aggressive ions attack, mainly chloride, present in underground water, soil and aggregate has been identified as the main cause of corrosion. An unacceptable degree of deterioration was observed within a short period of 5-7 years after construction as in Al-Basra airport [18].

1.2 Objective of the Research

The goal of this thesis is to investigate the influence of three synergic admixtures as corrosion inhibitors by using Linear Polarization Resistance technique on the reinforcement of concrete in addition to their activity on some properties of concrete like, compressive strength, splitting tensile strength, chloride concentration and absorption. These synergic admixtures are (Calcium Nitrate + Ethanolamine), (Potassium Dichromate + Styrene Butadiene Rubber) and (Sodium Silicate + Sodium Benzoate), where each of these synergies are used in three concentrations.

1.3 Research Layout

The present study consists of five chapters as follows:
Chapter one represents the introduction. Chapter two which represents the literature review contains the mechanism of corrosion process, causes of concrete corrosion, types of corrosion, corrosion rate, factors influencing corrosion rate and corrosion inhibitors.

Chapter three deals with materials properties, mix proportions and methods of testing the specimens.

Results of the experimental work and the discussion are presented in chapter four.

Chapter five includes the conclusions (which are obtained from the results) and the recommendations for future works.

Chapter Two

Literature Review

2.1 General

Deterioration of reinforced concrete structures exposed to man-made or atmospheric aggressive conditions is a common problem in many countries of the world. Frequently, due to corrosion, the resistance of structures decreases much earlier than their expected service life and the need to carry out repairs of degraded structures is increasing exponentially [17].

2.2 Mechanism of Corrosion Process

The corrosion of reinforcement is an electrochemical process, in which anodic reaction and cathodic reaction progress simultaneously. So, it is possible to suppress the corrosion of the reinforcement, if one side or both of the reactions are stopped. In this electrochemical process the moist concrete forms the electrolyte [18].

The potential difference between anode and cathode is the driving electrical force for steel corrosion. Usually, the process can be divided into primary electrochemical processes and secondary processes:

I* Primary Electrochemical Processes

For steel in concrete, as the passive film is degraded by chloride ions or the pH is reduced by carbonation, the metallic *Fe* at the anode is oxidized to form ferrous ions (Fe^{+2}):



The electrons released at the anode flow through the steel to the cathodic areas, as illustrated in Figure (2.1). The above reaction is

initially balanced by cathodic reaction of dissolved oxygen (O_2) to hydroxyl ions (OH^-):

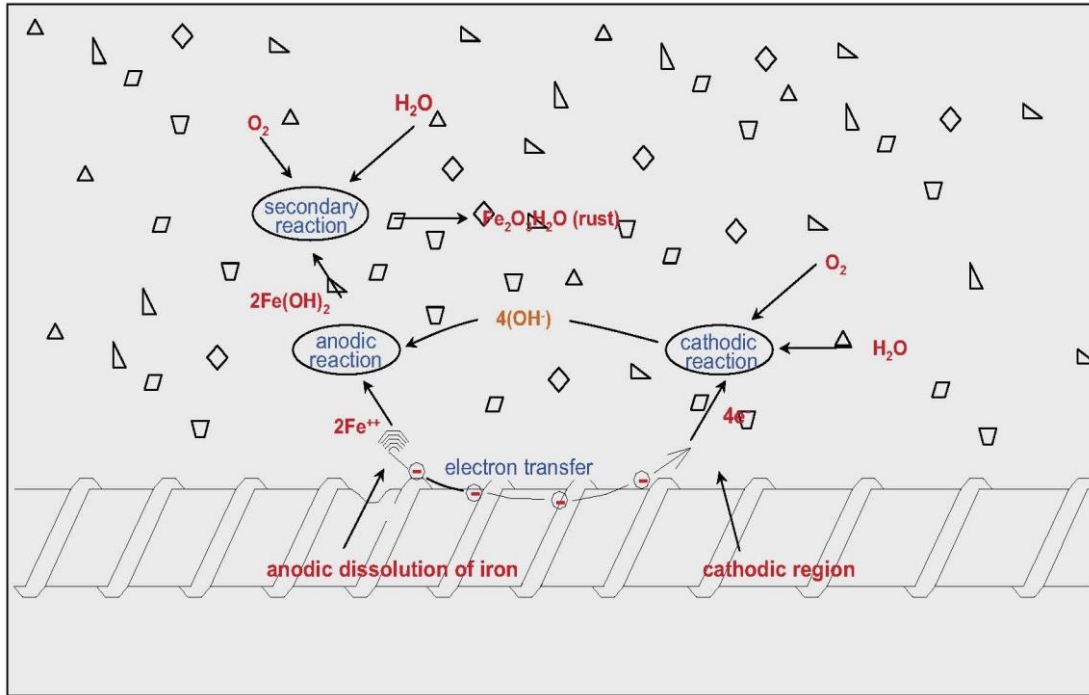
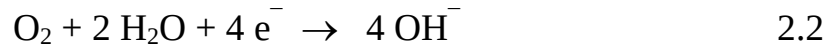


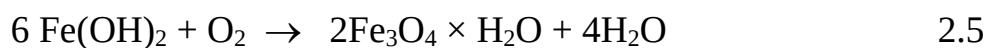
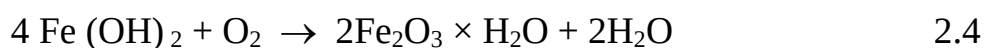
Figure (2.1) Electrochemical process of anode and cathode [19].

The anodic product (Fe^{+2}) reacts with the cathodically formed hydroxyl ions to produce a ring of a white precipitate of ferrous hydroxide ($Fe(OH)_2$) [20]:



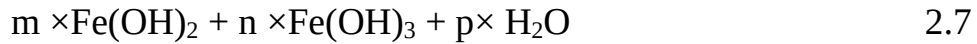
II* Secondary Processes

The $Fe(OH)_2$ can be further converted to hydrated ferric oxide ($Fe_2O_3 \times H_2O$), also known as ordinary red-brown rust, and black magnetite (Fe_3O_4) preceded by the formation of green hydrated magnetite ($Fe_3O_4 \times H_2O$):





The composition of rust on iron may be expressed as a general formula:



Where, the values of m , n and p vary considerably, depending on conditions such as pH of the solution, the oxygen supply and moisture content [21].

The corrosion process of steel can be summarized with the following reactions:

1. The oxidation of iron (*anodic process*) that liberates electrons in the metallic phase and gives rise to the formation of iron ions whose hydrolysis produces acidity. (eq: 2.1)
2. The reduction of oxygen (*cathodic process*) that consumes these electrons and produces alkalinity. (eq: 2.2)
3. The transport of electrons within the metal from the anodic regions where they become available, to the cathodic regions where they are consumed (since the electrons carry a negative charge, this gives rise to a nominal electrical current flowing in the opposite direction);
4. Finally, in order for the circuit to be complete the flow of current inside the concrete from the anodic regions to the cathodic ones, transported by ions in the pore solution [15].

The previously discussed reactions at the anode and cathode result in corrosion of reinforcing steel. Ferrous ions (Fe^{+2}) produced in the anodic reaction combine with the hydroxyl ions produced in the cathodic reaction to form the corrosion product ferric hydroxide Goethite ($\text{Fe}(\text{OH})_2$) [22].

The transformation of metallic iron to rust is accompanied by an increase in volume that, depending on the state of oxidation, may be as

large as 600 percent of the original metal Figure (2.2). This volume increase is believed to be the principal cause of concrete expansion and cracking, see Figure (2.3) [16].

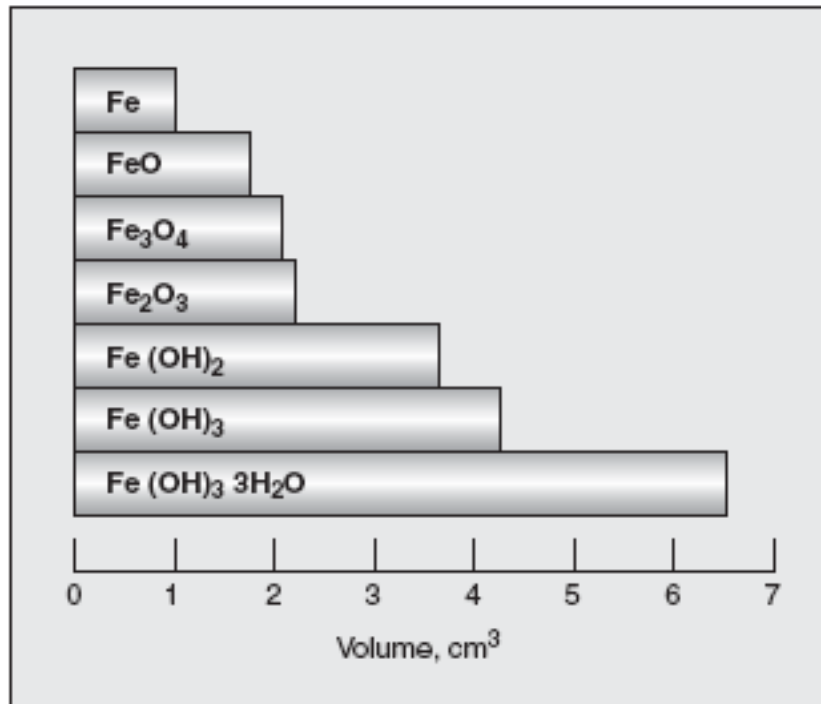


Figure (2.2) Increasing the volume of iron due to corrosion [23].

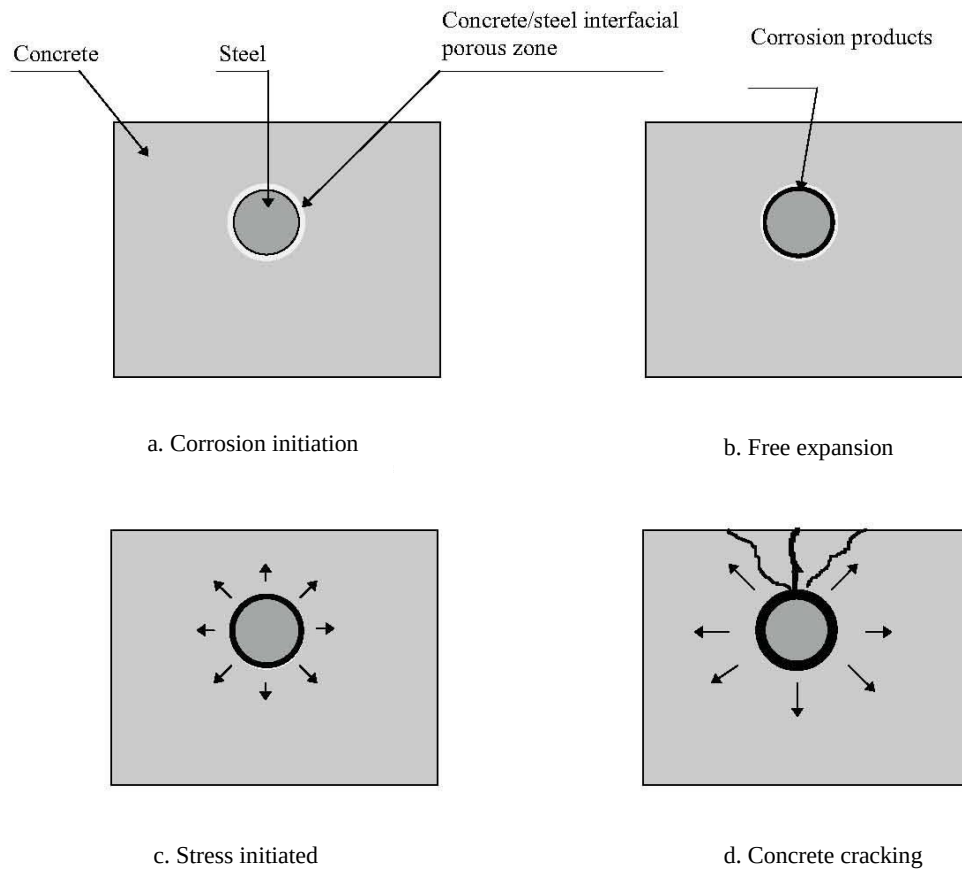


Figure (2.3) A schematic diagram of the corrosion-cracking processes [24].

2.3 Pourbaix Diagrams

Based on thermodynamic data on reactions between metal and water, Pourbaix [25] developed potential versus pH diagrams which indicate thermodynamically stable phases as a function of electrode potential and pH. The Pourbaix diagram for iron is shown in Figure (2.4).

There are three general regions described as regions of corrosion, passivity and immunity. A soluble product is formed under a range of acidic conditions and under narrow range of alkaline conditions. These are regions of corrosion. Between these two regions an insoluble film is formed, and that region is referred as a passive region. The third region,

immunity, shows that metal is thermodynamically stable and no corrosion will occur. Pourbaix diagrams provide a thermodynamic basis for understanding corrosion reactions [26].

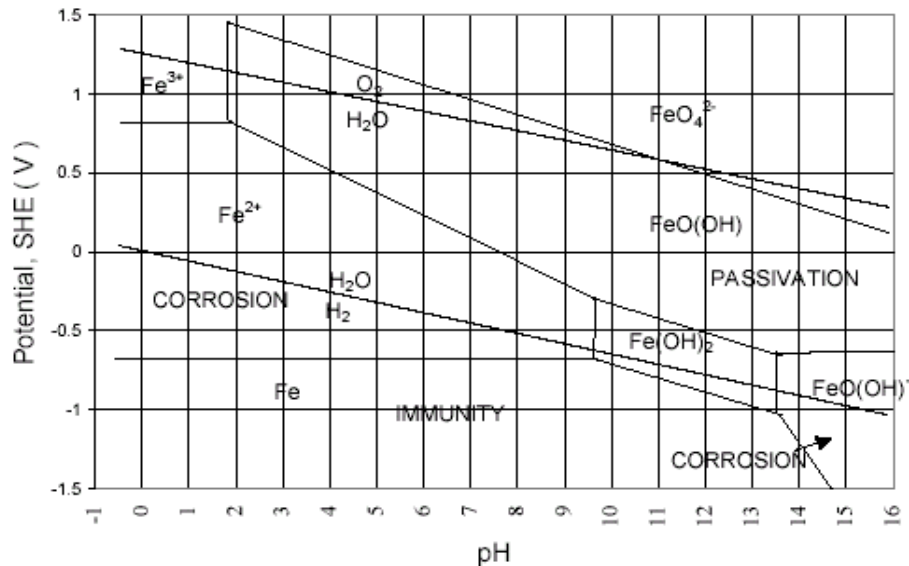


Figure (2.4) Pourbaix diagram for the FeO-H₂O system at (25°C) for 10⁻⁶M, activities of all metal ions [26].

2.4 Passive State

Passivity occurs when the corrosion product is insoluble and adherent and results in the formation of an ultra-thin protective film on the surface of the metal. Passivity is of two kinds, chemical and mechanical passivity:

Chemical Passivity. This type of passivity is due to an invisible thin but dense and semi conducting oxide film on the metal surface, displacing the electrode potential of the metal strongly in the positive direction.

Mechanical Passivity. Mechanical passivity is due to the precipitation of solid salts on the metal surface. The cause of strongly reduced corrosion

rate in this case is a thick but more or less porous salt layer, usually non-conducting [24].

2.5 Causes of Concrete Corrosion

2.5.1 Carbonation

Carbonation is one of the major factors to cause corrosion deterioration. Carbonation is the reaction of the hydration products dissolved in the pore water with the carbon dioxide in the air which reduces the pH of concrete pore solution from 12.6 to less than 9 and steel passive oxide film may be destroyed and accelerating uniform corrosion [27].

Carbonation and the resulting loss in alkalinity will typically begin at the concrete surface and will move in the form of a "carbonation front" toward the center of the concrete section. The gas (CO_2) and its solution in water, carbonic acid (H_2CO_3), react with the calcium hydroxide cement paste — a process termed “carbonation”. Nitrous and sulfurous oxides can also react in this way. Carbonation of calcium hydroxide ($\text{Ca}(\text{OH})_2$) present in the hydrated cement paste is shown by the reactions below [28]:



Jones et al [2001] [29] have focused their research work on the development of carbonation of hardened concrete. Ten different common cement mixes, at an equal grade of 37 MPa have been tested and compared to a benchmark Portland cement with 30% pulverized fuel ash (PFA) mix. The effect of storage condition and the type of cement on carbonation were determined. The potential carbonation resistance of concrete was determined to be dependant on both permeation and alkalinity of the cover concrete. A comparison of water vapor diffusivity

and total $\text{Ca}(\text{OH})_2$ in the cover concrete showed that concretes with lower water vapor diffusivity properties still exhibited higher carbonation depths due to the fact that the cover concrete alkalinity was relatively low.

An experimental investigation was carried out by **Chi et al** [2002] [30] to study the effect of carbonation on mechanical properties and durability of concrete. Ordinary Portland concretes (OPC) with water/cement ratios of 0.58 and 0.48 and self-compacting concretes (SCC) with water/binder ratios of 0.40 and 0.36 were used in that study. Compressive strength test, splitting strength test, electrical resistivity test, rapid chloride penetration test (RCPT), open circuit potential method and alternative current (AC) impedance method were performed to estimate the properties of concrete.

Test results showed that carbonation may improve some concrete properties such as compressive strength, splitting strength, electrical resistivity and chloride ion penetration. However, corrosion test results showed that carbonation increases corrosion rate of reinforcing steel.

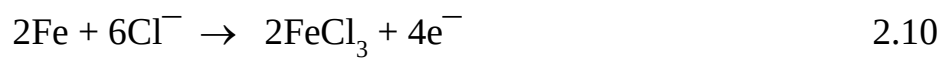
A1-Khayat et al [2002] [31] studied the influence of concrete carbonation in arid climate. Fifty-four different concrete mixes were exposed to hot arid weather in Kuwait to monitor their extent of carbonation. Various parameters affecting carbonation such as water/cement ratio, cement content, type of cement, type and dosage of admixture, water-curing period, type of coating, and the addition of silica fume or pulverized fuel ash were investigated. For many of these variables, the carbonation depth and rate constant (K) were reported for an exposure period of 8.6 years.

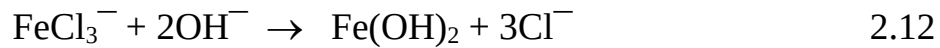
The results showed that the water/cement ratio is one of the main factors affecting carbonation. The values of (K) ranged from 2.1 to 7.8 as the water/cement ratio increased from 0.45 to 0.8. Concrete made with

white Portland cement carbonated less than ordinary or sulphate resisting cements. All curing compounds (C1 was based on sodium silicate, C2 on resin, C3 on wax emulsion, while C4 was based on white resin) were effective in reducing carbonation while two coating materials (CW1 and CW2 based on ethylene copolymer and acrylic resin, respectively) prevented carbonation after eight years of exposure.

2.5.2 Chloride Attack

Chlorides may be introduced when seawater or water with a high chloride concentration is used as mixing water, when chloride contaminated coarse or fine aggregates are used, or when chloride containing admixtures such as calcium chloride are used. In addition, chloride present in the surrounding environment may penetrate the concrete [32]. The chloride ions from these sources slowly penetrate into the concrete, mostly through the pores in the hydrated cement paste. The chloride ions will eventually reach the steel and at a certain concentration level the protective film is destroyed and the steel begins to corrode, when oxygen and moisture are present at the steel-concrete interface. The chloride ions initiate the corrosion reaction by depassivating the natural oxide film on the steel surface, allowing the iron to dissolve into solution. On reaching the iron substrate, the chloride ions oxidize the iron to form FeCl_3 and that draws its unstable ferrous ion into solution, where it reacts with the available hydroxyl ions to form $\text{Fe}(\text{OH})_2$. This releases the Cl^- back into the solution and consumes the hydroxyl ions, as seen in the following reactions [33]:





The effect of internal chloride was studied by **Mohammed et al** [2004] [34] by using seawater as a chloride source, they summarized mineralogy, chloride ingress, and corrosion of steel bars embedded in concrete made with seawater and tap water based on the several long-term exposure investigations under tidal environment. And they showed that the initial amount of chloride (due to the use of seawater) may cause the initiation of corrosion at the locations of the steel bars having voids/gaps at the steel–concrete interface immediately after casting concrete. The use of seawater results in the formation of deeper corrosion pits compared to the same with tap water.

Poupard et al [2006] [35] investigated the effect of the chloride on the corrosion damage which was performed on a 40 years old reinforced concrete beam exposed to marine environment. Visual observations, electrochemical measurements, carbonation depth and total chloride content were carried out. Half-cell potential measurements were used to locate corrosion areas. Complementary destructive methods were applied to observe the real corrosion state of steel rebars and characterize the corrosion products and the steel/concrete interface (optical and electronic microscope).

All these data indicated that there were two types of areas on the beam: (high-corrosion zones) and (low-corrosion zones). Given the fact that the (high corrosion zones) were found to be close to corrosion induced cracks and that they have a different morphology, this contribution concludes that the position of these areas did not shift in time. However, non destructive measurements as confirmed by visual observation suggest a heterogeneous corrosion along the rebar surface.

2.6 Chloride Threshold

A small concentration of chloride ions in concrete pore water will not break down the passive layer, especially if the system is effectively reestablishing itself. However, there is a chloride threshold for corrosion, given in terms of the chloride-hydroxyl ratio, which represents the concentration of chloride ions required to initiate corrosion [36].

In the presence of chloride ions, depending on the Cl^-/OH^- ratio, it is reported that the protective film is destroyed even at pH values considerably above 11.5. It seems that when Cl^-/OH^- molar ratio is higher than 0.6, steel is no longer protected against corrosion probably because the iron-oxide film becomes either permeable or unstable under these conditions. For the typical concrete mixtures normally used in practice, the threshold chloride content to initiate corrosion is reported to be in the range 0.6 to 0.9 kg Cl^- per cubic meter of concrete. Furthermore, when large amounts of chloride are present, concrete tends to hold more moisture, which also increases the risk of steel corrosion by lowering the electrical resistivity of concrete [16].

Diamond [1986] [37] stated that at the range of pH present in typical cement paste, the Cl^-/OH^- ratio of 0.3 at which risk of corrosion significantly drops. Table (2.1).

Hussain et al [1995] [38] presented a study on the factors which affecting threshold chloride for reinforcement corrosion in concrete. Three cements with variable C_3A contents were mixed with different levels of chloride, alkali and sulfate contents. Effect of exposure temperature was also studied by curing the chloride-treated specimens at 20 and 70 C°. The results showed that C_3A content and exposure temperature have very strong influence on threshold chloride content. Alkali content of cement has marginal effect whereas presence of sulfates

along with chlorides has moderate effect on the threshold chloride content.

Thomas [1996] [39] studied the effect of fly ash on the chloride threshold in reinforced concrete specimens exposed to tidal conditions were retrieved at ages ranging from 1 to 4 years. He found that the threshold chloride level decreased with increasing fly ash content; values obtained were 0.70%, 0.65%, 0.50% and 0.20% acid-soluble chloride (by mass of cementitious material) for concrete with 0%, 15%, 30% and 50% ash, respectively.

Table (2.1) $[\text{Cl}^-]/[\text{OH}^-]$ ratios for various pH values [37].

Point	pH	Estimated $[\text{Cl}^-]:[\text{OH}^-]$ ratio
1	11.8	0.57
2	12.1	0.48
3	12.6	0.29
4	13.0	0.27
5	13.3	0.30

Manera et al [2007] [40] investigated the effect of silica fume on the chloride threshold for the initiation of pitting corrosion of steel in concrete. Laboratory tests were carried out in concrete specimens made with ordinary Portland cement and with 10% of silica fume. Chloride contents up to 2% by mass of cement were added to the mixes, in order to investigate the corrosion rate of embedded bars made of both strengthened and mild steel. The results showed that a lower chloride threshold was observed in the bars which were embedded in concrete

with silica fume compared to those embedded in concrete made of Portland cement.

2.7 Initiation and Propagation of Corrosion

The service life of reinforced-concrete structures can be divided in two distinct phases (Figure 2.5). The first phase is the *initiation of corrosion*, in which the reinforcement is passive but phenomena that can lead to loss of passivity, e. g. carbonation or chloride penetration in the concrete cover, take place. The second phase is *propagation of corrosion* that begins when the steel is depassivated and finishes when a limiting state is reached beyond which consequences of corrosion cannot be further tolerated [15].

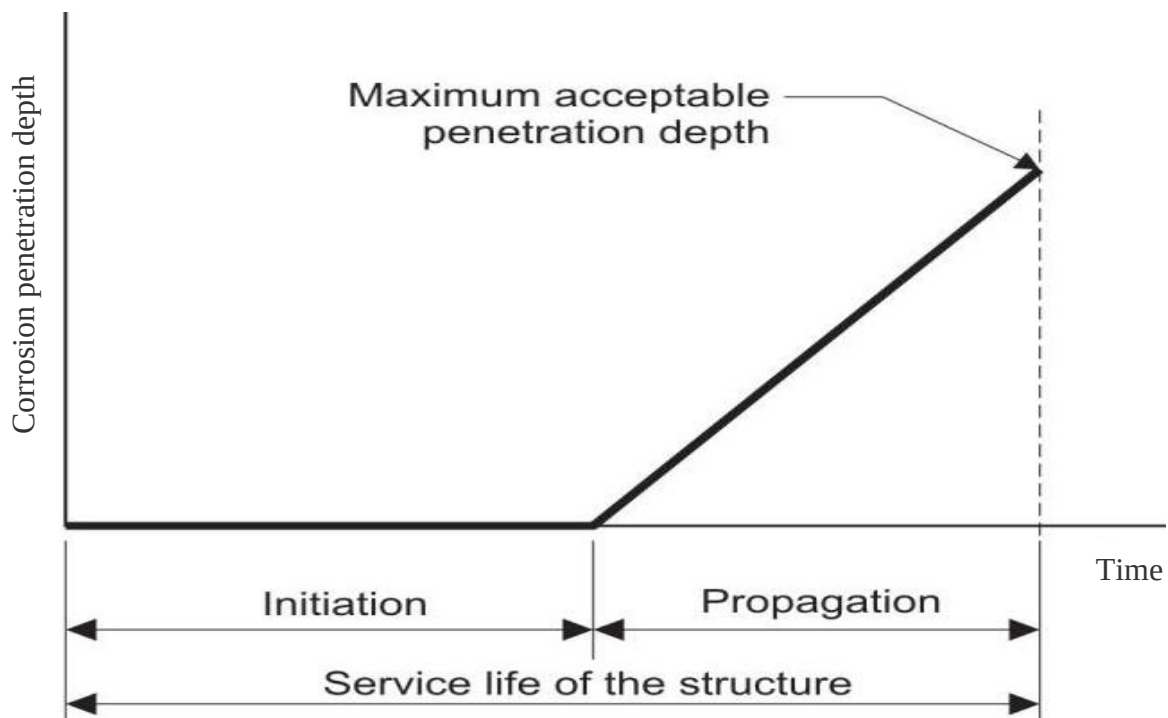


Figure (2.5) Initiation and propagation periods for corrosion in a reinforced-concrete structure [15].

2.7.1 Initiation Period

During which the aggressive agents (CO_2 , Cl^-) will ingress into the concrete.

1. *Initiation by carbonation:* Ingress of (CO_2) from the air will react with the calcium hydroxide in the concrete under formation of calcium carbonate and reduction of pH to approximately 9 as shown in equations (2.8 and 2.9). The concrete coating which makes the reinforcement passive is degraded when the carbonation front reaches the reinforcement. At this stage corrosion is initiated [41].

2. *Initiation by chloride ingress:* Chloride will diffuse from the surface into the concrete and the concentration most commonly increases with time. Chlorides can have their origin from e.g. de-icing salts, sea water or admixtures. When the chloride concentration reaches a critical level, called the threshold value, corrosion will be initiated [41].

2.7.2 Propagation Period

Breakdown of the protective layer is the necessary prerequisite for the initiation of corrosion. Once this layer is destroyed, corrosion will occur only if water and oxygen are present on the surface of the reinforcement. The corrosion rate determines the time required to reach the minimally acceptable state of the structure (Figure 2.5) but it should be borne in mind that this rate can vary considerably depending on temperature and humidity [15].

2.8 Types of Corrosion

2.8.1 General Corrosion

Depassivation arises in concrete if the pH value of pore-water at the depth of the reinforcement becomes substantially lower than its initial, high level. This can happen as a result of carbonation, which involves

penetration into the material of acidic gases (CO₂ etc.) from the surrounding air, and it gives rise to general corrosion of steel [43].

2.8.2 Pitting Corrosion

Corrosion of steel in concrete generally starts with the formation of pits. These increase in number, expand and join up leading to the generalized corrosion. Pitting corrosion is likely to occur in reinforced concrete containing significant amount of chloride, derived either from the service environment or from the use of contaminated mix materials [42].

2.8.3 Black Rust

There is an alternative to the formation of ‘normal’ red rust described in sections 2.8.1, 2.8.2 above. If the anode and cathode are well separated (by several hundred millimeters) and the anode is starved of oxygen (say be being underwater) the iron as Fe⁺² will stay in solution. This means that there will be no expansive forces to crack the concrete, so corrosion may not be detected. This type of corrosion (known as ‘black’ or ‘green’ rust due to the color of the liquid seen on the rebar when first exposed to air after breakout) is found under damaged waterproof membranes and in some underwater saturated conditions. There is no indication of corrosion by cracking and spalling of the concrete and the reinforcing steel may be severely weakened before corrosion is detected. Rebars may be hollowed out in such deoxygenated conditions, particularly under membranes or when water is permanently ponded on the surface [9].

2.8.4 Bacterial Corrosion

Another complication comes from bacterial corrosion. Bacteria in the soil (thiobacilli) convert sulphur and sulphides to sulphuric acid. This acid attacks steel causing corrosion. There are other species (ferrobacilli) that attack the sulphides in steel (FeS). This is often associated with a smell of hydrogen sulphide (rotten eggs) and smooth pitting, with a black corrosion product when rebars are exposed having been in water saturated conditions. In anaerobic (oxygen starved) conditions such bacteria can contribute to the pitting corrosion discussed above [9].

2.8.5 Stray Current Corrosion

Stray current corrosion (interference corrosion) is corrosion caused by direct current from an external source that travels through paths other than the intended circuit. Although alternating current (AC) can cause corrosion, it is generally considered insignificant (more than a thousand times less) when compared to corrosion from direct current (DC) [44]. Stray current, arising for instance from railways, cathodic protection systems, or high-voltage electroducts, often induces corrosion on buried metal structures, leading to severe localized attack [45].

2.9 Effects of the Concrete Environment on Corrosion

2.9.1 Portland Cement

When Portland cement hydrates, the silicates react with water to produce calcium silicate hydrate and calcium hydroxide. The high alkalinity of the chemical environment normally present in concrete protects the embedded steel because of the formation of a protective oxide film on the steel. The integrity and protective quality of this film depends on the alkalinity (pH) of the environment [2].

Differences in the types of cement are a result of variation in composition or fineness or both, and as such, not all types of cement have the same ability to provide protection of embedded steel [2].

Joukoski et al [2004] [46] studied the influence of cement type on the resistance and durability of reinforced concrete samples with 25 mm cover thickness, when submitted to aging in a 3.4% sodium chloride aqueous solution and in a high salinity marine environment. Two concrete mixtures were made using CII-F 32 (filler-modified Portland cement): a mix with no admixture and a mix with addition of 8% silica fume swapping fine aggregates. Another mixture was batched with CPV-ARI RS (high-early-strength Portland cement, with sulfur resistance). All the three mixtures were designed with cement content of about 350 kg/m³. The performance of the structures was evaluated from the results of physicochemical, mechanical and electrochemical testing, after over a year of natural aging. Corrosion potentials of the reinforced concrete samples and of the cast utility poles were measured in terms of the aging time at the natural environment and under chloride ion accelerated aging at laboratory.

The half-cell potential measurements showed that the best results were obtained from the mixture containing CII-F 32 cement and silica fume, followed by the concrete made with CPV-ARI RS cement. The mixture batched with CII-F 32 cement without admixture presented the worst durability performance.

Herrera et al [2006] [47] investigated the influence of C₃A of the cement on electrochemical chloride extraction (ECE) treatment efficiency. ECE was applied using cylindrical specimens made from concrete containing two levels of C₃A (4.3% and 9.05%). Specimens were 5 cm in diameter and 10 cm in height. Steel was placed in the axial direction with an embedded length of 7 cm. These specimens were

immersed in a NaCl solution and dried in a stream of air at 40 C° for 10 months. The corrosion was monitored by half-cell potential and polarization resistance measurements. After steel depassivation, ECE was applied for 20, 30, 40 and 50 days using a constant current density of 1 A/m² of steel. At the end of the treatment, the specimens were maintained at 20 C° and 70% RH (relative humidity) in order to observe the evolution of the steel (electrochemical measurements).

The results showed that, after 30 days of treatment, the chloride content remained constant in the specimen. Concerning the C₃A content, ECE efficiency was slightly affected by C₃A because only a part of the bound chloride ions was released. From the point of view of corrosion, half-cell potential showed a shift in the positive direction, indicating little corrosion activity at 20 C° and 70% RH. However, polarization resistance measurements showed that 2 months post treatment corrosion rates were significant, although the corrosion rate decreased from 6 µA/cm² to 2.5 µA/cm².

2.9.2 Aggregate

The effects of the aggregate in concrete on corrosion of embedded steel relate to the degree of their chloride contamination and their effect on permeability and absorptive characteristics of concrete. The gradation of the aggregates may have a significant effect on corrosion of embedded steel if gradations are such as a result in segregation and bleeding of the concrete mixture [48].

An attempt is made by **Hobbs** [1999] [49] to predict the probable effect of the aggregate on chloride ion diffusion into saturated concrete.

It is shown that if the chloride ion diffusion coefficient of an aggregate ranges from 0.2 to 10 times that of the cement paste matrix,

then this could result of changes in the concrete chloride ion diffusion coefficient of up to ten times.

2.9.3 Water

A high moisture content will substantially reduce the rate of diffusion of carbon dioxide and hence the rate of carbonation of the concrete [2]. However, the high water content effect the durability of concrete by increasing its permeability, and allowing the ingress of chloride ions which lead to corrosion of reinforcing bars.

Hong and Hooton [2000] [50] studied the effects of fresh water exposure on chloride contaminated concrete. It was found that continuous or cyclic exposure of chloride contaminated concrete to distilled water will decrease the chloride concentration at the surface of the concrete, but increase at depths below the convection zone. In saturated pores, free chloride ions continue to diffuse to regions of lower chloride concentrations, both outside the concrete surface, and deeper into the concrete.

2.9.4 Mineral Admixtures

Mineral admixtures have been studied by many researchers to investigate their effect on corrosion of steel reinforcement in concrete.

As reported in Abdul Amir [76], **Yousif** [1997] [51] studied the effect of high range water –reducing admixture (HRWA) and the joint action of Rice husk ash (RHA) and (HRWA) on the strength development, electrical resistance and corrosion behavior of steel in concrete containing various amounts of cementitious materials. Concrete column samples were prepared and partially submerged in $\text{Cl}^- + \text{SO}_4^{2-}$ solutions at concentration that tended to simulate severely aggressive environment. Results indicated that the addition of HRWA produced

considerable increases in strength and electrical resistance compared to reference concrete and the use of RHA and HRWA can produce additional improvement in these vital characteristics relative to the corresponding HRWA concrete. The study also revealed that the use of HRWA resulted in considerable reduction in corrosion activity, and significantly further improvement was achieved when RHA + HRWA were used.

Marcotte and **Hansson** [2003] [52] presented a study about the influence of silica fume on the corrosion behaviour of steel in high performance concrete (HPC) by comparing the behaviour of HPC concretes with and without a 10% by mass of cement addition of silica fume. Reinforced concrete prisms ($500 \times 100 \times 100$) mm with embedded corrosion probes were loaded in three-point bending to achieve a 0.3 mm crack and exposed to simulated sea water for up to four years. Corresponding prisms without induced cracks were also studied as controls.

For the HPC with silica fume, pore size distribution measurements showed that after exposure to the simulated sea water, the hydration and pozzolanic reactions near the induced crack blocked almost all continuous pores in the 0.01 to 10 μm range. This affected the type and distribution of corrosion products that formed by restricting the access of chlorides and oxygen to the surface of the steel. Thus, the formed magnetite (Fe_3O_4) confined the space provided by the induced crack, effectively plugging the crack. In HPC without silica fume, oxygenated corrosion products such as goethite ($\alpha\text{-FeOOH}$) and akaganeite ($\beta\text{-FeOOH}$) formed in the induced crack region.

Moon and **Shin** [2004] [53] evaluated the corrosion of steel bar embedded in antiwashout underwater concrete. Accelerated steel bar corrosion tests have been performed for three series of steel bar-

reinforced antiwashout underwater concrete specimens manufactured with different admixtures and under different environments. The three series of antiwashout underwater concrete were: concrete constituted exclusively by ordinary portland cement (OPC), concrete composed by ordinary Portland cement mixed with fly-ash in 20% ratio (FA20) and concrete with ground granulated blast furnace slag was mixed in 50% ratio (BFS50). The three different environments were: exposure to air, tap water, and artificial seawater.

Measurement results using half-cell potential surveyor showed that, among all the specimens, steel bar in OPC manufactured in artificial seawater was the first one that exceeded the threshold value proposed by ASTM C 876 with a potential value below -350 mV after 14 cycles. And, the corresponding corrosion current density and concentration of water soluble chloride were measured as $0.3 \mu\text{A}/\text{cm}^2$ and 0.258%. On the other hand, for the other specimens that are FA20 and BFS50, potential values below -350 mV were observed later at 18 and 20 cycles, respectively. Results confirmed the expectation that mineral admixtures may be more effective in delaying the development of steel bar corrosion in antiwashout underwater concrete.

Yeau and **Kim** [2005] [54] presented experimental test on corrosion resistance of concrete containing ground granulate blast-furnace slag (GGBS) and ASTM Type I or ASTM Type V cement. Test results showed that the coefficient of permeability of Type I cement concrete was lower than that of Type V cement concrete. All the concrete mixed with GGBS exhibited lower diffusion coefficient, compared to GGBS-free concrete. Moreover, the corrosion probability of steel bar in Type V cement concrete was higher than that of steel bar in Type I cement concrete.

2.9.5 Temperature

Temperature changes have important effects on concrete resistivity. A higher temperature causes the resistivity to decrease and vice versa (for a constant relative humidity). This is caused by changes in the ion mobility in the pore solution and by changes in the ion–solid interaction in the cement paste [15].

Katwan [2001] [55] investigated the corrosion of steel reinforcement in hot countries by studying an acute case of widespread corrosion damage observed on a ground slab of a huge prestigious building complex constructed at the southern part of Iraq in the late eighties. The remedial measures necessary for extending the service life of the structure were described. The concrete cores were subjected to different chemical and physical tests.

Chemical and electrochemical survey clearly indicated that the corrosion damage was confined to the top slab reinforcement and that corrosion was induced by internal chloride attack. Chloride ions were introduced into concrete by the initial use of chloride contaminated sand in the concrete mixes and the subsequent application of saline water used for concrete curing. The curing process resulted in distinct increase of chloride concentration in the first 6 cm layer of concrete. Chloride content as high as 0.76% was obtained.

Živica [2002] [56], studied the significance and influence of the ambient temperature as a rate factor of steel reinforcement corrosion.

The effects of ambient temperature on the rate of chloride induced corrosion were: (i) acceleration of the rate when the ambient temperature is increased to about 40 C°, and (ii) inhibition of the rate when the ambient temperature is increased over the given value of the temperature.

A thorough analysis of the corrosion process showed that the decrease of oxygen content and water in the pores of the corroding system (concrete– steel) is a result of above two effects.

2.9.6 Concrete Cracks

In concrete, microcracks already exist due to its unstable condition as a composite material. Some other cracks develop when concrete is exposed to environmental gradients or service loads [57].

Cracks can be induced in concrete by load, volumetric change due to plastic settlement, high curing temperature, various types of shrinkage, creep, and deteriorating mechanisms such as frost and alkali aggregate reaction [58].

In any case, cracks may reduce the corrosion initiation time by providing a preferential path for the penetration of carbonation or chlorides (Figure 2.6). Experiments with sectioned steel bars in intentionally cracked concrete beams have shown that the depassivation time decreases as the crack width increases; however, there is no relationship between crack width and corrosion rate; actually the corrosion rate decreases with increasing cover of the uncracked concrete (between cracks) due to the influence of the cathodic process [59].

Generally, if the crack width is modest (e. g. it is below 0.3–0.5 mm), after the initiation of corrosion on the steel surface, the corrosion rate is low. Chemical processes in the cement paste and formation of corrosion products may seal the crack near the reinforcement and allow the protective oxide film to form again [15].

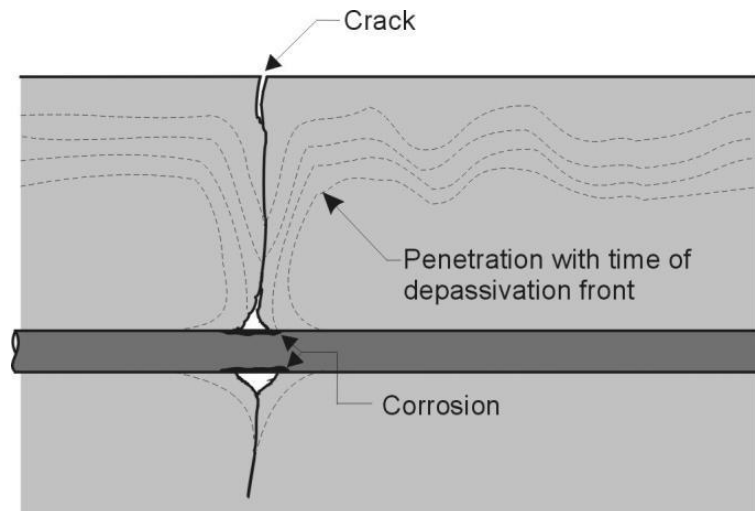


Figure (2.6) Illustration of the penetration of the depassivation front (as a consequence of carbonation or chloride ingress) in time in cracked concrete [59].

The effects of crack width and calcium nitrite based corrosion inhibitor on the corrosion process of steel reinforcing bars in high performance concrete were investigated by **Montes et al** [2004] [57]. Small-scale concrete slabs containing steel reinforcement were cast with a concrete cover depth of 20 mm. The slabs were subjected to a simulated marine environment with two cycles of wetting and drying per day. The specimens were also visually inspected on a regular basis.

It was found that calcium nitrite alone, in general, has no effect in decreasing corrosion, and that the crack condition of the specimens strongly affects the corrosion process. A significant effect of crack width on corrosion was also found.

Shafiqul et al [2006] [60] made an experimental study to investigate the effect of different crack widths on CO_2 ingress into concrete repair patch. The cement used was ordinary Portland cement (specific gravity: 3.15), the coarse aggregate was crushed stone (specific gravity: 2.7); and the fine aggregate was river sand (specific gravity: 2.63; FM: 2.9).

Polymer modified cementitious mortar was used as a repair patch named Emaco S98P. Emaco S98P was a ready to use polymer modified cementitious mortar mixed with cement, standard various powder polymer.

From the results the conclusions attained there were: within limited 4 weeks exposure duration the crack width did not have any significant influence on the penetration of CO_2 from exposed surface, crack was similar to exposed boundary since CO_2 was found on the crack face and with the increase of crack width corrosion was localized near crack and CO_2 did not penetrate inside the concrete or Emaco from the crack surface.

2.10 Corrosion Rate

The presence of the diffusing reactants, including chloride, oxygen and moisture, are fundamental to the rate at which corrosion progresses. Environmental factors such as temperature and pH of the concrete will also affect the rate of corrosion. Reactions in various zones of a concrete member or structure will likely occur at different rates and times, depending upon variations in environmental exposure and electrochemical interaction between the zones. It was stated previously that, as the corrosion process continues, the volume of corrosion product increases until the tensile strength of the concrete is exceeded and cracking occurs. Such cracking will emanate from the reinforcement to the nearest surface, and a direct path is created for further ingress of chloride, oxygen and water to the steel surface. As further amounts of corrosion products accumulate, the crack will evolve into a delaminating or spall, resulting in the effective or actual loss of concrete cover, and leaving the steel directly exposed to the source of reactants, the environment [13].

2.11 Factors Influencing Corrosion Rate

Once a sufficient amount of aggressive agents reached the steel reinforcing bars to depassivate the bars and initiate corrosion, factors influencing the corrosion rate of steel reinforcing bars embedded in concrete include [61]:

First: Availability of water and oxygen.

Second: Ratio of the steel surface area at the anode to that at the cathode.

Third: Amount of chloride ions in the pore water.

Fourth: Resistivity of the concrete.

Fifth: Temperature.

Sixth: Relative humidity (both internal and external).

Seventh: Concrete microstructure

2.12 Methods of Corrosion Monitoring

Techniques for corrosion monitoring are well established for reinforced concrete structures. Because corrosion is an electrochemical process, the collection and interpretation of data is relatively easy. As introduced during the corrosion of steel reinforcement, electrons are released as a product of the anode chemical reaction. The electrons flow from the site of corrosion (anode) to a non-corroding site (cathode). This allows for corrosion risk and corrosion rate to be evaluated through electronic means (i.e., voltmeter measurements) [36].

There are many methods used in corrosion monitoring such as: Half-cell potential, electrochemical impedance spectroscopy, Open circuit potential measurements, Ultrasonic pulse velocity technique and linear polarization resistance technique (that was used in this research).

2.13 Polarization Resistance Technique (LPR)

The LPR technique has become a well-established method of determining the instantaneous corrosion rate measurement of reinforcing steel in concrete. Due to the widespread corrosion of reinforcing steel in concrete structures there has been a concerted demand for the development of non-destructive techniques to enable accurate assessment of the condition of reinforced concrete structures. LPR monitoring has been developed to address this need. The technique is rapid and non-intrusive, requiring only a connection to the reinforcing steel. The data provides a valuable insight into the instantaneous corrosion rate of the steel reinforcement, giving more detailed information than a simple potential survey. The LPR data enables a more detailed assessment of the structural condition and is a major tool in deciding upon the optimum remedial strategy to be adopted. It is thus imperative that the LPR measurements obtained are accurate [7].

The polarization resistance, R_p , is equal to the slope of the curve ($\Delta E / \Delta i_{app}$). The corrosion rate can then be determined through the relations of the Stern-Geary equation:

$$R_p = \Delta E / \Delta i_{app} \quad B = \beta_a \beta_c / 2.3 (\beta_a + \beta_c) \quad I_{corr} = B / R_p$$

where β_a and β_c are the anodic and cathodic Tafel slopes, respectively, B is the Tafel constant, and I_{corr} is the corrosion current. By dividing I_{corr} (Amps) by the surface area (cm^2) of the polarized steel, then the corrosion current density, I_{corr} is obtained. The Tafel slopes are difficult to obtain without damaging the system. For this reason, many researchers assume values for the Tafel slopes. Their basis for assumption comes from related published work. The assumed Tafel slopes (both anodic and cathodic) for corrosion of reinforcement in concrete are typically 0.120V [62].

Linear polarization was derived from experimental data that showed that the slope of the linear curve of applied cathodic and anodic current vs. potential is inversely proportional to the corrosion rate. Figure (2.4) illustrates how linear polarization is derived graphically [63].

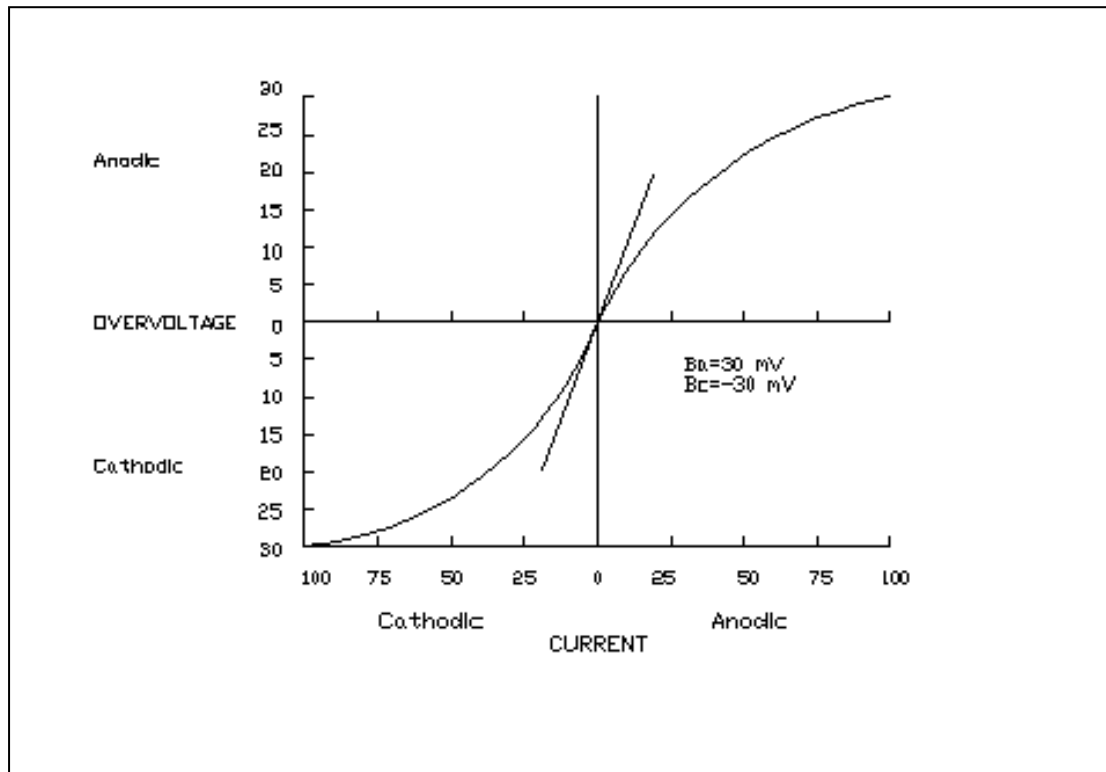


Figure (2.4) Hypothetical anodic and cathodic polarization curve [63].

2.14 Corrosion Inhibitors

Corrosion inhibitors are chemical admixtures added to Portland cement concrete mixes during batching-usually in very small concentrations- as a corrosion-protecting measure [61].

Inhibitors are often used in combination with low- permeability concrete and usually they have the effect of increasing the threshold chloride concentration needed to initiate corrosion [61].

Corrosion inhibitors are widely used to prevent or delay corrosion of reinforcing steel in concrete. There are three general groups into which corrosion inhibitors can be classified: anodic, cathodic and adsorption inhibitors [64].

Anodic inhibitors react with the ions of the corroding metals increasing the polarization of the anode and producing thin passive film or salt layers which coat the anode [8]. Two types of anodic corrosion inhibitors are important for steel, those which are oxidizing agents and those which require dissolved oxygen to be effective. Anodic inhibitors are said to be dangerous because the corrosion rate will increase if the inhibitor is not enough [65].

Cathodic inhibitors affect cathodic reactions. They react with the hydroxyl ions to precipitate insoluble compounds on the cathode site and prevent access of oxygen or form a layer of adsorbed hydrogen on the cathode surface [65]. They are said to be safe because the active cathode area is reduced even if little inhibitor is added [8].

From the two corrosion inhibitor groups, anodic inhibitors were found to be more efficient than cathodic corrosion inhibitors. Presently a combination of both is being used to provide most corrosion protection [65].

Andrade et al [1991] [66] presented a study on the inhibition action of sodium monofluorophosphate MFP ($\text{Na}_2\text{PO}_3\text{F}$) for reinforcement in concrete. In that work it has been considered either when added to the mixing water or penetrating from outside. The inhibitor effect has been measured by using electrochemical techniques. The mixing water contained (0.5 M/L) of chloride and (0, 0.05, 0.1 and 0.5 M/L) of MFP.

Results indicate that $\text{Na}_2\text{PO}_3\text{F}$ may act as inhibitor of reinforcement corrosion although it seems that the inhibition effect enhances when

$\text{Na}_2\text{PO}_3\text{F}$ penetrates through the hardened concrete. It was shown that the minimum ratio of MFP/Cl^- must be equal to 1 to get efficient inhibitor.

Sagoe-Crentsil et al [1993] [67] investigated the using of water soluble carboxylic acids as corrosion inhibitors. NaCl was introduced into some mix formulation at a fixed level of 2.5% by weight of dry cement to give a corresponding initial chloride ion concentration in the mix water equivalent to 862 mM/L. The level of the organic admixtures was also kept constant, at 2.5% of the anhydrous salt by weight of dry cement. They remain largely soluble after curing in cement for up to 90d.

Corrosion current measurements showed that water soluble carboxylic acids (malonic acid, a dicarboxylic acid) to be a very effective corrosion inhibitor even in the presence of 2.5% wt chloride. Unfortunately, it has an initial retarding effect on the set of Portland cement.

Abd El-Rehim et al [1999] [68] studied the effectiveness of 4-aminoantipyrine (AAP) as a corrosion inhibitor for mild steel in 2 M HCl solution using different techniques: weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

The results showed that 4-aminoantipyrine (AAP) behaves as an anodic inhibitor for mild steel corrosion in 2 M HCl . And the protection efficiency increases with increase in inhibitor concentration but decreases with increase in temperature.

Refaey et al [2000] [69] investigated the inhibition effect of phosphate (PO_4^{-3}), chromate (CrO_4^{-2}), molybdate (MoO_4^{-2}) and nitrite (NO_2^-) ions on the pitting corrosion of steel in 0.1 M NaCl solution by using potentiodynamic polarization and scanning electron microscope (SEM) techniques. The addition of increasing concentrations of (PO_4^{-3}), (CrO_4^{-2}), (MoO_4^{-2}) and (NO_2^-) anions causes a shift of the pitting potential (E_{pit}) in the positive direction, indicating the inhibitive effect of the added

anions on the pitting attack. The adsorption characteristics of these anions on the steel surface play a significant role in the inhibition processes. The (PO_4^{-3}) anion has a strong inhibitive effect on chloride pitting corrosion.

Kahraman [2002] [70] evaluated the effectiveness of sodium benzoate as an inhibitor to slow down or prevent atmospheric corrosion/discoloration of the local mild steel during storage in the Arabian Gulf region. Test specimens were prepared from locally produced reinforcing steel products. The inhibitor solution was applied on steel specimens at a concentration of 100 mM for 1 day at room temperature. Corrosion was evaluated through weight loss determination and electrochemical technique.

It has been found that the treatment of steel with sodium benzoate lowered its corrosion rate during initial days of its exposure to the atmosphere. Atmospheric corrosion inhibition performance of sodium benzoate deteriorated with exposure time for longer exposure durations and the atmospheric corrosion rates of sodium benzoate-treated specimens reached that of the unprotected specimens at the end of 90 days of atmospheric exposure.

Al-Amoudi et al [2003] [71] studied the effectiveness of four types of inhibitors in mitigating corrosion of reinforcement in concrete at five levels of contamination, i.e, 0.8% chloride plus 1.5% SO_3 ; sea water , brackish water and unwashed aggregates. These inhibitors were: calcium nitrite at two dosages (2%, 4%) by weight of cement, calcium nitrate at three dosages (2%, 3% and 4%) by weight of cement and two organic inhibitors (CI, CII) at their recommended dosages.

The results showed that all the four inhibitors investigated were effective in delaying the initiation of reinforcement corrosion, and all inhibitors were equally effective in retarding the rate of reinforcement corrosion in the chloride contaminated concrete specimens. In the

concrete specimens prepared with sea water, 2% calcium nitrite was more effective in retarding reinforcement corrosion than the other inhibitors. And in the specimens contaminated with 0.8% chloride plus 1.5% sulfate, the minimum corrosion current values were noted on the steel in the concrete specimens incorporating 4% calcium nitrite and 3% calcium nitrate. The compressive strength of the concrete specimens incorporating all the four inhibitors was more than control specimens. And the concrete specimens admixed with 4% calcium nitrate showed the best increasing of compressive strength (about 14.5%).

De Schutter and **Luo** [2004] [72] presented an experimental study on the effect of different corrosion inhibiting admixtures on concrete properties. The effect of four different corrosion inhibiting admixtures is evaluated: a calcium nitrite-based inhibitor, an amino and ester-based organic inhibitor, an aminoalcohol-based inhibitor and a migrating corrosion inhibitor. The properties of the fresh concrete (density, workability and air content) and of the hardened concrete (compressive strength, splitting tensile strength) were evaluated.

It has been found that calcium nitrite-based corrosion inhibitor increased the early age compressive strength, showing the accelerating properties. And it increased somewhat the air content as well as the workability of the fresh concrete. Splitting tensile strength is reduced by about 5.5% at 28 days age. For amino and ester-based organic inhibitor, the results showed that it caused a decrease of the compressive strength by about 10–20%. And it decreased the splitting tensile strength by about 20.5%. The effect on workability is not clear. The air content might be slightly increased. The results showed also that the aminoalcohol-based inhibitor seems to decrease the compressive strength, while, the workability tends to be increased. Splitting tensile strength is decreased by about 17%. The air content might be slightly increased. A migrating

corrosion inhibitor decreased somewhat the early age concrete strength, while the ultimate compressive strength seems to be improved. The effect on workability might depend on the way in which the inhibitor is added (powder or emulsion). The splitting tensile strength is increased by about 7%. The air content might be slightly increased.

Fedrizzi et al [2005] [73] studied the effectiveness of migrating corrosion inhibitors (MCIs) and repair mortars against rebar corrosion in concrete specimens made by ordinary Portland cement with w/c ratio equal to 0.6 and containing 1% wt. of chlorides. An alkanolamine-based inhibitor was tested in addition with a common mortar and two repair mortars. Electrochemical techniques, measurements of corrosion potential and electrochemical impedance spectroscopy (EIS) were used to determine the corrosion behaviour of the specimens when a cell containing a 3.5% NaCl solution was applied on the rehabilitation mortar.

Results demonstrated that the simultaneous use of the alkanolamine-based inhibitor with a good barrier coating offers protection against rebar corrosion and allows rehabilitation of deteriorated concrete structures.

The performance of an organic, penetrating corrosion inhibitor in reducing the rate of corrosion and delaying the onset of corrosion in carbonated concrete was investigated by **Heiyantuduwa et al** [2006] [74]. Laboratory trials were undertaken on specimens treated with the corrosion inhibitor before and after accelerated carbonation. Corrosion monitoring was undertaken for 11 months measuring corrosion rate, rebar potential and resistivity.

Results indicated that the penetrating corrosion inhibitor is capable of reducing corrosion rates and delaying the onset of corrosion under carbonation conditions. The effectiveness of the inhibitor was also assessed on site structures exhibiting severe carbonation-induced

corrosion. Corrosion monitoring on site was done for a period of nine months. Findings from site studies confirmed that surface application of the corrosion inhibitor significantly reduced the corrosion rate of reinforcement embedded in carbonated concrete when compared with untreated elements.

Saraswathy and song [2007] [75] investigated the performance of the anodic inhibitors (sodium nitrite and zinc oxide), cathodic inhibitors (mono ethanol amine, diethanol amine and tri ethanol amine) and mixed inhibitors to control rebar corrosion. The concrete specimens were immersed in 3% sodium chloride solution for 120 days. Compressive strength test, tensile strength test, chloride diffusion test and macro cell corrosion test were conducted by varying the type of inhibitors and varying the concentration of inhibitors. Inhibitors used were (control(OPC)-System1, sodium citrite- System2, zinc oxide- System3, mixed (sodium nitrite + zinc oxide)- System4, monoethanolamine-System5, diethanolamine-System6, triethanolamine- System7). Percentages of inhibitor used were (1%, 2%, 3%) by weight of cement.

Electrochemical results indicated that the zinc and mixed inhibitor added systems are found to perform better than the control and other inhibitor added systems. And it was observed that the optimum percentage addition of inhibitor is 2% by weight of cement.

Compressive strength measurements revealed that, all the inhibitor admixes concretes at 2% addition level showed a maximum compressive strength, and zinc oxide and (sodium nitrite + zinc oxide) admixed concrete systems have shown higher compressive strength values than other systems. Measurements revealed that the tensile strength of concrete is not at all affected by addition of inhibitors.

Abdul Amir [2008] [76] investigated the effectiveness of using sodium benzoate, potassium dichromate as corrosion inhibitors in three

concentrations (1%, 2% and 3% by weight of cement) and SBR (Styrene-Butadiene- Rubber) emulsion in three concentrations (10%, 15% and 25% by volume of water) on corrosion of steel reinforcement (by using linear polarization technique) and their effectiveness on concrete properties; compressive strength, splitting tensile strength, flexural strength and absorption for three ages (28, 60 and 90 days) with mix proportion 1:1.8:2.5 (cement : sand : gravel). The reinforced specimens were partially immersed in 3.5% sodium chloride solution for three months.

The polarization results indicated that the sodium benzoate and potassium dichromate with 2% concentration by weight of cement have the best corrosion inhibition (about 98%). And SBR emulsion in concentration 25% by volume of mixing water led to inhibition about 97%.

The concrete properties test results showed that the use of sodium benzoate, potassium dichromate in 2% concentration by weight of cement cause a considerable reduction in compressive strength about 15% and 4% at 28 days respectively, but in the later ages the compressive strength increased about 7% and 11% at 90 days respectively. The adding of these admixtures led to considerable improvement in the other mechanical properties of concrete mixes with increasing in; splitting tensile strength about 17% for sodium benzoate and 21% for potassium dichromate, flexural strength about 18% and 20% respectively, also they caused reduction in absorption with 38% and 42% respectively. The test results of SBR emulsion in concentration 25% by volume of mixing water led to a considerable improvement in all mechanical properties of concrete mixes with an increase in; compressive strength about 8%, 11% and 7% at ages 28, 60 and 90 days respectively, splitting tensile strength and flexural strength about 37%, and caused a maximum reduction in absorption about 77%.

2.15 Inhibitor Efficiency

The inhibitor efficiency can be expressed as in the following equation [77]:

$$\text{Inhibitor efficiency (\%)} = 100 (CR_{\text{uninhibited}} - CR_{\text{inhibited}}) / CR_{\text{uninhibited}} \quad (2-1)$$

Where;

$CR_{\text{uninhibited}}$ = corrosion rate of the uninhibited system.

$CR_{\text{inhibited}}$ = corrosion rate of the inhibited system.

Kondratova et al [2003] [78] presented an investigation of two types of commercial corrosion inhibitors (OCI, CNI) that were added to concrete for corrosion protection. Reinforced concrete slabs were cast with dimensions (55×230×300) mm and concrete cover 20mm. The water to cement ratio was 0.4, and the concrete slabs were uncracked and precracked. A simulated crack 0.2 or 0.4 mm wide was formed transverse to the axis of the reinforcing bar during the casting. According to the manufacturer's recommendations, the addition of the inhibitors were (OCI=5 l/m³, CNI=25 l/m³). The specimens were visually inspected and the corrosion rates were measured annually using the linear polarization technique. Some of the concrete slabs were broken open after 12 months of exposure and corrosion damage was evaluated. Water-soluble chloride content analysis was performed at this time. After three years of exposure, it was found, that OCI was more efficient than CNI in terms of corrosion rate reduction in uncracked concrete; and in cracked concrete both corrosion inhibitors were relatively inefficient.

The suitability of some inhibitors (potassium dichromate, calcium nitrite and formaldehyde) in reducing corrosion of mild steel reinforcement in concrete (immersed in sea water and dilute sulphuric

acid to simulate two factors) was investigated by **Burubai** and **Dagogo** [2007] [79] by using the potential monitoring technique. Two sets of concrete blocks were made with nominal mix ratio 1:2:4 (cement: sand: gravel). The dimensions of blocks were similar each being 160mm long, 100mm wide and 1000mm thick. The first set of five specimens were admixed with different inhibitors (specimen 1: prepared with 100g calcium nitrite plus 100g sodium chloride salts to accelerate corrosion, specimen 2: prepared with 100g formaldehyde plus 100g sodium chloride salts to accelerate corrosion, specimen 3: prepared with 100g potassium dichromate plus 100g sodium chloride salts, specimen 4: prepared with 100g potassium dichromate plus 100g formaldehyde plus 100g sodium chloride salts to accelerate corrosion and specimen 5: prepared with 100g chloride salts). The second set had no chemicals or inhibitors admixed with the concrete. Two specimens were made for each case. One partially immersed in sea water (to simulate marine environment) and the other partially immersed in dilute sulfuric acid (to simulate microbial environment).

The experimental results showed that, after 12 months in sea water, admixtures of potassium dichromate and formaldehyde were identified as a good inhibitor for concrete mix, but it caused substantial loss of compressive strength while calcium nitrite exhibit the best inhibiting qualities with no effect on the compressive strength of the concrete blocks. By comparison with reference specimens, the efficiency of the inhibitors were: 54% for potassium dichromate, 53% for formaldehyde, 55% for (potassium dichromate + formaldehyde) and 59% for calcium nitrite. It is also evidence from the results, that all the inhibitors tested showed good inhibiting properties when the blocks were immersed in dilute sulphuric acid solution.

Mohammed and **Mohana** [2008] [80] investigated the effectiveness of sodium benzoate (SB) and sodium 4-(phenylamino) benzenesulfonate (SPABS) on the corrosion behavior of low carbon steel by using gravimetric method in the temperature range of 30– 80 C°, velocity range of 1.44–2.02 m s⁻¹ and concentration range of 6.94 ×10⁻⁴ to 4.16 × 10⁻³ mol dm⁻³ SB and 3.69 ×10⁻⁴ to 2.06 ×10⁻³ mol dm⁻³ SPABS. The obtained results indicated that the inhibition efficiency (w_{IE} %) at 1.56 m s⁻¹ is not in excess of 81.5% at 4.16 × 10⁻³ mol dm⁻³ SB and 84.4% at 2.06 × 10⁻³ mol dm⁻³ SPABS. The inhibitive performance of these compounds showed an improvement with increasing concentration up to critical values of SB and SPABS; beyond these concentrations no further effectiveness is observed. These inhibitors retard the anodic dissolution of low carbon steel by protective layer bonding on the metal surface.

2.16 Concluding Remarks

1. Corrosion inhibitors can reduce corrosion rate in reinforced concrete structures and then extend its service life. Inhibitors are affected by many factors like alkalinity of cement and concentration of (Cl⁻) ions.
2. Anodic inhibitors are the most using in prevention of reinforcement from corrosion. That may be attributed to the direct effect of these inhibitors on the dissolution of the anode, which is considered the first step in corrosion process.
3. Quantity of C₃A in cement is important for reducing free chloride ions, which are responsible for reinforcement corrosion.
4. Chloride percentage is important to control the corrosion of reinforcement in concrete.
5. Chemical admixtures (fly ash, silica fume and rice husk ash) can delay corrosion initiation by reducing permeability of concrete.

Chapter Three

Experimental work

3.1 General

Corrosion of reinforcing steel in concrete is one of the greatest threats to the durability of reinforced concrete. It is the most single expensive corrosion related problem, and affects the integrity of thousands of reinforced concrete structures. Bridges located in aggressive environments, such as exposure to seawater or deicing salts are highly susceptible to corrosion activity [63].

This chapter includes description of materials properties, preparation and mixing, mechanical tests of concrete specimens and electrochemical tests.

3.2 Materials

3.2.1 Cement

Ordinary Portland cement (Type 1) is used in this study. The cement is (Tasluja). It is stored in a dry place to avoid exposure to atmospheric condition.

The chemical composition and physical properties of this cement (as tested in cement test laboratory/ Babylon University) are shown in Tables (3.1) and (3.2) respectively. Test results indicated that the adopted cement conforms to the Iraqi specification No.5/1984 [81].

Table (3.1) Chemical composition and main compounds of Cement

Oxides Composition	Content %	Limits of (I.O.S.) No.5/1984 %
CaO	62.28	-
SiO ₂	20.82	-
Al ₂ O ₃	4.34	-
Fe ₂ O ₃	4.2	-
MgO	3.15	<5
SO ₃	2.45	<2.5
Free lime	1.4	
L.O.I.	2.33	<4
Insoluble residue	1.26	<1.5
Lime Saturation Factor, L.S.F.	0.89	0.66-1.02
Main Compounds (Bogue's equations)		
C ₃ S	47.46	-
C ₂ S	23.88	-
C ₃ A	4.39	-
C ₄ AF	12.87	-

Table (3.2) Physical properties of cement

Physical Properties	Test Results	Limits of (I.O.S.) No.5/1984
Specific surface area (Blaine method), m ² /kg	328	≥230
Setting time (Vicat apparatus), Initial setting, min Final setting, min	110 225	≥45 ≤600
Compressive strength, MPa 3 days 7 days	21.5 31.2	≥15 ≥23

3.2.2 Fine Aggregate

Natural sand brought from Al-Ekhaider region is used as a fine aggregate in this research. Table (3.3) illustrates the sieve analysis of fine aggregate used throughout this work. Table (3.4) illustrates the physical properties and sulfate content of the fine aggregate used.

Results indicate that the fine aggregate grading and the sulfate content are within the requirements of the Iraqi specification No.45/1984 [82]. This test is made in the laboratories of Engineering College/Babylon University.

Table (3.3) Sieve analysis of fine aggregate

Sieve Size (mm)	Cumulative Passing %	Cumulative Passing % Limits of (I.O.S.) No.45/1984 Zone (2)
10	100	100
4.75	97.4	90-100
2.36	88	75-100
1.18	77	55-90
0.60	59.1	35-90
0.3	22	8-30
0.15	5.1	0-10

Table (3.4) Physical properties and sulfate content of fine aggregate

Properties	Test Results	Limit of Specification %
Specific gravity	2.7	-
Absorption %	0.7	-
Sulfate content as SO ₃ %	0.44	≤0.5

3.2.3 Coarse Aggregate

Rounded gravel of maximum size (19) mm from Al-Niba'ee region is used. The grading and physical properties (with sulfate content) are shown in Tables (3.5) and (3.6) respectively. They were within the requirements of the Iraqi specification No.45/1984 [82]. This test is made in the laboratories of Engineering College/Babylon University.

Table (3.5) Grading of coarse aggregate

Sieve Size (mm)	Cumulative Passing %	Cumulative Passing % Limits of (I.O.S.) No.45/1984
37.5	100	100
20	96.5	95-100
10	45	30-60
5	6	0-10

Table (3.6) Physical properties and sulfate content of coarse aggregate

Properties	Test Results	Limit of Specification %
Specific gravity	2.65	-
Absorption %	0.5	-
Sulfate content as SO ₃ %	0.0813	≤0.1

3.2.4 Steel Reinforcing Wires

Locally available, smooth mild steel wires are used throughout this work. The wire diameter is 0.5 cm. The steel bars are cleaned by wetted grinding paper to remove any rust deposits from their surface (see Plate (3.1)). Table (3.7) shows the properties of the steel wires.

Table (3.7) Properties of steel wires.

Diameter (cm)	Cross Section Area (cm ²)	Length (cm)	Surface Properties
0.5	0.196	30	Smooth



a



b

Plate (3.1) (a) Steel wires before cleaning and (b) steel wires after cleaning.

3.2.5 Water

Tap water is used for both mixing and curing of concrete.

3.3 Admixtures

Corrosion inhibitors and permeability admixture are used in this study.

3.3.1 Calcium Nitrate (CN)

The trade mark of Calcium Nitrate is (Calcium Nitrat). It has a white color (see Plate (3.2)). Properties of Calcium Nitrate are illustrated in Table (3.8).

Rozenfeld [1981] [83] stated that the best concentration of adding (CN) was (2% by weight of cement). Calcium Nitrate is used in this study

in three percentages (20%, 50% and 80% of the best concentration) by combination with Ethanolamine admixture (see mix design). The inhibitor was mixed with a small part of mixing water for dissolving it before adding.

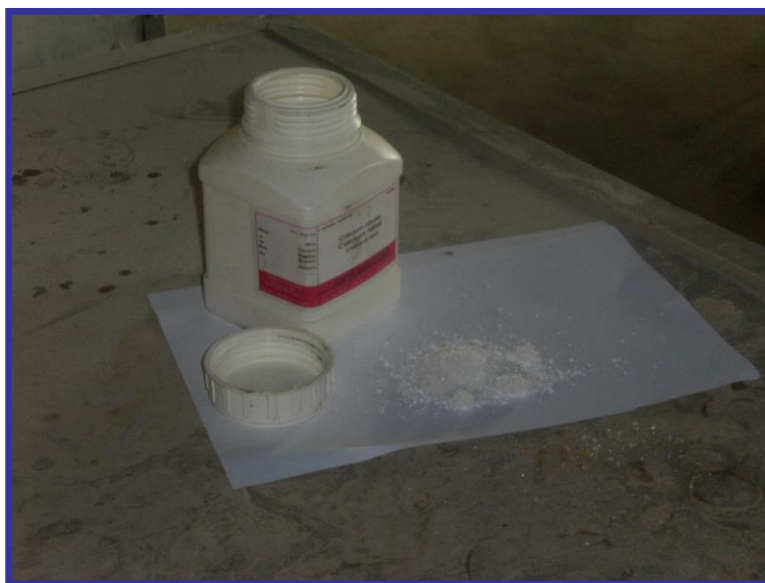


Plate (3.2) Calcium Nitrate

Table (3.8) Properties of Calcium Nitrate

Chemical Composition	Ca(NO ₃) ₂ .H ₂ O
Assay	98%
Impurities	(0.005%)Cl, (0.005%) Fe, (0.005%) SO ₄ , (0.005%) Cu
Color	White
Package	0.5 kg

3.3.2 Ethanolamine (EA)

Ethanolamine is a liquid like water organic base that acts as corrosion inhibitor for steel. Table (3.9) gives some properties of Ethanolamine. Plate (3.3) shows the Ethanolamine package.

Saraswathy and **Song** [2007] [75] declared that the best concentration of adding (EA) is (2% by weight of cement). Ethanolamine is used in this work in three percentages (80%, 50% and 20% of the best concentration) as a synergic with Calcium Nitrate admixture (see mix design). The weight of (EA) added is considered as a part of the weight of water required.

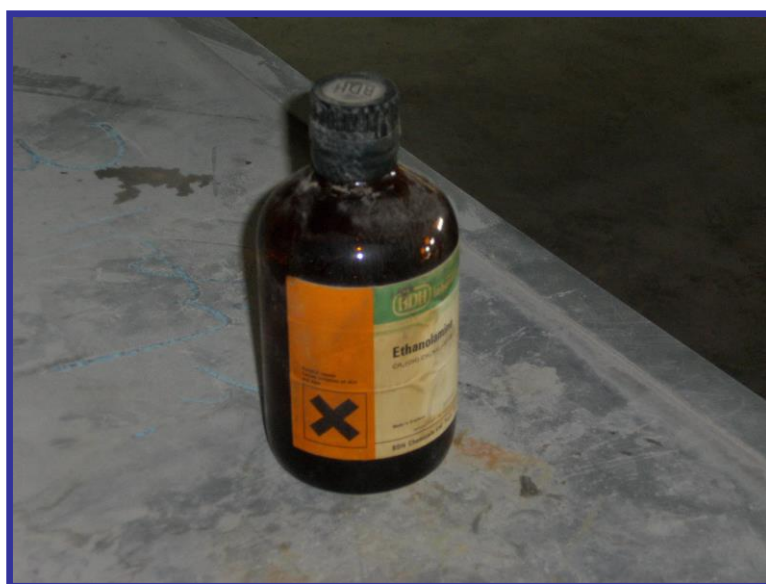


Plate (3.3) Ethanolamine

Table (3.9) Properties of Ethanolamine

Chemical Composition	Color	Assay	Package	Specific Gravity
$\text{CH}_2(\text{OH}).\text{CH}_2.\text{NH}_2$	Like water	99%	0.5 kg	1.014

3.3.3 Sodium Benzoate (SB)

Sodium Benzoate is an anodic, inorganic inhibitor. The trade name is 71300 Natriumbenzoat. It has white color (see Plate (3.4)). Table (3.10) illustrates some properties of Sodium Benzoate.

Abdul Amir [2008] [76] found that (2% by weight of cement) is the best concentration of adding (SB) to act as a good inhibitor. Also, Sodium Benzoate is used in three percentages (80%, 50% and 20% of the best concentration) by combination with Sodium Silicate (see mix design). Sodium Benzoate is dissolved in small quantity of mixing water before adding.



Plate (3.4) Sodium Benzoate [76].

Table (3.10) Properties of Sodium Benzoate

Chemical Composition	Color	Assay	Package
C_6H_5COONa	White	>97%	0.5 kg

3.3.4 Sodium Silicate (SS)

Liquid Sodium Silicate known as water glass, is produced by melting high purity silica sand along with sodium carbonate at 1100-1200C°. It is known as corrosion inhibitor since 1945 [84]. Sodium Silicate has a grey color as shown in Plate (3.5). Table (3.11) illustrates some properties of Sodium Silicate.

Rozenfeld [1981] [83] mentioned that the best concentration of adding (SS) was (1% by weight of cement). Then (SS) is used in three percentages (20%, 50% and 80% of the best concentration) by mixing with Sodium Benzoate admixture (see mix design).



Plate (3.5) Liquid Sodium Silicate

Table (3.11) Properties of Sodium Silicate

Chemical Composition	Color	Package
Na_2SiO_3	Grey	5 Liter

3.3.5 Potassium Dichromate (PD)

It is an inorganic inhibitor with grains look like sugar grains in size and shape with orange color as shown in Plate (3.6). Table (3.12) illustrates some properties of Potassium Dichromate.

Abdul Amir [2008] [76] showed that the best concentration of adding (PD) is (2% by weight of cement). Thus, (PD) is used in this investigation in three percentages (20%, 50% and 80% of the best concentration) by composing with Styrene Butadiene Rubber admixture (see mix design). Potassium Dichromate is dissolved in small quantity of mixing water before adding.



Plate (3.6) Potassium Dichromate

Table (3.12) Properties of Potassium Dichromate

Chemical Composition	$K_2Cr_2O_7$
Assay	99.8 %
Impurities	(0.003%) Insoluble matter, (0.005%) Cl, (0.02%) SO_4
Package	0.5 kg
Color	Orange

3.3.6 Styrene Butadiene Rubber (SBR)

SBR 100 is single component styrene butadiene rubber latex. It is designed to improve the physical properties of cement mixes and slurries. Plate (3.7) and Table (3.13) show the package and some properties of SBR 100.

Abdul Amir [2008] [76] concluded that the best concentration of adding (SBR) to the concrete to make a good inhibition for corrosion of steel was (25% by volume of water). Also, Styrene Butadiene Rubber is used in three percentages (80%, 50% and 20% of the best concentration) by composition with Potassium Dichromate admixture (see mix design).

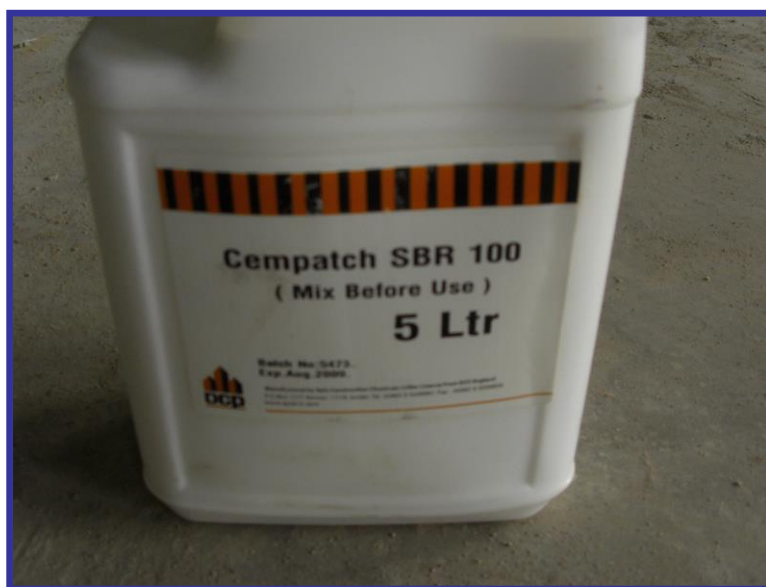


Plate (3.7) Styrene Butadiene Rubber (SBR 100)

Table (3.13) Properties of SBR 100

Color	Specific Gravity	Package	Fire
White	Around 1@25C°	(5, 25) Liter	Non-flammable

3.4 Mix Design

Concrete mixes are designed according to the American mix design method ACI 211[85] to have a compressive strength 25 MPa at age of 28 days. The proportions of mix (by weight) were 1:1.8:2.5 (cement : sand : gravel), with water to cement ratio (w/c) equal to 0.5. Table (3.14) shows the materials quantities for 1m³.

Table (3.14) Materials quantities for the concrete mix per 1 m³

Cement (kg)	Sand (kg)	Gravel (kg)	Water (l)
370	777	1023	185

Eleven concrete mixes are cast, two reference mixes and nine concrete mixes containing synergic admixtures, with three percentages for each synergic as shown in Figure (3.1).

Notes about Figure (3.1):

B_{SBR}: Best concentration of adding Styrene Butadiene Rubber = 25% by volume of water.

B_{PD}: Best concentration of adding Potassium Dichromate = 2% by weight of cement.

B_{EA}: Best concentration of adding Ethanolamine = 2% by weight of cement.

B_{CN}: Best concentration of adding Calcium Nitrate = 2% by weight of cement.

B_{SS}: Best concentration of adding Sodium Silicate = 1% by weight of cement.

B_{SB}: Best concentration of adding Sodium Benzoate = 2% by weight of cement.

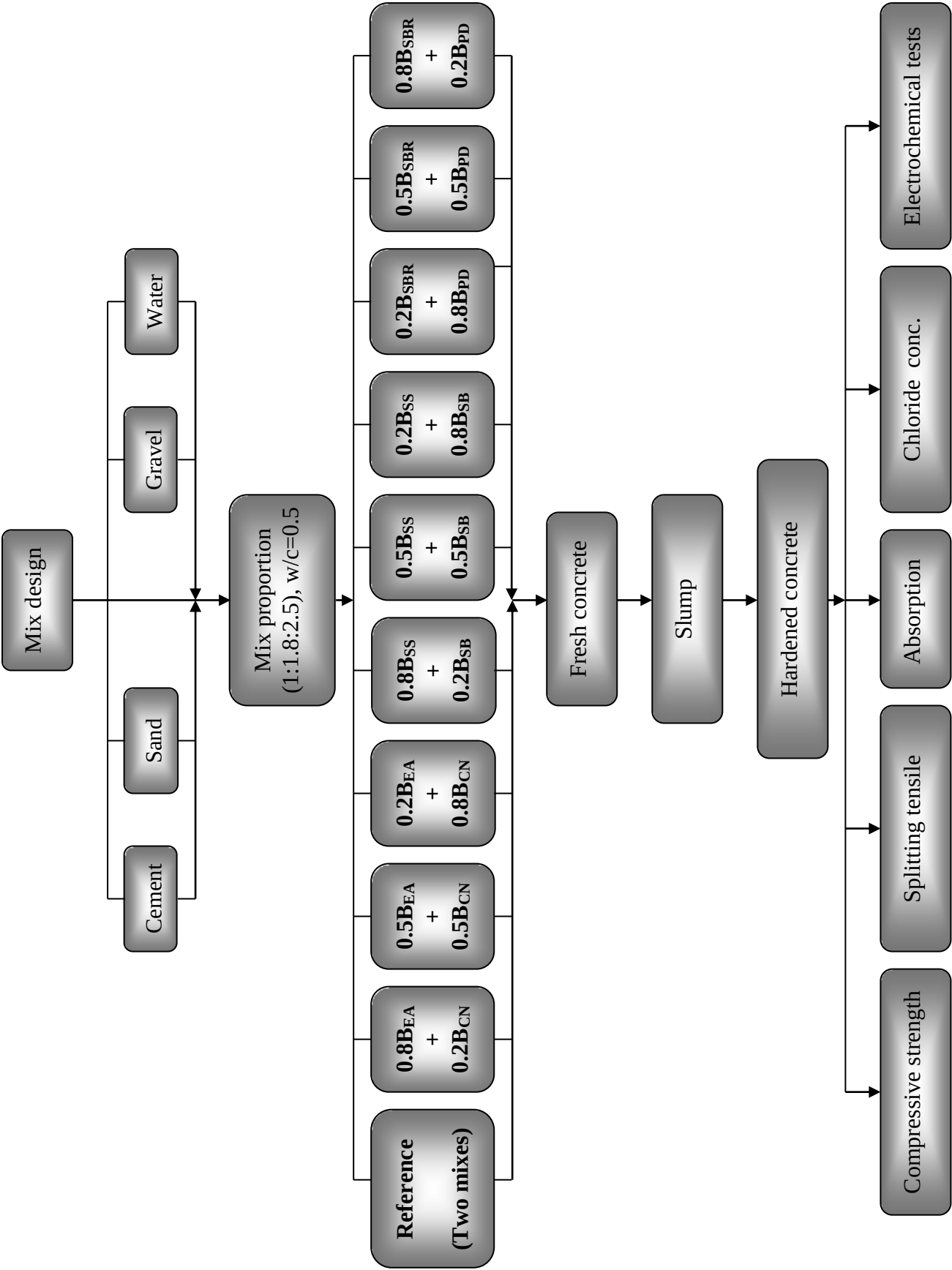


Figure (3.1) Schematic representation of experimental program

3.5 Mixing

Mixing process is carried out by using 0.1 m³ pan type mixer. The coarse and fine aggregate of reference mixes with about 2/3 of the required amount of water are initially mixed for about 1.5 minutes. The cement and remaining part of water are then added, and the whole mix ingredients are mixed for 1.5 minutes.

Concrete mix containing synergic admixtures (Calcium Nitrate + Ethanolamine), (Potassium Dichromate + Styrene Butadiene Rubber) and Sodium Silicate + Sodium Benzoate) is mixed similarly except that the corrosion inhibitor or permeability reducer is added to the mixing water to ensure uniform dispersion throughout the mixing water. Table (3.15) illustrates slump values for fresh concrete mixes.

Table (3.15) Slump properties of fresh concrete mixes.

Admixtures	Mixes Symbols	Percentage of Adding	Slump (mm)
Reference	R	Nil	56
Calcium Nitrate + Ethanolamine	CN + EA	20%B _{CN} +80%B _{EA}	59
		50%B _{CN} +50%B _{EA}	50
		80%B _{CN} +20%B _{EA}	70
Sodium Benzoate + Sodium Silicate	SB + SS	80%B _{SB} +20%B _{SS}	55
		50%B _{SB} +50%B _{SS}	70
		20%B _{SB} +80%B _{SS}	60
Potassium Dichromate + Styrene Butadiene Rubber	PD + SBR	20%B _{PD} +80%B _{SBR}	45
		50%B _{PD} +50%B _{SBR}	35
		80%B _{PD} +20%B _{SBR}	40

3.6 Preparing, Casting and Curing of Concrete Specimens

3.6.1 Preparing, Casting and Curing of Plain Concrete Specimens

Standard cubic steel moulds of 150 mm are used for compressive strength test. 100 × 200 mm cylindrical steel moulds are used for splitting tensile strength test. For absorption test, standard cubic steel moulds of 100 mm are used. The moulds are carefully cleaned and oiled before casting to avoid adhesion with the concrete surface. Placing of concrete is done in three layers. While placing concrete; a vibrator table is used in each layer to achieve good compaction then the specimens are leveled and covered with nylon sheets for 24 hr to prevent moisture evaporation from the surface. After demoulding, the specimens are completely immersed in tap water for (except compressive strength specimens) a period of 28 days. The compressive strength specimens are cured in tap water for periods of (28, 60 and 90 days).

3.6.2 Preparing, Casting and Curing of Reinforced Concrete Specimens

Prism steel moulds of 200 × 150 × 140 mm are used (see Figure (3.2)) for casting reinforced concrete specimens with three (5 mm) diameter steel wires. 18 cm of each wire is buried in concrete. The part wire 2 cm above the upper surface of concrete and 2 cm below the upper surface of concrete (inside the block) was isolated to avoid the corrosion of and around the interface (see Plate (3.8-a)). The casting and curing (see Plate (3.8-b)) are similar to plain specimens.

After the curing period (28 days) was completed, the reinforced specimens are partially immersed in water contaminated 3.5% NaCl for three months (see Plate (3.8-c)) to accelerate corrosion process.

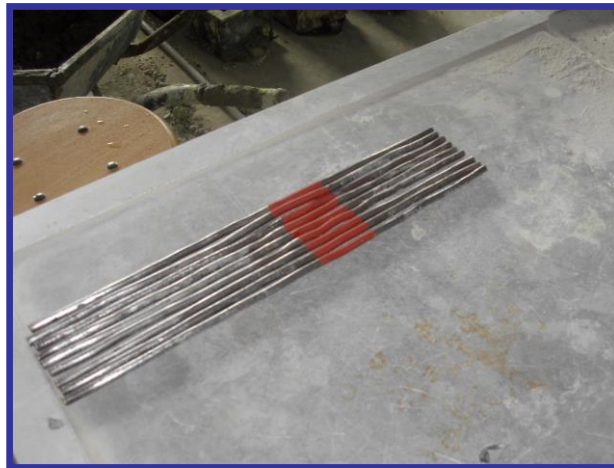
**a****b****c**

Plate (3.8) (a) Steel wires with 4 cm insulation, (b) curing of reinforced specimens and (c) partially immersed of reinforced concrete specimens in 3.5% NaCl.

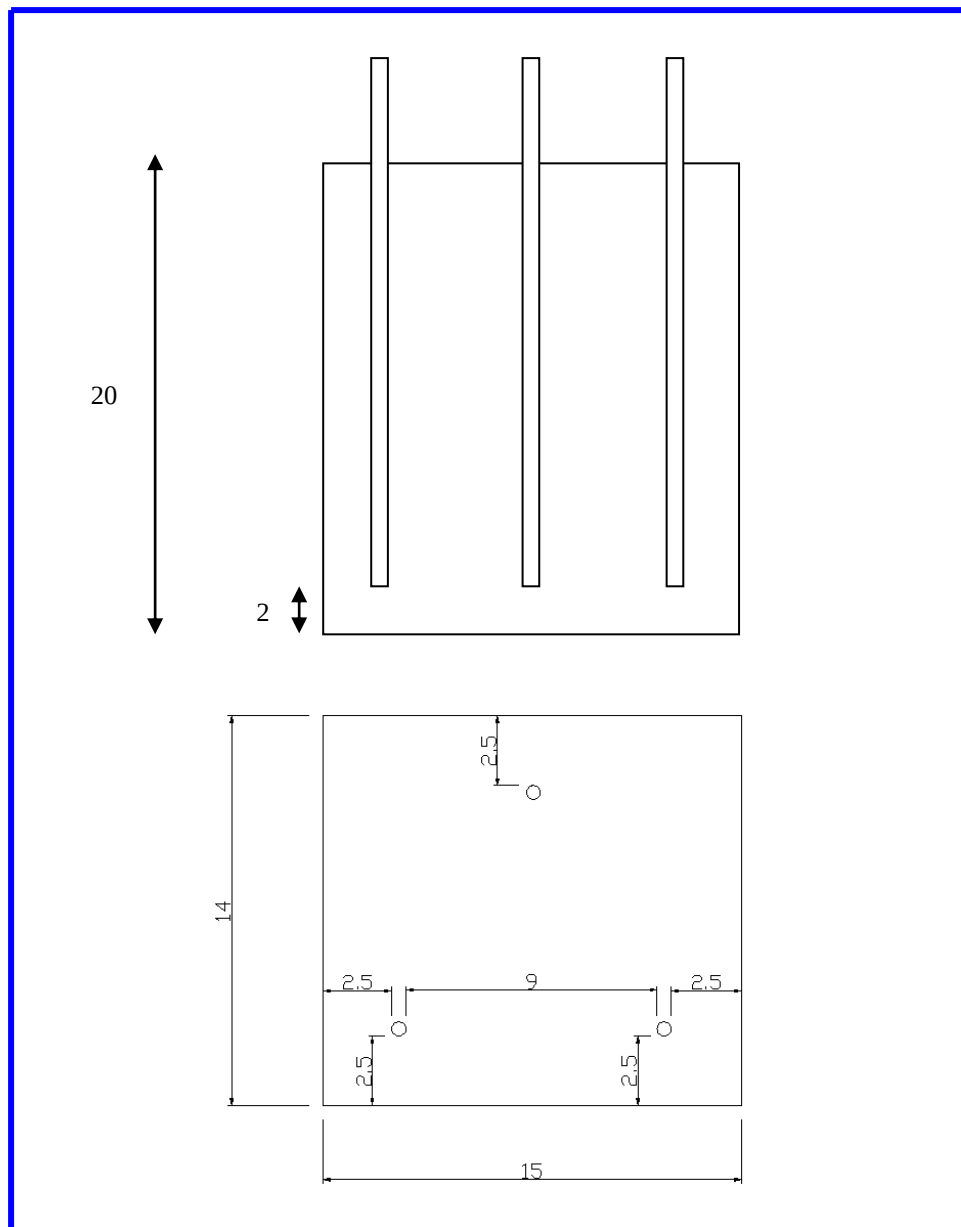


Figure (3.2) Dimensions of reinforced specimens, (cm).

3.7 Concrete Tests

3.7.1 Compressive Strength

Cubes of (150) mm are cast and tested (according to B.S. 1881: Part 116, 1989) [86] for determining the compressive strength of the concrete mixes for three ages of testing (28, 60 and 90) days. A total (99) specimens are cast, (33) for each age. Average of three specimens is

considered. The test is made via compressive strength machine (2000 KN of capacity) in the laboratories of Engineering College/Babylon University.

3.7.2 Splitting Tensile Strength

For splitting tensile strength test (33) cylindrical specimens are cast with dimensions (100×200) mm, in accordance with ASTM C496–86 [87]. The average of three cylinders is taken for each value. Tests are performed by using compressive strength machine in the laboratory of Engineering Collage/Babylon University. The splitting tensile strength is given by the following equation:

$$f_t = 2P/\pi DL \quad (3-1)$$

Where;

f_t : splitting tensile strength, (MPa).

P: maximum applied load, (N).

D: diameter of cylinder, (mm).

L: length of cylinder, (mm).

3.7.3 Absorption Test

Absorption test is determined according to ASTM C 642-97 [88]. In this test, 100mm cube specimens are used. At 28 days age, the absorption of the average of three specimens is determined. At this age the specimens mass is determined and dried in an oven at a temperature of (100-110) C° for 24h. After removing each specimen from the oven, it is allowed to cool in dry air to a temperature of (20-25) C° and the mass is determined. The specimens are placed in the oven for a second drying treatment of 24h again to determine the mass, and the procedure is repeated until the difference between any successive values becomes less

than 0.5% of the lowest value obtained. After final drying, cooling, and determination of mass, the specimens are immersed in water at approximately (21) C° for 48h and until two successive values of the mass of the surface-dried sample at intervals of 24h show an increase in mass of less than 0.5% of the largest value. The specimens are surface dried by removing surface moisture with a towel, and the mass is determined. Average of three specimens is considered. This test is made in the laboratories of Engineering College/Babylon University.

Absorption is calculated using the following formula:

$$A = [(M_s - M_d) / M_d] * 100 \quad (3-2)$$

Where:

A: absorption value (%).

M_s: mass of surface dry specimen in air, (kg).

M_d: mass of oven-dry specimen in air, (kg)

3.8 Chloride Concentration (Cl⁻) Test

Chloride concentration in hardened concrete is obtained by analysis of small parts (at depth: 2.5-3 cm) from reinforced concrete specimens and concrete cubes specimens that tested by compressive strength machine. These cubes were cast from the same batch of concrete and cured under the same conditions. This test is conducted in the Environment Laboratory/Engineering College/Babylon University.

3.9 Electrochemical Tests

3.9.1 Polarization Test

In this investigation direct current (D.C) measurements are performed on (150×140×200) mm prisms. The circuit used (according to ASTM STP 908) [89] is as shown in Plate (3.9).

3.9.1.1 Instrument

The setup used to determine the corrosion current, consists of:

1. Stabilized power supply, type "EISCO", its main function is to obtain a constant D.C voltage with different levels. The D.C voltage ranged between (120 to -120) mV.
2. Two high digital Multimeters, type "MX 553 – Metcix ", one of them is used as a voltage measuring device and the other as a current measuring device (see Plate (3.9)).

3.9.1.2 Test Procedure

The details of the electrochemical techniques (three electrode method) are according to ASTM STP 908 [89]. **The Working Electrode (W.E)** potential is measured against the reference electrode, provided that an ohmic resistance gradient is significantly reduced and current flows only between the auxiliary electrode and the working electrode. **The Auxiliary Electrode (A.E)**: It passes current to the working electrode (specimen) to be tested. **The Reference Electrode (R.E)** does not carry the polarizing current [89]. To calculate linear polarization resistance and corrosion rate, the three electrodes considered as follows:

1. Wire1 is a Reference electrode (R.E).
Wire2 is a Working electrode (W.E).
Wire3 is an Auxiliary electrode (A.E).

2. The electrical circuit for polarization and corrosion rate measurement is connected as shown in Plate (3.9).
3. The following voltages are applied [-120mv, -90mv, -60mv, 60mv, 90mv and 120mv], in each value of these voltages the current value is recorded. The readings are recorded before and after immersing in (3.5% NaCl solution) along three.

After six weeks of immersing the reinforced concrete specimens in 3.5% NaCl solution, low corrosion rate was recorded for the reference mix (without any admixture) because of the slowly development of corrosion process.

To increase corrosion rate (low corrosion in concrete samples without any adding), 10% of the compressive strength load was applied over two of the three reinforced concrete specimens after 6 weeks of immersing in 3.5 % NaCl solution by compressive strength test machine. This procedure was adopted to make initial micro cracks in the concrete specimens to make a path for chlorides to ingress and reach the steel wires faster.

3.9.2 Electrical Resistance Test

Measurements are conducted on the same specimens that are used for linear polarization measurements.

3.9.2.1 Instrument

The electrical resistance for the reinforced concrete specimens is measured by using Ohmmeter machine (MX 553 – Metcix) digital multimeter as shown in Plate (3.10).

3.9.2.2 Test Procedure

Two steel wires are required in this test. After connecting the steel wires to the Ohmmeter machine, the electrical resistance is taken. The reading of the machine is in $K\Omega$ (Kilo Ohm) units. The results of the electrical resistance before and after partial immersing of specimens in [3.5% NaCl solution] for three months are measured and given in the next chapter.

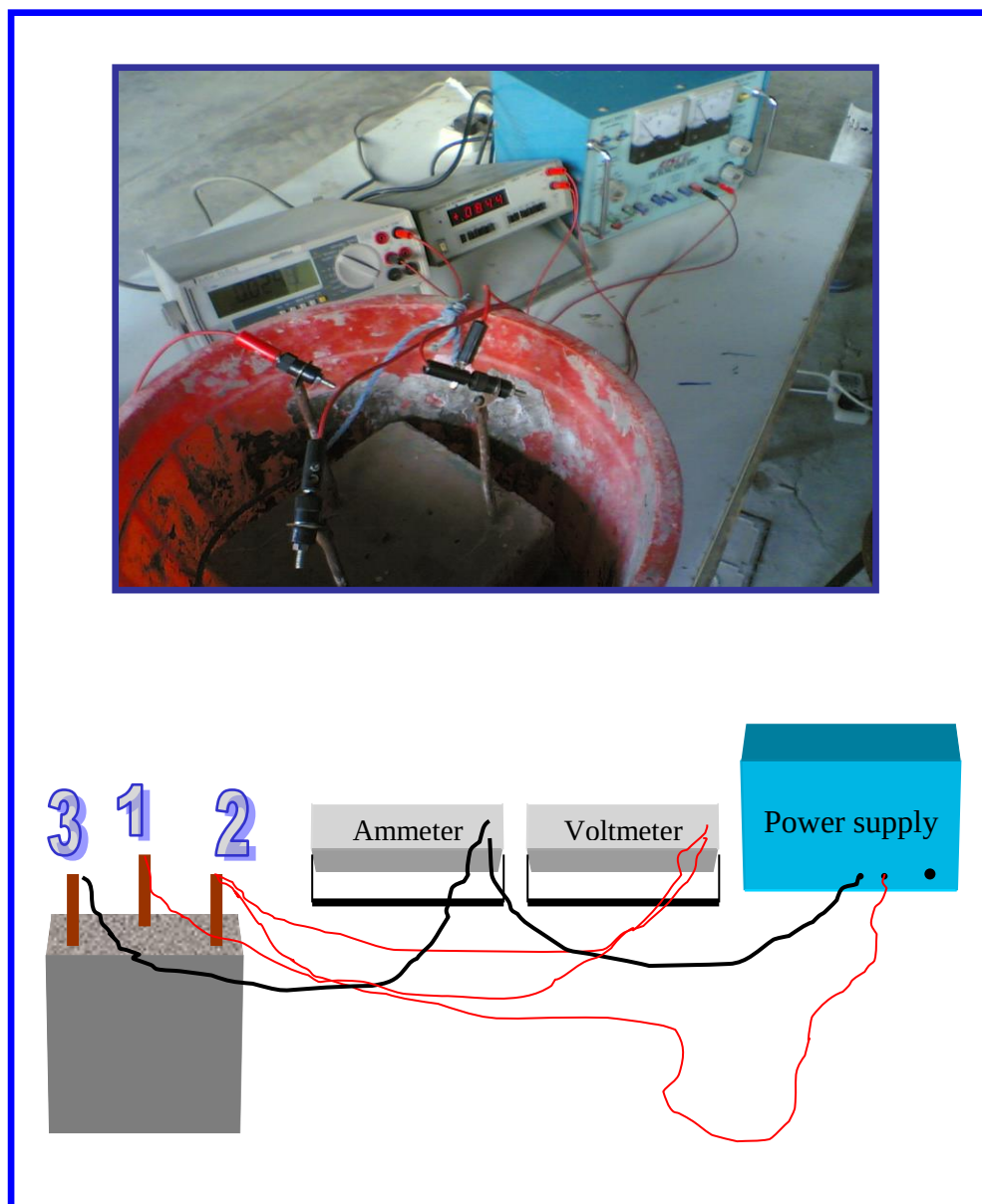


Plate (3.9) Polarization resistance circuit.

Chapter Four

Results and Discussion

4.1 General

The experimental results obtained in the present study are mentioned and discussed in this chapter. The results of the specimen tests that contained inhibiting admixtures are compared with the results of the tests of the reference specimens (without any admixture) in compression strength test, splitting tensile strength test, absorption test, chloride concentration test and electrochemical tests.

4.2 Mechanical Tests

4.2.1 Compressive Strength of Concrete

The results of this test are shown in Table (4.1) and Figures (4.1) to (4.3). Every data point represents the average of three test specimens. Results demonstrated that, in general, all concrete specimens with corrosion inhibitors exhibited a considerable decrease in compressive strength for 28, 60 and 90 ages in comparison with reference specimens.

For specimens which contain (CN + EA) admixtures, it is noticeable that the decrease in compressive strength is higher at later ages (60 and 90 days of curing) than that at early age. At 90 days age, the decrease in compressive strength is 16.4% for (0.2 $\mathbf{B_{EA}}$ + 0.8 $\mathbf{B_{CN}}$) mix, 17.9% for (0.5 $\mathbf{B_{EA}}$ + 0.5 $\mathbf{B_{CN}}$) mix and 22.4% for (0.8 $\mathbf{B_{EA}}$ + 0.2 $\mathbf{B_{CN}}$) mix relative to the reference mix. Also, it is observed that the decrease in compressive strength is reduced (at 28 and 60 days) with the increasing of Ethanolamine dosage or reducing Calcium Nitrate dosage.

These results agree with De Schutter and Luo [72] but, disagree with Al-Amoudi et al [71].

For (SB + SS) mixes, the results showed that the mixes ($0.8\mathbf{B}_{SB} + 0.2\mathbf{B}_{SS}$) and ($0.5\mathbf{B}_{SB} + 0.5\mathbf{B}_{SS}$) have the same reduction in the compressive strength at 28 and 90 days. The reduction is 26.4% and 28.4% for 28 and 90 days respectively with respect to the control mix. The reduction, for 60 days age, was 30% and 20% for ($0.8\mathbf{B}_{SB} + 0.2\mathbf{B}_{SS}$) and ($0.5\mathbf{B}_{SB} + 0.5\mathbf{B}_{SS}$) mixes respectively. For ($0.2\mathbf{B}_{SB} + 0.8\mathbf{B}_{SS}$) mix, the decrease in compressive strength is 15%, 16.7% and 19.4% at 28, 60 and 90 days, sequentially. These results disagree with Abdul Amir [76].

For (SBR + PD) mixes, the results indicated that the mix which contains ($0.5\mathbf{B}_{SBR} + 0.5\mathbf{B}_{PD}$) admixtures has given the lowest compressive strength with decreasing about 30%, 33.3% and 34.3% at ages 28, 60 and 90 days respectively. And, for ($0.8\mathbf{B}_{SBR} + 0.2\mathbf{B}_{PD}$) mix, the reduction in compressive strength is 24.5%, 28.3%, 26.9% for 28, 60 and 90 days respectively. However, ($0.2\mathbf{B}_{SBR} + 0.8\mathbf{B}_{PD}$) has got less reduction in compressive strength with respect to all other mixes with lowering about 11.3%, 15% and 16.4% at 28, 60 and 90 days, sequentially. These results agree with Burubai and Dagogo [79] who found that in sea water, admixture of potassium dichromate and formaldehyde were identified as good inhibitors for concrete mix, but they caused a substantial loss of compressive strength. However, Abdul Amir [76] stated that potassium dichromate admixture caused a clear increase in compressive strength at later ages. This difference with Abdul Amir may be due to used single inhibitor, but in this investigation two inhibitors were used together and this may cause the differences in some mechanical properties of concrete.

That reduction in compressive strength in all mixes which contain inhibitive admixtures may be due to these inhibitors curbing or slowing the reactions which occur in concrete mix (hydration) within the curing

period of concrete with a resulting effect on the compressive strength development.

Table (4.1) Compressive strength values for concrete specimens with and without adding of corrosion inhibitors after (28, 60 and 90 days) of curing in tap water.

Mixes Symbols	Percentage of Adding	Compressive Strength (MPa)		
		28 day curing	60 day curing	90 day curing
R	Nil	26.5	30	33.5
CN + EA	$0.8B_{EA} + 0.2B_{CN}$	23	25.5	26
	$0.5B_{EA} + 0.5B_{CN}$	22.5	25	27.5
	$0.2B_{EA} + 0.8B_{CN}$	22	24	28
SB + SS	$0.8B_{SB} + 0.2B_{SS}$	19.5	21	24
	$0.5B_{SB} + 0.5B_{SS}$	19.5	24	24
	$0.2B_{SB} + 0.8B_{SS}$	22.5	25	27
PD + SBR	$0.8B_{SBR} + 0.2B_{PD}$	20	21.5	24.5
	$0.5B_{SBR} + 0.5B_{PD}$	18	20	22
	$0.2B_{SBR} + 0.8B_{PD}$	23.5	26.5	28

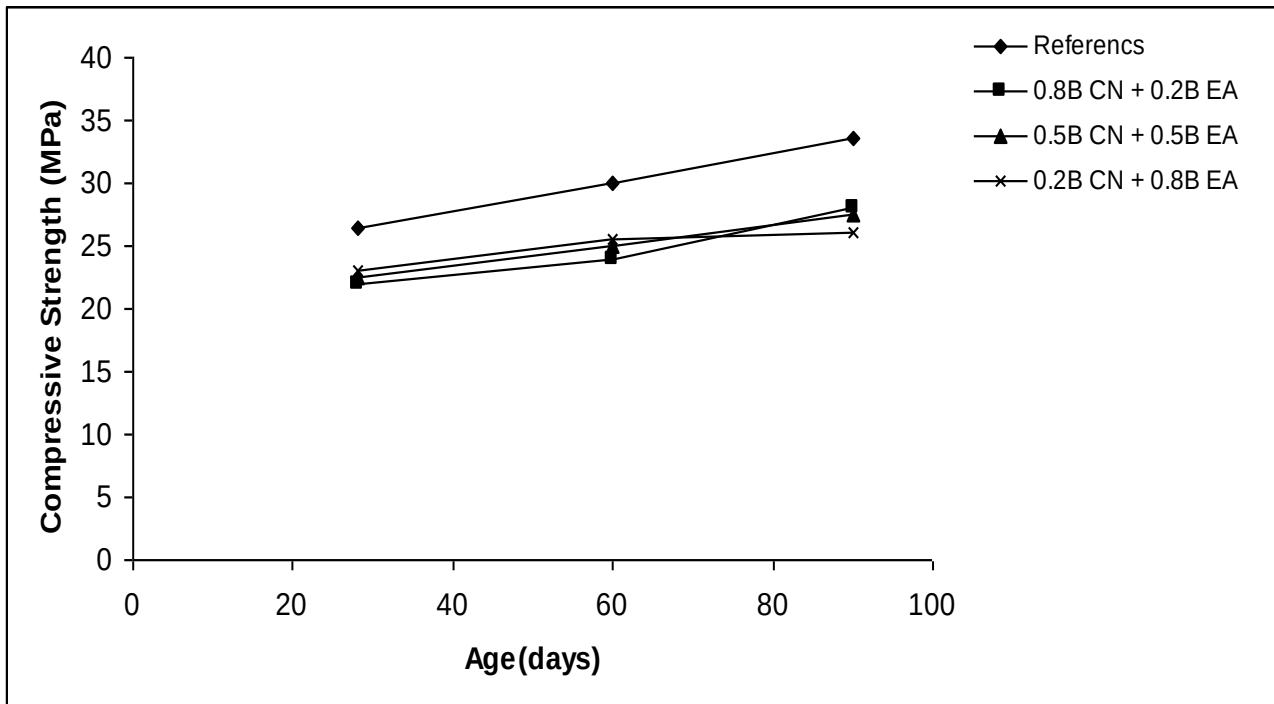


Figure (4.1) Compressive strength development with age for (CN + EA) mixes.

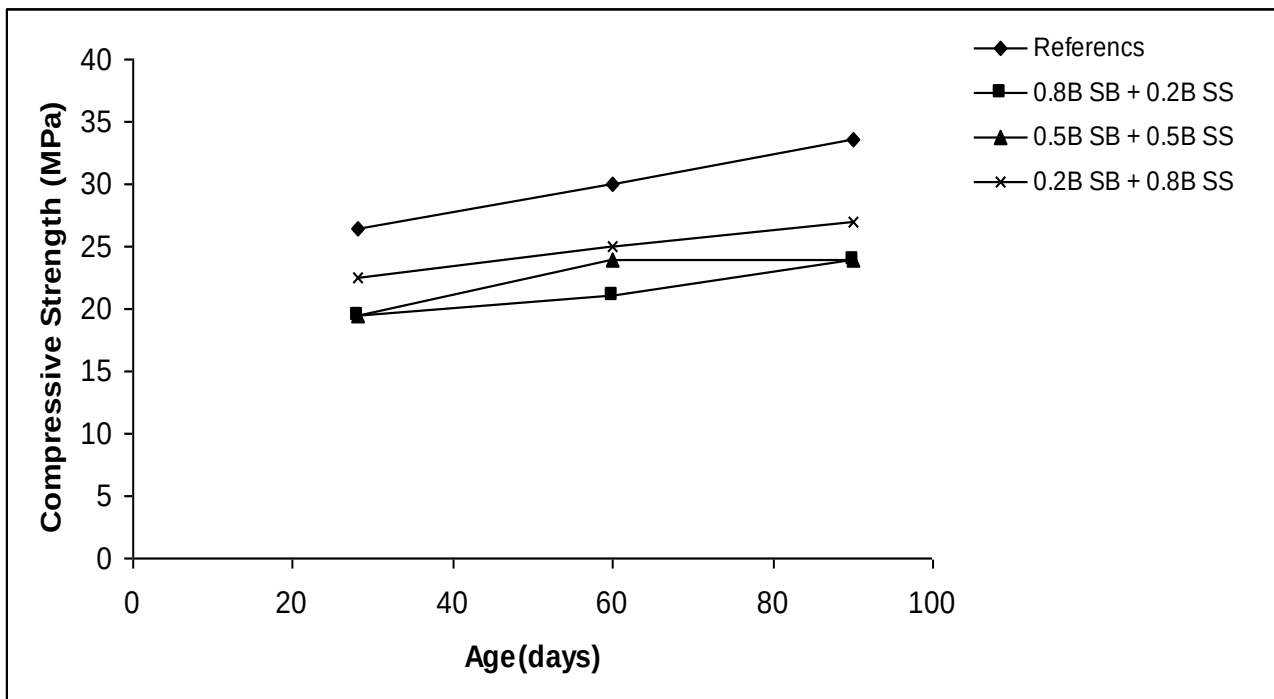


Figure (4.2) Compressive strength development with age for (SB + SS) mixes.

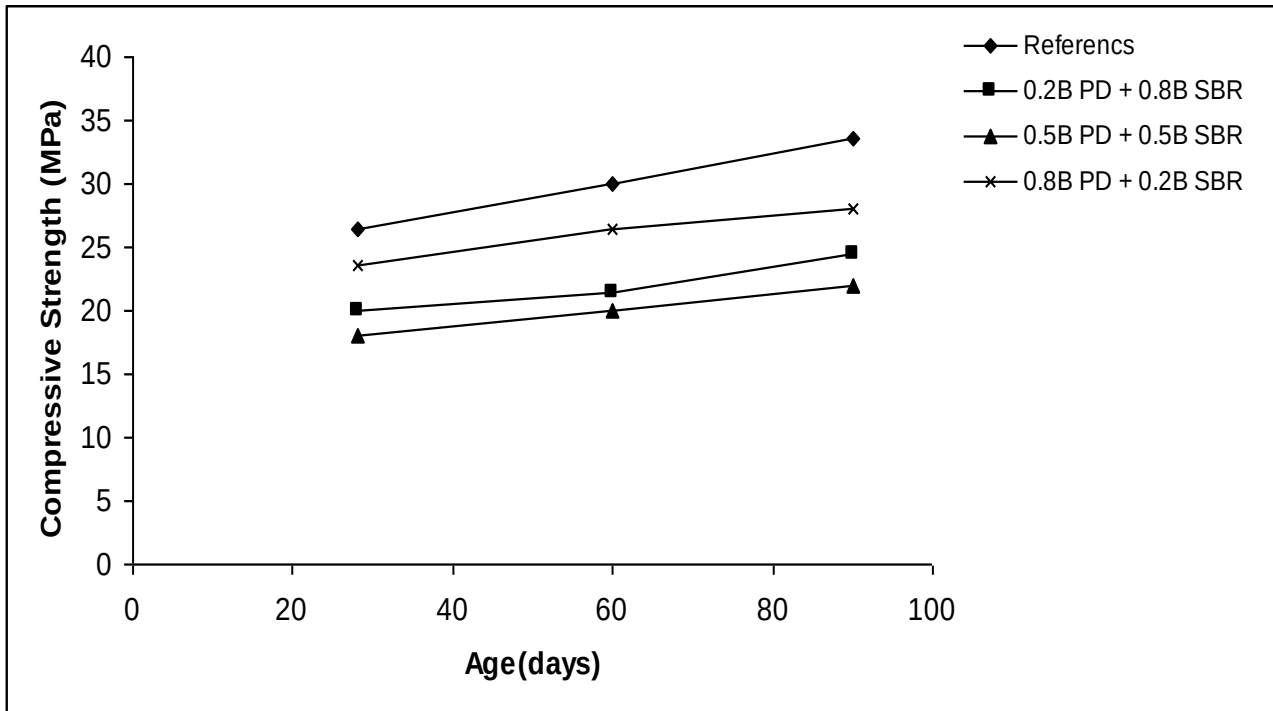


Figure (4.3) Compressive strength development with age for (SBR + PD) mixes.

4.2.2 Splitting Tensile Strength

The results of this test are shown in Table (4.2), and Figure (4.4). Average of three specimens is considered for each result. These results, for all specimens, are made after 28 days of curing in tap water. The test results showed that there is an obvious decreasing in splitting tensile strength for all mixes which have inhibitive admixtures with respect to control mix.

For specimens which contain (CN + EA) admixtures, the results showed that the decrease in splitting tensile strength is 31%, 15.4%, 21.6% for (0.2 $\mathbf{B}_{EA}$ + 0.8 $\mathbf{B}_{CN}$) mix, (0.5 $\mathbf{B}_{EA}$ + 0.5 $\mathbf{B}_{CN}$) mix and (0.8 $\mathbf{B}_{EA}$ + 0.2 $\mathbf{B}_{CN}$) mix respectively. These results agree with De Schutter and Luo [72] who found that, after using aminoalcohol-based inhibitors, there is a reduction about 17% in splitting tensile strength.

For mixes that hold with (SB + SS) admixtures, results demonstrated that the reduction in splitting tensile strength is minimized with increasing of Sodium Silicate dosage upon Sodium Benzoate admixture. The reduction, for $(0.8\mathbf{B}_{\text{SB}} + 0.2\mathbf{B}_{\text{SS}})$ mix, $(0.5\mathbf{B}_{\text{SB}} + 0.5\mathbf{B}_{\text{SS}})$ mix and $(0.2\mathbf{B}_{\text{SB}} + 0.8\mathbf{B}_{\text{SS}})$ mix respectively, is 44%, 34% and 19%. These results are not compatible with Abdul Amir [76].

For samples which include (SBR + PD) admixtures, the percentage of decreasing in splitting tensile strength (in comparison with reference samples), for $(0.8\mathbf{B}_{\text{SBR}} + 0.2\mathbf{B}_{\text{PD}})$, $(0.5\mathbf{B}_{\text{SBR}} + 0.5\mathbf{B}_{\text{PD}})$ and $(0.2\mathbf{B}_{\text{SBR}} + 0.8\mathbf{B}_{\text{PD}})$ mixes, is 24.8%, 20.9 and 23.9%, respectively. These results are in contrary with Abdul Amir [76] when she used SBR or PD each alone as a corrosion inhibitor in the mix.

Figure (4.2) Tensile strength values for all mixes after 28 days curing.

Mixes symbols	Percentage of adding	Splitting Tensile Strength (MPa)
R	Nil	3.06
CN + EA	$0.8\mathbf{B}_{\text{EA}} + 0.2\mathbf{B}_{\text{CN}}$	2.4
	$0.5\mathbf{B}_{\text{EA}} + 0.5\mathbf{B}_{\text{CN}}$	2.59
	$0.2\mathbf{B}_{\text{EA}} + 0.8\mathbf{B}_{\text{CN}}$	2.11
SB + SS	$0.8\mathbf{B}_{\text{SB}} + 0.2\mathbf{B}_{\text{SS}}$	1.71
	$0.5\mathbf{B}_{\text{SB}} + 0.5\mathbf{B}_{\text{SS}}$	2.02
	$0.2\mathbf{B}_{\text{SB}} + 0.8\mathbf{B}_{\text{SS}}$	2.48
PD + SBR	$0.8\mathbf{B}_{\text{SBR}} + 0.2\mathbf{B}_{\text{PD}}$	2.3
	$0.5\mathbf{B}_{\text{SBR}} + 0.5\mathbf{B}_{\text{PD}}$	2.42
	$0.2\mathbf{B}_{\text{SBR}} + 0.8\mathbf{B}_{\text{PD}}$	2.33

It was found from the results of absorption test that the splitting tensile strength could be minimized due to the existence of inhibitors in the concrete pores and its effect on the rate and nature of concrete reactions.

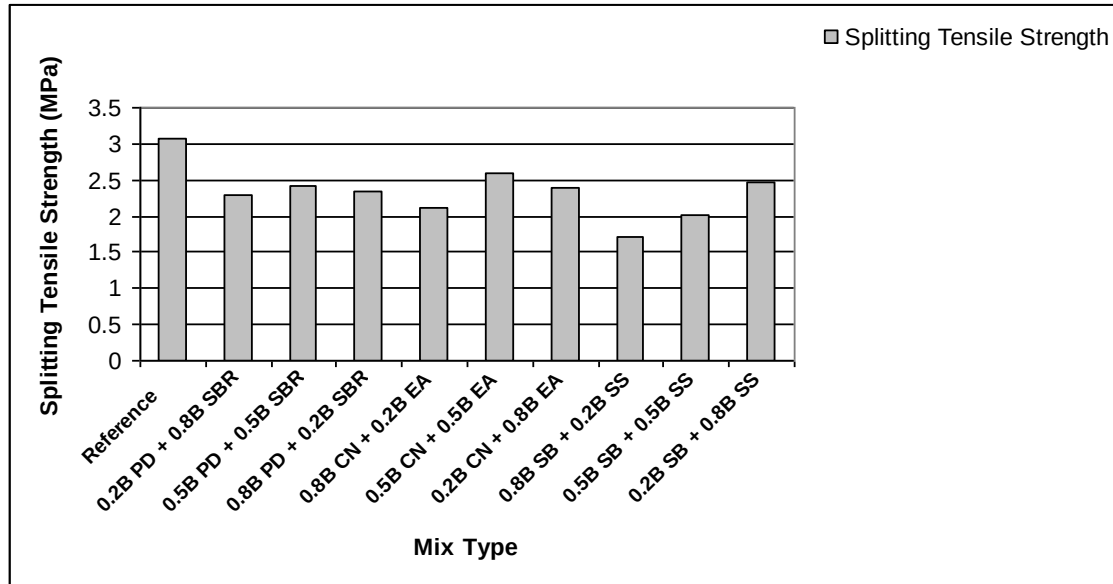


Figure (4.4) Splitting tensile strength results for concrete with and without adding of corrosion inhibitors.

4.2.3 Absorption

The results of this test are shown in Table (4.3), and Figure (4.5). Each result is representing an average of three readings.

The results indicated that all mixes, except $(0.8\mathbf{B}_{EA} + 0.2\mathbf{B}_{CN})$ mix, revealed increase in the absorption in comparison with reference mixes. Also, results demonstrated that $(0.2\mathbf{B}_{PD} + 0.8\mathbf{B}_{SBR})$ mix has given higher absorption with respect to other mixes. However, $(0.8\mathbf{B}_{EA} + 0.2\mathbf{B}_{CN})$ mix had lower absorption, that's equal to reference mix. This increase in absorption may be attributed to the affinity of inhibitors to dissolve in water which make it easy for water to be absorbed by concrete mix through pores and soluble materials exist.

Table (4.3) Absorption values for concrete specimens with and without adding of corrosion inhibitors.

Mixes symbols	Percentage of adding	Absorption %
R	Nil	6.3
CN + EA	$0.8B_{EA} + 0.2B_{CN}$	6.3
	$0.5B_{EA} + 0.5B_{CN}$	6.6
	$0.2B_{EA} + 0.8B_{CN}$	6.5
SB + SS	$0.8B_{SB} + 0.2B_{SS}$	6.8
	$0.5B_{SB} + 0.5B_{SS}$	7.4
	$0.2B_{SB} + 0.8B_{SS}$	6.9
PD + SBR	$0.8B_{SBR} + 0.2B_{PD}$	7.9
	$0.5B_{SBR} + 0.5B_{PD}$	7.1
	$0.2B_{SBR} + 0.8B_{PD}$	7

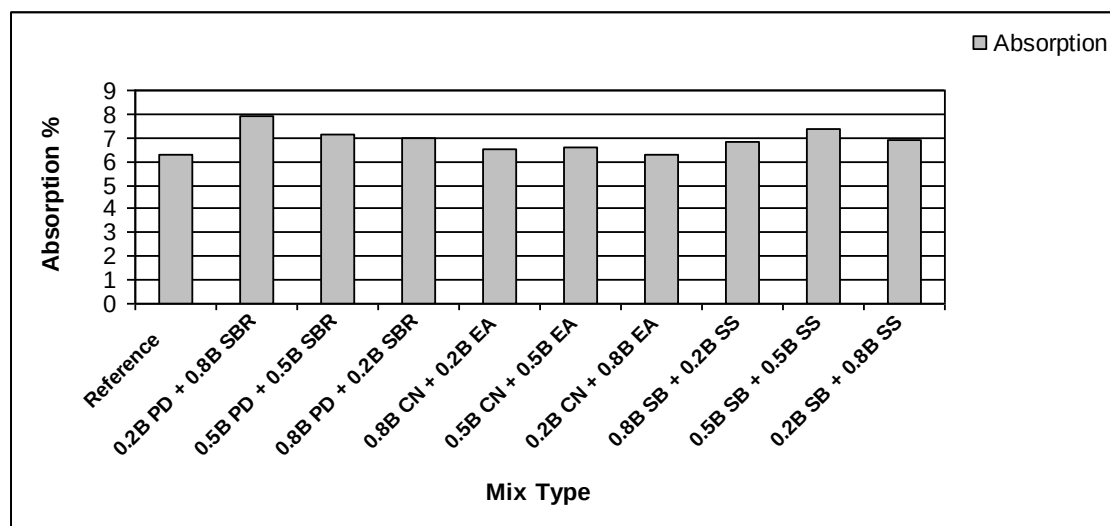


Figure (4.5) Absorption test values for all mixes

4.3 Chloride Concentration

Results of chloride concentration test, for precracked and non-precracked specimens, before and after three months of exposure to sodium chloride solution are presented in Tables (4.4) and (4.5).

Table (4.4) Chloride concentration for concrete specimens with and without adding of corrosion inhibitors before immersing in sodium chloride solution.

Mixes symbols	Percentage of adding	Chloride Concentration % (by wt. of Concrete)
R	Nil	0.001897
CN + EA	$0.2B_{CN} + 0.8B_{EA}$	0.00779
	$0.5B_{CN} + 0.5B_{EA}$	0.04998
	$0.8B_{CN} + 0.2B_{EA}$	0.03438
SB + SS	$0.8B_{SB} + 0.2B_{SS}$	0.01239
	$0.5B_{SB} + 0.5B_{SS}$	0.01559
	$0.2B_{SB} + 0.8B_{SS}$	0.01459
PD + SBR	$0.2B_{PD} + 0.8B_{SBR}$	0.02199
	$0.5B_{PD} + 0.5B_{SBR}$	0.01879
	$0.8B_{PD} + 0.2B_{SBR}$	0.01119

Results showed that chloride ions (Cl^-) concentration in most reinforced concrete specimens (precracked and non-precracked specimens) has increased after the three months of exposure. The decreasing of chloride ions, for some mixes, may be due to the reaction of these ions with C_3A in cement causing reduction in free chloride ions

(Cl⁻) concentration. Also, most precracked specimens have contained more concentration of chloride ions than non-precracked specimens. This observation is expected due to the existence of microcracks which allow the ingress of ions inside the concrete blocks easily. After three months of exposure, results demonstrated that mixes: (0.5B_{CN} + 0.5B_{EA}), (0.5B_{SB} + 0.5B_{SS}) and (0.8B_{PD} + 0.2B_{SBR}) which gave best inhibition against corrosion (see section 4.4.2.2) have decreased the chloride content in concrete specimens relative to reference samples. That may be due to the effect of synergies which works as reducer for permeability and porosity of concrete beside of its working as corrosion inhibitor [76].

Table (4.5) Chloride concentration for concrete specimens with and without adding of corrosion inhibitors after three months of exposure to sodium chloride solution.

Mixes Symbols	Percentage of Adding	Chloride Concentration % (by wt. of Concrete)	
		Non-Precracked Specimens	Precracked Specimens
R	Nil	0.019	0.0425
CN + EA	0.2B _{CN} + 0.8B _{EA}	0.022	0.043
	0.5B _{CN} + 0.5B _{EA}	0.024	0.032
	0.8B _{CN} + 0.2B _{EA}	0.043	0.0375
SB + SS	0.8B _{SB} + 0.2B _{SS}	0.039	0.0462
	0.5B _{SB} + 0.5B _{SS}	0.031	0.0412
	0.2B _{SB} + 0.8B _{SS}	0.029	0.04
PD + SBR	0.2B _{PD} + 0.8B _{SBR}	0.026	0.055
	0.5B _{PD} + 0.5B _{SBR}	0.026	0.045
	0.8B _{PD} + 0.2B _{SBR}	0.039	0.0375

4.4 Electrochemical Tests

4.4.1 Electrical Resistance of Concrete

The results of D.C. electrical resistance for all specimens tested at various ages of exposure to 3.5% NaCl solution are presented in Figures (4.6) to (4.11). (See appendix 1).

The trend lines (by using Microsoft Excel Program) of the results, for three months of exposure, are as follows:

For non-precracked specimens:

1. Reference mix : Corrosion rate = $0.0772x^2 + 0.3845x + 76.09$
2. $0.2B_{CN} + 0.8B_{EA}$: Corrosion rate = $4.2335x^2 - 71.479x + 316.07$
3. $0.5B_{CN} + 0.5B_{EA}$: Corrosion rate = $-0.2598x^2 + 3.6346x + 6.82$
4. $0.8B_{CN} + 0.2B_{EA}$: Corrosion rate = $0.0857x^2 - 2.7014x + 54.46$
5. $0.8B_{SB} + 0.2B_{SS}$: Corrosion rate = $2.746x^2 - 40.271x + 201.49$
6. $0.5B_{SB} + 0.5B_{SS}$: Corrosion rate = $2.9665x^2 - 42.276x + 155.91$
7. $0.2B_{SB} + 0.8B_{SS}$: Corrosion rate = $21.404 e^{0.1233X}$
8. $0.2B_{PD} + 0.8B_{SBR}$: Corrosion rate = $1.4313x^2 - 27.343x + 137.14$
9. $0.5B_{PD} + 0.5B_{SBR}$: Corrosion rate = $-0.5643x^2 + 4.5229x + 41.14$
10. $0.8B_{PD} + 0.2B_{SBR}$: Corrosion rate = $1.3996x^2 - 29.719x + 184.73$

For precracked specimens:

1. Reference mix : Corrosion rate = $-2.6699x^2 + 21.812x + 151.97$
2. $0.2B_{CN} + 0.8B_{EA}$: Corrosion rate = $0.406x^2 - 13.94x + 144.12$
3. $0.5B_{CN} + 0.5B_{EA}$: Corrosion rate = $1.2076x^2 - 33.232x + 237.33$
4. $0.8B_{CN} + 0.2B_{EA}$: Corrosion rate = $1.6938x^2 - 21.526x + 80.77$
5. $0.8B_{SB} + 0.2B_{SS}$: Corrosion rate = $166.94 e^{-0.1503X}$
6. $0.5B_{SB} + 0.5B_{SS}$: Corrosion rate = $95.83 e^{-0.0726X}$
7. $0.2B_{SB} + 0.8B_{SS}$: Corrosion rate = $0.7114x^2 - 12.804x + 153.19$
8. $0.2B_{PD} + 0.8B_{SBR}$: Corrosion rate = $3.656x^2 - 60.975x + 252.84$
9. $0.5B_{PD} + 0.5B_{SBR}$: Corrosion rate = $2.9786x^2 - 42.921x + 176.77$

$$10. 0.8B_{PD} + 0.2B_{SBR} : \text{Corrosion rate} = -0.1701x^2 + 1.957x + 81.62$$

Results showed that most mixes exhibit a decrease in electrical resistance with time of exposure to sodium chloride solution. This may be attributed to the continuous diffusion of chloride ions (Cl^-) into the hardened concrete leading to reduce the alkalinity of concrete (pH) and increasing the conductivity of the concrete and consequently the electrical resistance has decreased. Thus, electrical resistance is considered as an indication to the development of corrosion process in reinforced concrete specimens. These results are compatible with Abdul Amir [76].

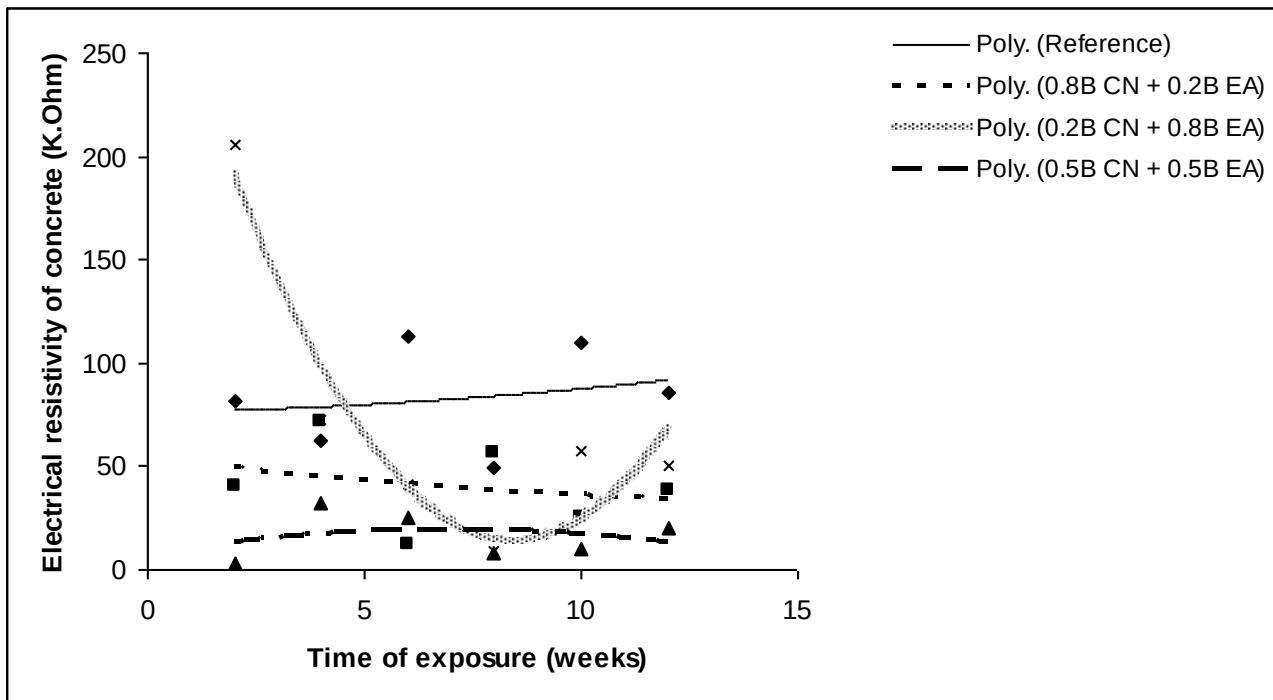


Figure (4.6) Electrical resistance for non-precracked (CN + EA) mixes in 3.5% NaCl solution vs. time.

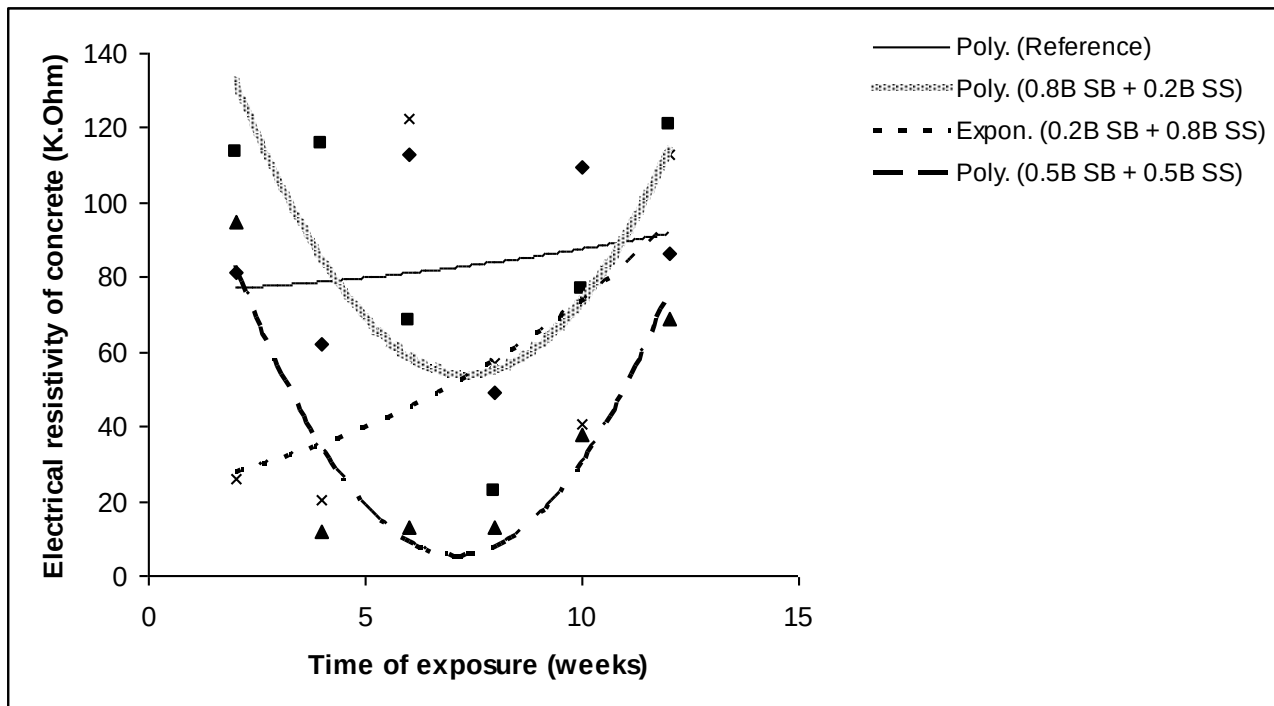


Figure (4.7) Electrical resistance for non-precracked (SB + SS) mixes in 3.5% NaCl solution vs. time.

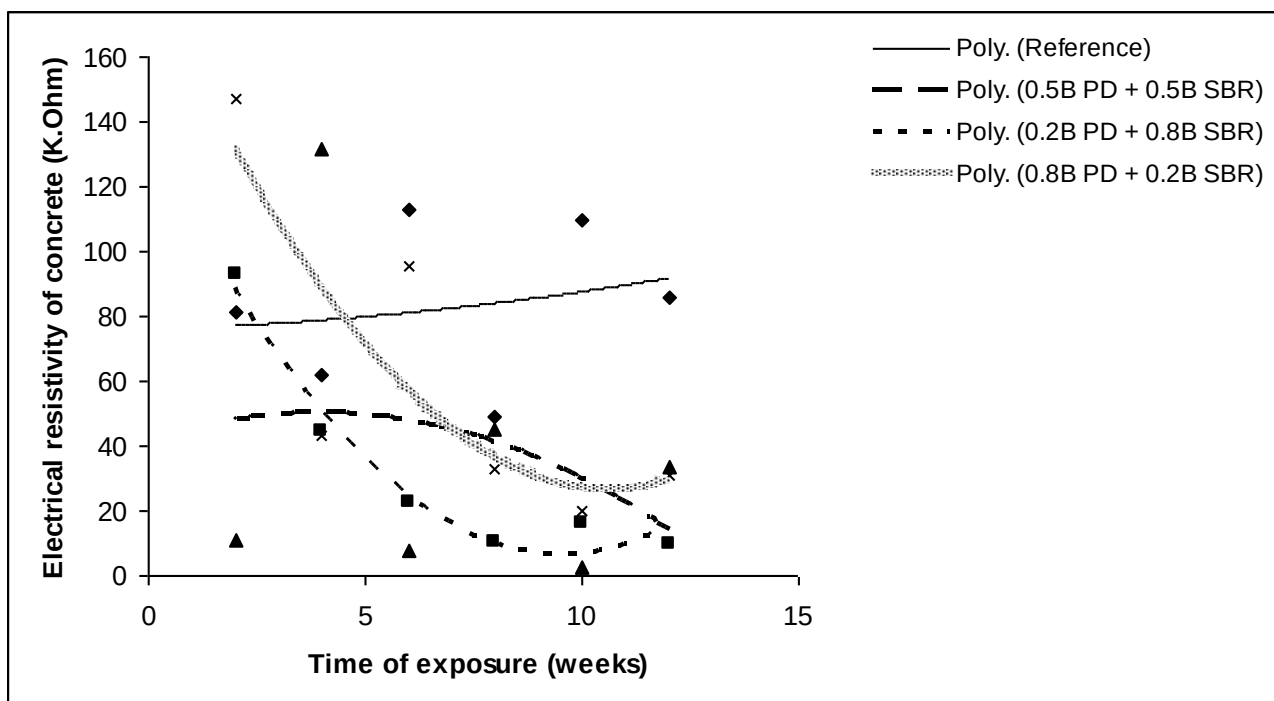


Figure (4.8) Electrical resistance for non-precracked (SBR + PD) mixes in 3.5% NaCl solution vs. time.

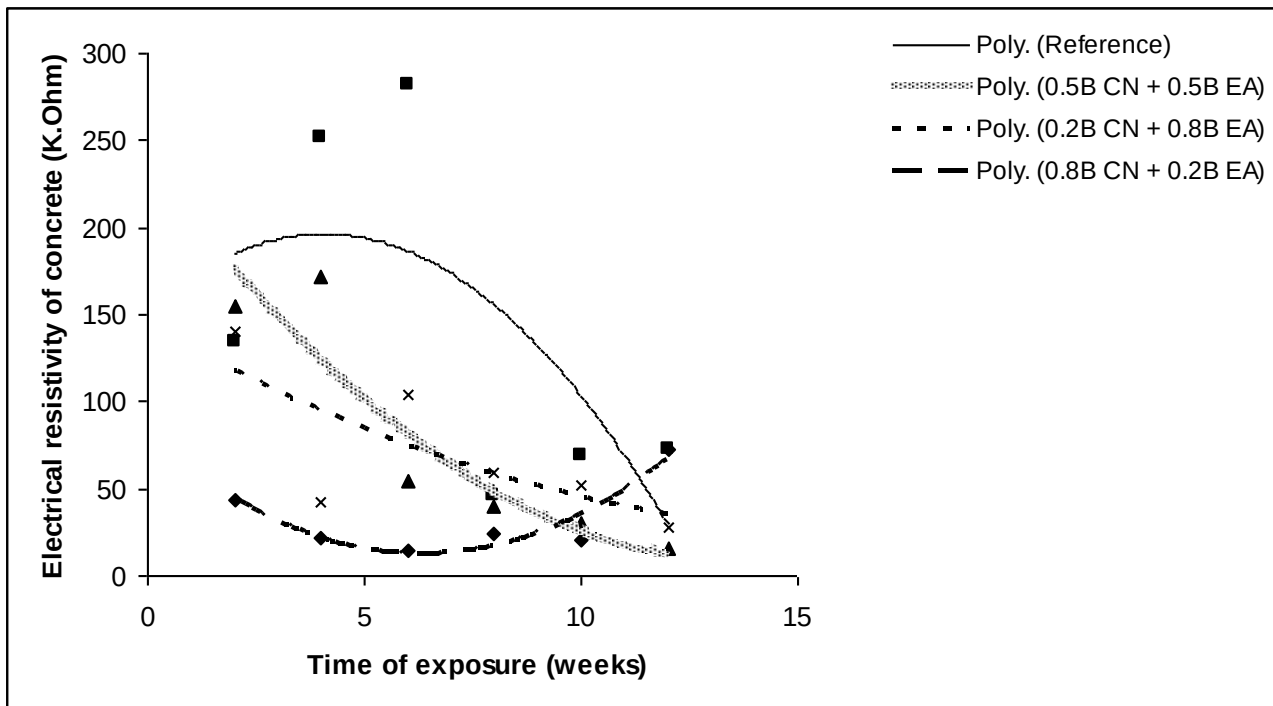


Figure (4.9) Electrical resistance for precracked (CN + EA) mixes in 3.5% NaCl solution vs. time.

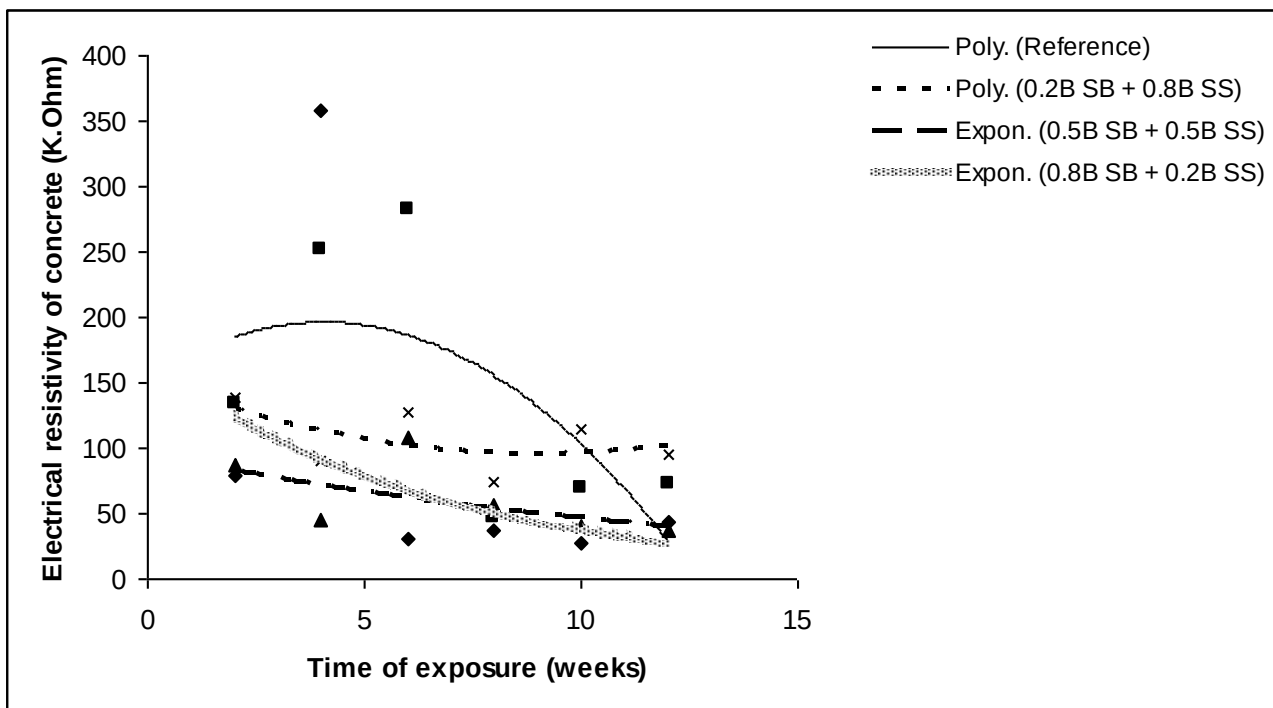


Figure (4.10) Electrical resistance for precracked (SB + SS) mixes in 3.5% NaCl solution vs. time.

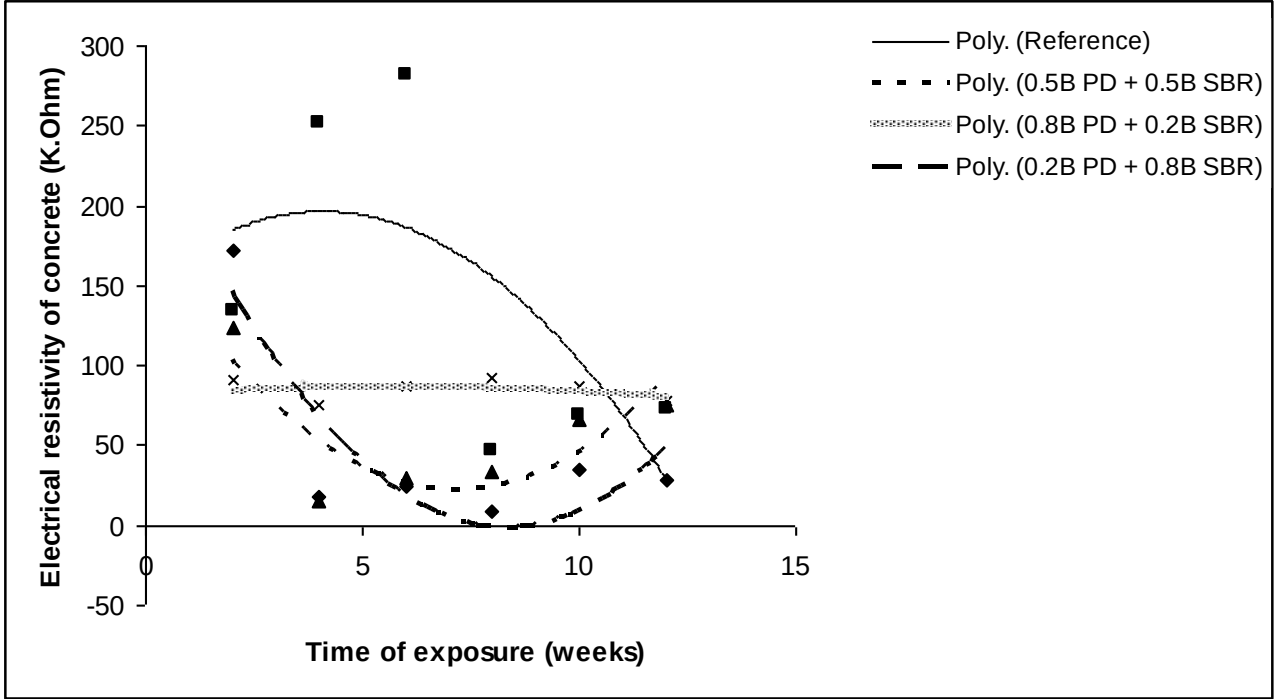


Figure (4.11) Electrical resistance for precracked (SBR + PD) mixes in 3.5% NaCl solution vs. time.

4.4.2 Corrosion Rate

In this study, the corrosion rate has been determined by using *Barnart Method* [90] as in the following equation: (see appendix 1, 2)

$$\text{Corrosion Rate (CR)} = I_{\text{corr.avg}} * \text{eq.wt} / (96500 * A) \quad (4-1)$$

Where ($I_{\text{corr.avg}}$) can be determined from the two equations below:

$$1. I_{\text{corr}1} = I_1 / (R_1 + 4R_2)^{0.5} \quad (4-2)$$

$$2. I_{\text{corr}2} = I_1 / ((R_3 * R_4)^2 + 4R_3)^{0.5} \quad (4-3)$$

$$I_{\text{corravg}} = (I_{\text{corr}1} + I_{\text{corr}2}) / 2 \quad (4-4)$$

$$\text{And: } R_1 = I_3 / I_1, \quad R_2 = R_3 = I_1 / I_4, \quad R_4 = I_6 / I_4$$

Where:

I_{corr} : Corrosion current (Ampere)

ΔE : The potential (voltage)

I_1 : The current in Amp. at $\Delta E_1 = 0.060$ volt

I_3 : The current in Amp. at $\Delta E_3 = 0.120$ volt

I_4 : The current in Amp. at $\Delta E_4 = -0.060$ volt

I_6 : The current in Amp. at $\Delta E_6 = -0.120$ volt

C.R: Corrosion Rate (kg / sec. m²)

A: Surface area of the steel wire (0.5 cm in diameter) that imbedded in concrete (m²)

eq. wt.: Equivalent weight of steel (kg)=56/2=28

96500: Faraday constant

Corrosion rate has taken every two weeks, for three months of exposure in 3.5% NaCl solution. After three months of exposure, it is noticed that there is an obvious fluctuation in the results of polarization resistance. That may be due to the limited period of the study. For this reason, it has been made fitting trend lines for the obtained results.

4.4.2.1 Corrosion Rate for Non-Precracked Specimens

Results of corrosion rate for non-precracked reinforced specimens before and after of exposure in 3.5% NaCl solution for three months are shown in Figures (4.12) to (4.14).

The trend lines (by using Microsoft Excel Program) of the results, for three months of exposure, are as follows:

1. Reference mix : Corrosion rate = $22.741e^{0.2912X}$
2. $0.2B_{CN} + 0.8B_{EA}$: Corrosion rate $y = 72.299e^{0.3155X}$
3. $0.5B_{CN} + 0.5B_{EA}$: Corrosion rate = $-19.527x^2 + 335.97x + 489.82$
4. $0.8B_{CN} + 0.2B_{EA}$: Corrosion rate = $829.81e^{0.0644X}$
5. $0.8B_{SB} + 0.2B_{SS}$: Corrosion rate $y = 6.3583e^{0.5899X}$
6. $0.5B_{SB} + 0.5B_{SS}$: Corrosion rate = $15.872x^2 - 69.864x + 98.487$

7. $0.2B_{SB} + 0.8B_{SS}$: Corrosion rate = $12.885x^2 + 17.278x + 320.7$
8. $0.2B_{PD} + 0.8B_{SBR}$: Corrosion rate = $-70.891x^2 + 931.78x - 576.46$
9. $0.5B_{PD} + 0.5B_{SBR}$: Corrosion rate = $-161.93x^2 + 1962x + 38.048$
10. $0.8B_{PD} + 0.2B_{SBR}$: Corrosion rate = $-30.284x^2 + 406.83x - 40.353$

It is noticed from the results, after three months of exposure, that the mixes which contained (SBR + PD), (SB + SS) and (CN + EA) admixtures have got adverse effect on the corrosion of reinforcing bars (increased the corrosion rate). This increase of corrosion rate may be attributed to the effect of anodic inhibitors which increase the corrosion rate if they do not exist in sufficient concentration at the corrosion system.

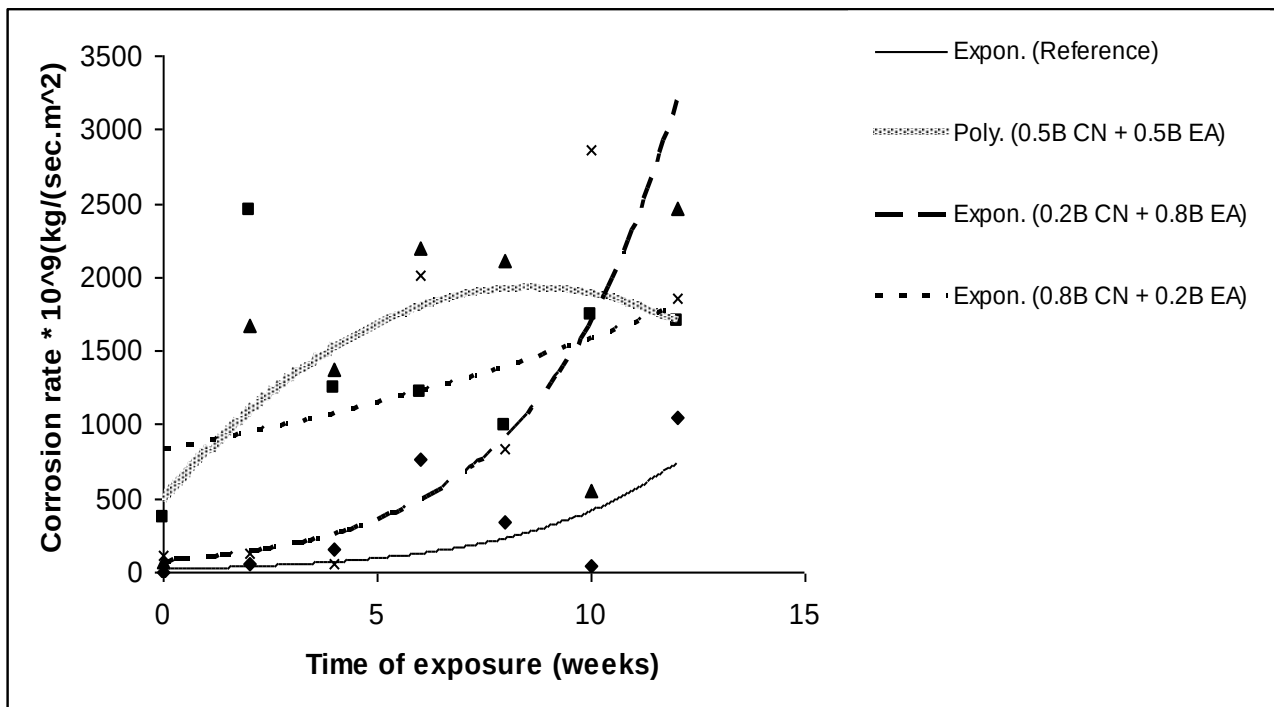


Figure (4.12) Corrosion rate for non-precracked (CN + EA) mixes with time of exposure to 3.5% NaCl solution.

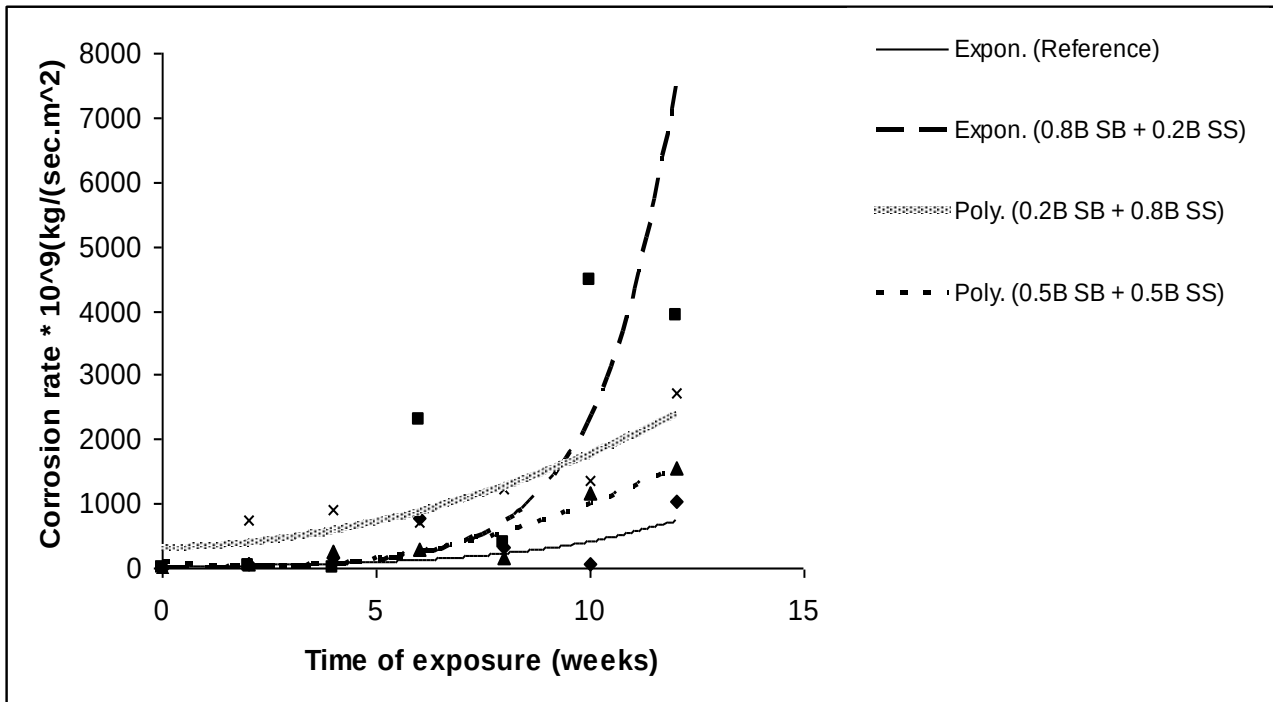


Figure (4.13) Corrosion rate for non-precracked (SB + SS) mixes with time of exposure to 3.5% NaCl solution.

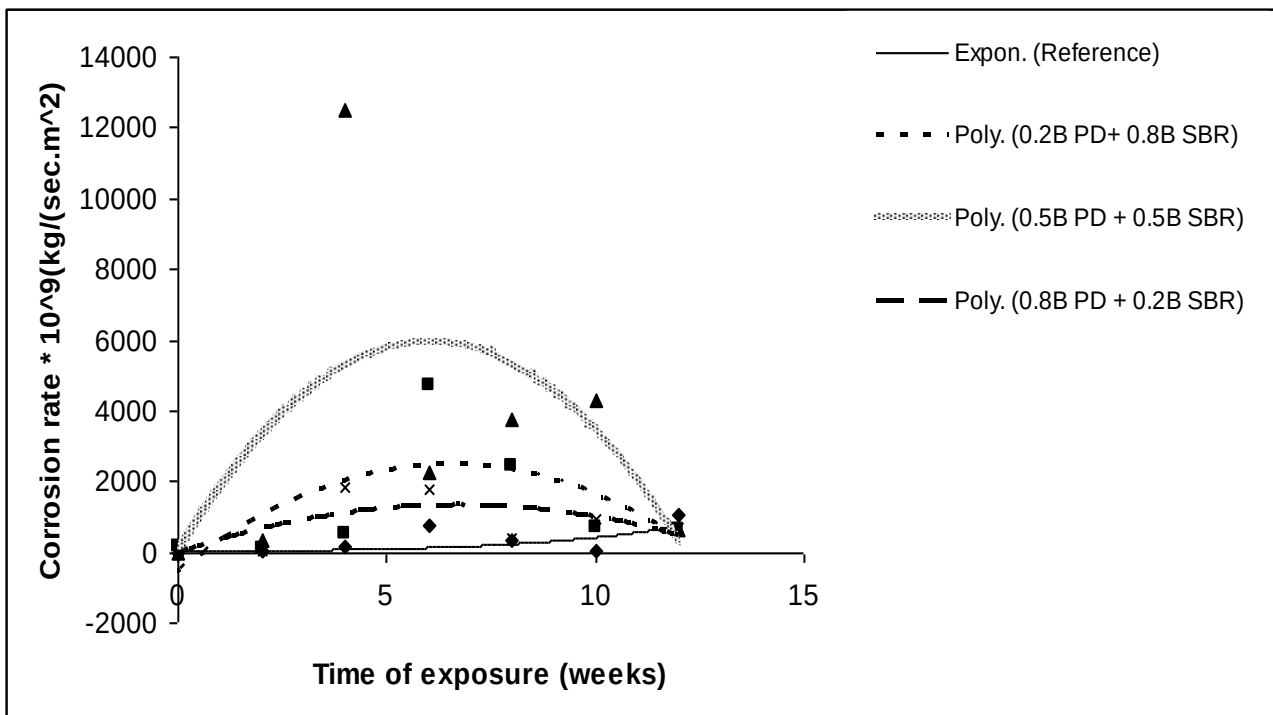


Figure (4.14) Corrosion rate for non-precracked (SBR + PD) mixes with time months of exposure to 3.5% NaCl solution.

4.4.2.2 Corrosion Rate for Precracked Specimens

Results of corrosion rate for the precracked reinforced specimens before and after of exposure to 3.5% NaCl solution are shown in Figures (4.15) to (4.17). Every data point represents the average of two test specimens.

The trend lines (by using Microsoft Excel Program) of the results, for three months of exposure, are as follows:

1. Reference mix : Corrosion rate = $50.655x^2 + 77.044x + 389.57$
2. $0.2B_{CN} + 0.8B_{EA}$: Corrosion rate = $19.95x^2 - 114.48x + 443.09$
3. $0.5B_{CN} + 0.5B_{EA}$: Corrosion rate = $6.5656x^2 + 20.925x + 204.35$
4. $0.8B_{CN} + 0.2B_{EA}$: Corrosion rate = $162.18e^{0.2819X}$
5. $0.8B_{SB} + 0.2B_{SS}$: Corrosion rate = $-18.42x^2 + 367.91x - 94.629$
6. $0.5B_{SB} + 0.5B_{SS}$: Corrosion rate = $44.306e^{0.3734X}$
7. $0.2B_{SB} + 0.8B_{SS}$: Corrosion rate = $214.55e^{0.2433X}$
8. $0.2B_{PD} + 0.8B_{SBR}$: Corrosion rate = $-8.8346x^2 + 342.04x - 104.68$
9. $0.5B_{PD} + 0.5B_{SBR}$: Corrosion rate = $35.324x^2 + 7.5759x + 81.526$
10. $0.8B_{PD} + 0.2B_{SBR}$: Corrosion rate = $289.85e^{0.1228X}$

After three months of exposure it is found:

For specimens which contain (CN + EA) admixtures, results indicated that there is no significant difference in corrosion rate between $(0.8B_{EA} + 0.2B_{CN})$ and $(0.2B_{EA} + 0.8B_{CN})$ mixes. The results, also, demonstrated that $(0.5B_{EA} + 0.5B_{CN})$ mix has presented better inhibition than $(0.8B_{EA} + 0.2B_{CN})$ and $(0.2B_{EA} + 0.8B_{CN})$ mixes (about 82%). That stability of corrosion may be due to the protecting film that formed on the anode by Calcium Nitrate and Ethanolamine to prevent the dissolution of the anode metal or the aggressive ions reaching to the anode. In addition to the adsorption film that formed on the cathode by Ethanolamine

inhibitor. These results agree with the researches Al-Amoudi et al [71] and Saraswathy and song [75].

For mixes with (SB + SS) admixtures, the results indicated that $(0.8\mathbf{B}_{\text{SB}} + 0.2\mathbf{B}_{\text{SS}})$ mix is better than $(0.2\mathbf{B}_{\text{SB}} + 0.8\mathbf{B}_{\text{SS}})$ mix. Wherever, $(0.5\mathbf{B}_{\text{SB}} + 0.5\mathbf{B}_{\text{SS}})$ mix has handed the best inhibition for corrosion with efficiency about 84%. That may be attributed to the role of Sodium Silicate in the adhering of the corrosion by formation of precipitates on the surface of the metal (reinforcement), thereby providing a protective film. Besides the thin passive layer that may be formed by, the anodic inhibitor, Sodium Benzoate. These results agree with the researches Abdul Amir [76] and Mohammed and Mohana [80].

For specimens which include (SBR + PD) admixtures, the results indicated that the corrosion rate of $(0.5\mathbf{B}_{\text{SBR}} + 0.5\mathbf{B}_{\text{PD}})$ mix is lower than $(0.8\mathbf{B}_{\text{SBR}} + 0.2\mathbf{B}_{\text{PD}})$ mix. And it has found that the $(0.2\mathbf{B}_{\text{SBR}} + 0.8\mathbf{B}_{\text{PD}})$ mix has got the lowest corrosion rate with efficiency about 85%. This is attributed to the inhibitive action of Potassium Dichromate inhibitor which considerably reduced the cathodic activities by forming a protective film on the steel bar. And the SBR is reducing the pores in concrete and resulting in increasing resistance against ions diffusion and decreasing diffusion of aggressive ions. These results are compatible with the researches Abdul Amir [76] and Burubai and Dagogo [79].

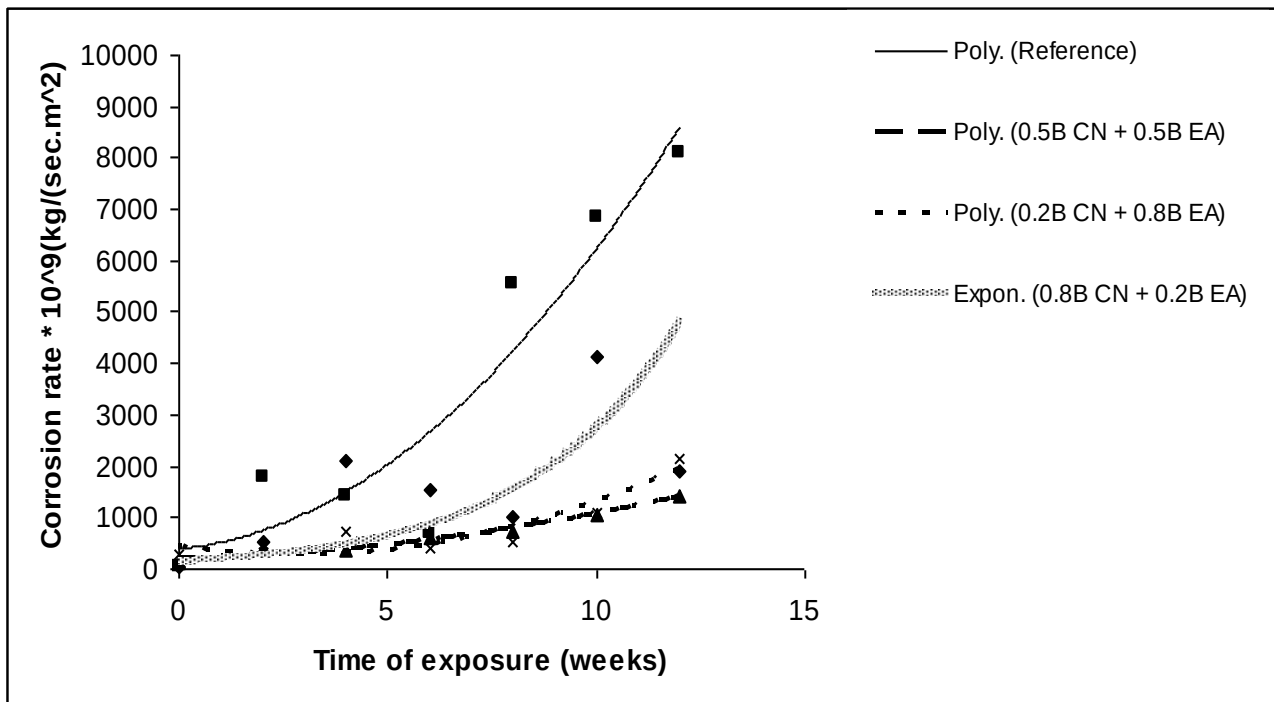


Figure (4.15) Corrosion rate for precracked (CN + EA) mixes with time of exposure to 3.5% NaCl solution.

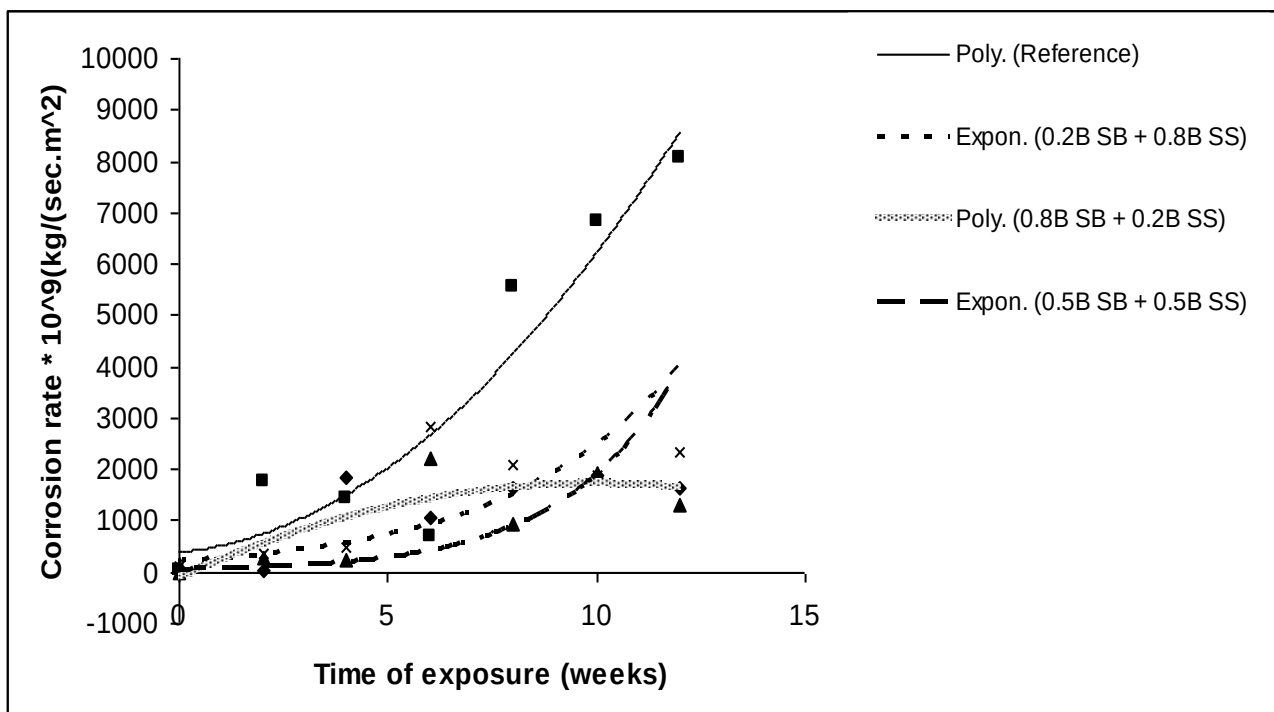


Figure (4.16) Corrosion rate for precracked (SB + SS) mixes with time of exposure to 3.5% NaCl solution.

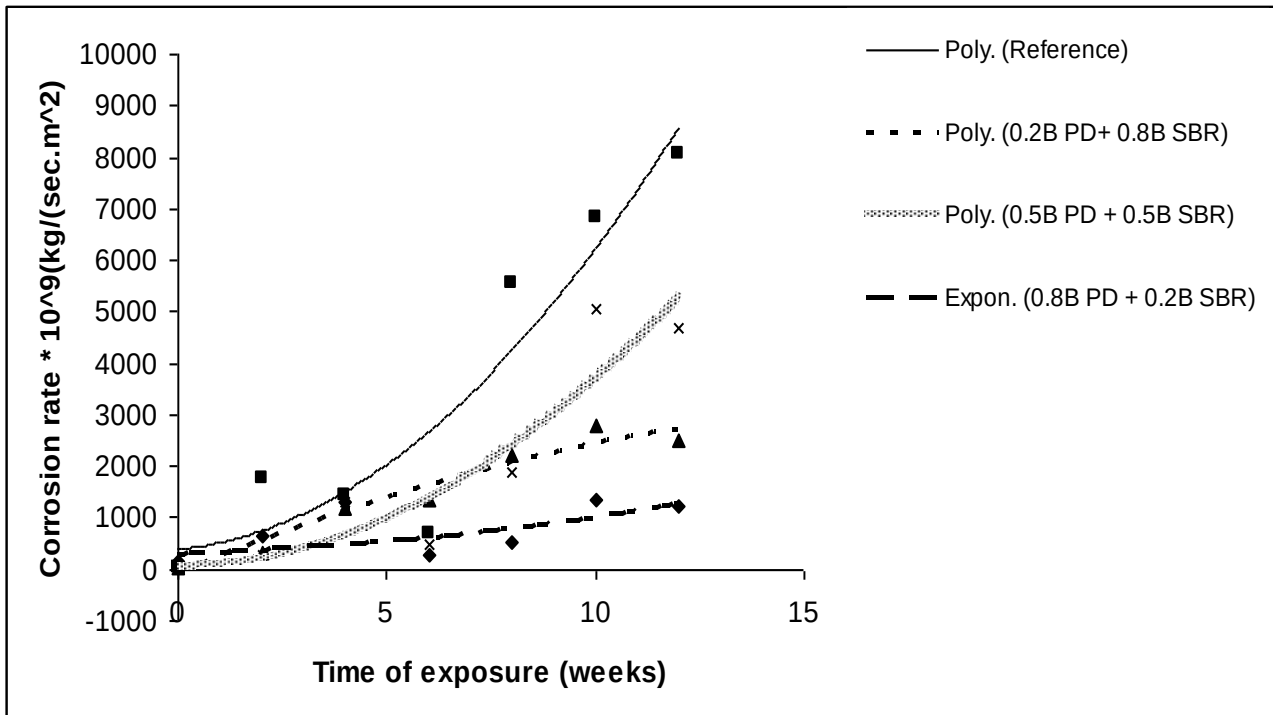


Figure (4.17) Corrosion rate for precracked (SBR + PD) mixes with time of exposure to 3.5% NaCl solution.

4.5 Corrosion Current Categorization

The following broad criteria for corrosion have been developed from field and laboratory investigation with the sensor controlled guard ring device (Broomfield criteria) [91]:

Passive condition : $I_{\text{corr}} < 0.1 \mu\text{A} / \text{cm}^2$

Low to Moderate corrosion : $I_{\text{corr}} (0.1 - 0.5) \mu\text{A} / \text{cm}^2$

Moderate to high corrosion : $I_{\text{corr}} (0.5 - 1) \mu\text{A} / \text{cm}^2$

High corrosion : $I_{\text{corr}} > 1 \mu\text{A} / \text{cm}^2$

Depending on the previous criteria, the Categorization degrees of non-precracked and precracked specimens (after three months of exposure) are tabulated in Tables (4.6) and (4.7).

Table (4.6) Categorization degree of corrosion current for non-precracked reinforced specimens after three months of exposure to 3.5% sodium chloride solution.

Mixes Symbols	Percentage of Adding	Corrosion Current for Non-Precracked Specimens ($\mu\text{A}/\text{cm}^2$)	Categorization Degree of Corrosion
R	Nil	0.361236	Low
CN + EA	$0.2B_{\text{CN}} + 0.8B_{\text{EA}}$	0.641389	Moderate
	$0.5B_{\text{CN}} + 0.5B_{\text{EA}}$	0.849851	Moderate
	$0.8B_{\text{CN}} + 0.2B_{\text{EA}}$	0.583678	Moderate
SB + SS	$0.8B_{\text{SB}} + 0.2B_{\text{SS}}$	1.35207	High
	$0.5B_{\text{SB}} + 0.5B_{\text{SS}}$	0.536526	Moderate
	$0.2B_{\text{SB}} + 0.8B_{\text{SS}}$	0.931932	Moderate
PD + SBR	$0.2B_{\text{PD}} + 0.8B_{\text{SBR}}$	0.220273	Low
	$0.5B_{\text{PD}} + 0.5B_{\text{SBR}}$	0.224422	Low
	$0.8B_{\text{PD}} + 0.2B_{\text{SBR}}$	0.242626	Low

Table (4.7) Categorization degree of corrosion current for precracked reinforced specimens after three months of exposure to 3.5% sodium chloride solution.

Mixes Symbols	Percentage of Adding	Corrosion Current for Precracked Specimens ($\mu\text{A}/\text{cm}^2$)	Categorization Degree of Corrosion
R	Nil	2.783639	High
CN + EA	0.2B _{CN} + 0.8B _{EA}	0.740498	Moderate
	0.5B _{CN} + 0.5B _{EA}	0.490714	Low
	0.8B _{CN} + 0.2B _{EA}	0.662455	Moderate
SB + SS	0.8B _{SB} + 0.2B _{SS}	0.559119	Moderate
	0.5B _{SB} + 0.5B _{SS}	0.444912	Low
	0.2B _{SB} + 0.8B _{SS}	0.810618	Moderate
PD + SBR	0.2B _{PD} + 0.8B _{SBR}	0.856823	Moderate
	0.5B _{PD} + 0.5B _{SBR}	1.612374	High
	0.8B _{PD} + 0.2B _{SBR}	0.428624	Low

4.6 Inhibitor Efficiency

Inhibitors efficiencies, after three months of exposure to 3.5% sodium chloride solution, for all mixes which contain inhibitive admixtures are presented in Table (4.8).

The results showed, for non-precracked specimens, that all mixes which have (SBR + PD), (CN + EA) and (SB + SS) admixtures have given opposite action (increased the corrosion rate). That may be due to these synergic inhibitors did not access the steel reinforcement with enough concentration and curb the corrosion process. These results are

conforming to inhibitor definition "Corrosion inhibitors is a chemical substance that decreases the corrosion rate *when present in the corrosion system at suitable concentration*, without significantly changing the concentration of any other corrosion agent" [14].

For precracked specimens, it is noticed that there is an obvious role of inhibitor, for all mixes which have inhibitive admixtures, for adhering and minimizing corrosion process. Where, $(0.5\mathbf{B}_{EA} + 0.5\mathbf{B}_{CN})$ mix has given better inhibition (about 82%) than other $(CN + EA)$ mixes. And $(0.5\mathbf{B}_{SB} + 0.5\mathbf{B}_{SS})$ mix has handed higher efficiency (about 84%) than $(0.8\mathbf{B}_{SB} + 0.2\mathbf{B}_{SS})$ and $(0.2\mathbf{B}_{SB} + 0.8\mathbf{B}_{SS})$ mixes. The best efficiency (about 85%) by comparison with all other mix has obtained from $(0.2\mathbf{B}_{SBR} + 0.8\mathbf{B}_{PD})$ mix. That good inhibition which occurred, for most mixes contaminated inhibitive admixtures, may be related to sufficient concentration of inhibitor at steel reinforcement due to the bath that created by the micro cracks for motion of inhibitors toward the steel bars and make chemical protective film on part or all metal surface, depending on the inhibition mechanism of each inhibitor (anodic, cathodic or mixed), and steering to reduce the corrosion rate. These results agree with Abdul Amir [76].

Table (4.8) Inhibition efficiency of synergic inhibitors after three months of partially immersing in 3.5% NaCl solution.

Mixes Symbols	Percentage of Adding	Corrosion Efficiency %	
		Non-Precracked Specimens	Precracked Specimens
CN + EA	0.2B _{CN} + 0.8B _{EA}	Adverse Action	73.4
	0.5B _{CN} + 0.5B _{EA}	Adverse Action	82.4
	0.8B _{CN} + 0.2B _{EA}	Adverse Action	76.2
SB + SS	0.8B _{SB} + 0.2B _{SS}	Adverse Action	79.9
	0.5B _{SB} + 0.5B _{SS}	Adverse Action	84
	0.2B _{SB} + 0.8B _{SS}	Adverse Action	70.9
PD + SBR	0.2B _{PD} + 0.8B _{SBR}	39	69.2
	0.5B _{PD} + 0.5B _{SBR}	37.9	42.1
	0.8B _{PD} + 0.2B _{SBR}	32.8	84.6

4.7 Polarization Resistance (RP)

Results of polarization resistance of non-precracked and precracked specimens are shown in Tables (4.9) and (4.10). Polarization resistance can be determined by using the following equations (Barnart method) [90].

$$RP1 = [2 * M1 * (M1^2 - 1) * V1] / [2 * M1^2 * (I_1 + I_4) - (I_3 + I_6)]$$

$$RP2 = [2 * M2 * (M2^2 - 1) * V1] / [2 * M2^2 * (I_1 + I_4) - (I_2 + I_5)]$$

Where;

$$M1 = V_3/V_1 = 120/60 = 2 \quad M2 = V_2/V_1 = 90/60 = 1.5$$

It has been found from the results that the polarization resistance, for most mixes, has exhibited to decrease with time of exposure to sodium chloride solution. That may be attributed to the effect of the

diffusion of chloride ions into the reinforced concrete specimens and destroying the passive film on the steel surface causing a significant reduction in polarization resistance. These results are compatible with Abdul Amir [76].

Table (4.9) Polarization resistance for non-precracked specimens for three months of exposure to 3.5% sodium chloride solution.

Mixes Symbols	Percentage of Adding	RP1: M=2 RP2: M=1.5	Polarization Resistance *10 ³ (Amp./Volt.)						
			0 week	2 week	4 week	6 week	8 week	10 week	12 week
R	Nil	RP1	75.789	43.902	13.636	2.852	5.590	4.8	2.397
		RP2	375	17.374	6.503	1.735	3.251	2.767	1.471
CN + EA	0.2B _{CN} +0.8B _{EA}	RP1	30.769	21.752	16.326	1.091	2.274	0.775	1.112
		RP2	20.089	12.261	9.2402	0.725	1.385	0.505	0.651
	0.5B _{CN} +0.5B _{EA}	RP1	53.333	1.487	1.854	1.176	1.221	2.260	0.999
		RP2	49.450	0.922	1.009	0.665	0.755	1.479	0.578
	0.8B _{CN} +0.2B _{EA}	RP1	6.990	0.963	0.681	1.460	0.939	0.987	1.102
		RP2	4.0540	0.582	0.447	0.910	0.564	0.586	0.637
SB + SS	0.8B _{SB} +0.2B _{SS}	RP1	1800	69.902	107.46	1.114	6.25	0.574	0.588
		RP2	236.842	34.883	59.210	0.6805	3.9301	0.353	0.351
	0.5B _{SB} +0.5B _{SS}	RP1	130.909	15.720	6.997	7.651	16.941	1.758	1.402
		RP2	562.5	8.538	4.170	3.859	3.649	0.991	0.860
	0.2B _{SB} +0.8B _{SS}	RP1	3600	3.443	2.769	3.643	2.011	1.909	0.893
		RP2	500	2.153	1.707	2.062	1.266	1.107	0.575
PD+SBR	0.2B _{PD} +0.8B _{SBR}	RP1	9.638	20.454	3.748	0.476	0.830	0.896	2.112
		RP2	4.663	11.936	2.319	0.317	0.528	0.536	1.157
	0.5B _{PD} +0.5B _{SBR}	RP1	98.630	6.260	0.207	0.633	0.687	0.597	0.658
		RP2	93.75	3.982	0.127	0.382	0.420	0.389	0.433
	0.8B _{PD} +0.2B _{SBR}	RP1	100	12.903	1.331	1.438	5.240	1.855	3.217
		RP2	59.210	7.588	0.827	0.860	3.318	1.062	1.753

Table (4.10) Polarization resistance for precracked specimens for three months of exposure to 3.5% sodium chloride solution.

Mixes Symbols	Percentage of Adding	RP1: M=2 RP2: M=1.5	Polarization Resistance *10 ³ (Amp./Volt.)						
			0 week	2 week	4 week	6 week	8 week	10 week	12 week
R	Nil	RP1	50.526	1.360	1.381	2.414	0.456	0.379	0.317
		RP2	28.662	0.862	0.751	1.471	0.275	0.228	0.191
CN + EA	0.2B _{CN} +0.8B _{EA}	RP1	9.651	7.515	3.127	3.892	4.695	2.334	1.186
		RP2	6.224	4.513	1.663	2.374	2.738	1.308	0.690
	0.5B _{CN} +0.5B _{EA}	RP1	14.414	3.231	2.403	2.740	3.330	1.749	1.567
		RP2	8.919	2.027	1.421	1.557	2.073	1.054	0.959
	0.8B _{CN} +0.2B _{EA}	RP1	205.714	3.542	1.151	1.682	2.72	0.602	0.880
		RP2	58.823	2.09	0.694	0.961	1.500	0.362	0.527
SB + SS	0.8B _{SB} +0.2B _{SS}	RP1	42.352	96.644	1.393	1.417	1.222	1.211	0.901
		RP2	17.374	48.648	0.902	0.830	0.701	0.706	0.525
	0.5B _{SB} +0.5B _{SS}	RP1	100	4.395	10.397	0.902	4.091	1.185	1.158
		RP2	63.380	2.403	5.099	0.541	1.594	0.758	0.671
	0.2B _{SB} +0.8B _{SS}	RP1	18.556	5.008	3.495	0.916	1.216	1.274	0.634
		RP2	12.448	3.145	1.871	0.554	0.761	0.671	0.367
PD+SBR	0.2B _{PD} +0.8B _{SBR}	RP1	68.246	6.939	1.638	1.814	1.158	0.740	0.945
		RP2	40.178	3.971	1.027	1.031	0.688	0.4376	0.580
	0.5B _{PD} +0.5B _{SBR}	RP1	411.429	10.690	1.943	3.7	1.035	0.505	0.554
		RP2	204.545	7.188	1.142	2.073	0.657	0.287	0.323
	0.8B _{PD} +0.2B _{SBR}	RP1	12.182	3.807	1.947	8.475	5.091	1.387	2
		RP2	7.7653	2.178	1.205	3.578	2.736	0.825	1.253

4.8 Economical Cost

For determining economical cost for this study, the mixes (0.2B_{SBR} + 0.8B_{PD}), (0.5B_{EA} + 0.5B_{CN}) and (0.5B_{SB} + 0.5B_{SS}) are considered. The previous mixes of precracked specimens have given the best inhibition

for corrosion of reinforcement (after three months of exposure) by comparison with other mixes.

To determine the economical cost, the following equations are used:

$$1- \text{A.R.C.V for each mix} = \frac{\text{C.M for } 1\text{m}^3 \text{ con.} - \text{P. } 1\text{m}^3 \text{ con. after S. L}}{\text{No. Y. S.L}}$$

$$2- \text{Benefit over the av. of E.C} = \frac{(\text{C.M for } 1\text{m}^3 \text{ con.} + \text{P. } 1\text{m}^3 \text{ con. after S. L}) * B}{2}$$

Where:

A.R.C.V. for each mix: Annual Reduction for Capitalism Value for each mix.

C.M for 1m³ concrete: The cost of materials to cast 1m³ of concrete (ID).

P. 1m³ concrete after S.L: The price of 1m³ concrete after the service life (ID).

No. Y. S.L: Number of years of the building's Service Life (from Table (4-7)) as follow:

$$\text{No. Y. S.L} = (I_{\text{corr ref.}} / I_{\text{corr inhibitor}}) * 10$$

Where;

Abbas [2007] [18] stated that: an unacceptable degree of deterioration was observed within a short period of 5-7 years after construction as in Al-Basra airport. Thus, it has taken the number of years of the building's Service Life as 10 years.

Benefit over the average of E.C: Benefit over the average of the exploitation cost (ID).

B: The benefit (%).

1. Economical Cost for Reference Mix

- The cost of materials to cast 1m³ concrete = 250000 ID.
- The price of 1m³ concrete after the service life (ID) = 0.
- The cost of the work to cast 1m³ concrete (ID) = 180000 ID
- The cost of Durability (ID) = 125000 ID.
- The benefit (%) = 10%

$$1- \text{A.R.C.V for each mix} = \frac{250000 - 0}{10} = 25000 \text{ ID.}$$

$$2- \text{Benefit over the av. of E.C} = \frac{(250000 - 0) * 10\%}{2} = 12500 \text{ ID}$$

2. Economical Cost for (0.5B_{EA} + 0.5B_{CN}) Mix

- The cost of materials to cast 1m³ concrete = 250000 ID.
- The cost of Ethanolamine inhibitor for casting 1m³ concrete = 3.7kg * 65000 = 240500 ID.
- The cost of Calcium Nitrate inhibitor for casting 1m³ concrete = 3.7 kg * 60000 = 222000 ID.
- Because of there is no method in the literature for determining the cost of the reducing in compressive strength, the following method is suggested:

The compressive strength of reference mix @ 28 day = 26.5 MPa.

The compressive strength of (0.5B_{EA} + 0.5B_{CN}) mix @ 28 day = 22.5 MPa.

The cost of (0.5B_{EA} + 0.5B_{CN}) mix for casting 1 m³ = 712500 ID.

The cost of 1 MPa of compressive strength = $712500 / 22.5 \approx 31500$ ID.

The difference in compressive strength between reference mix and $(0.5\mathbf{B}_{EA} + 0.5\mathbf{B}_{CN})$ mix = $26.5 - 22.5 = 4$ MPa.

The cost of the reducing in compressive strength = $4 * 31500 = 126500$ ID.

- The total cost for casting 1 m^3 from $(0.5\mathbf{B}_{EA} + 0.5\mathbf{B}_{CN})$ mix = $250000 + 240500 + 222000 + 126000 = 838500$ ID.
- The price of 1m^3 concrete after the service life (ID) = 0.
- No. of years of the building's Service Life = 57 years.
- The cost of the work to cast 1m^3 concrete (ID) = 180000 ID.
- The cost of Durability = 75000 ID.
- The benefit (%) = 10.

$$1\text{- A.R.C.V for each mix} = \frac{838500 - 0}{57} \approx 14750 \text{ ID.}$$

$$2\text{- Benefit over the av. of E.C} = \frac{(838500 - 0) * 10\%}{2} \approx 42000 \text{ ID.}$$

3. Economical Cost for $(0.5\mathbf{B}_{SB} + 0.5\mathbf{B}_{SS})$ Mix

- The cost of materials to cast 1m^3 concrete = 250000 ID.
- The cost of Sodium Benzoate inhibitor for casting 1m^3 concrete = $3.7 \text{ kg} * 5000 = 18500$ ID.
- The cost of Sodium Silicate inhibitor for casting 1m^3 concrete = $1.85 \text{ kg} * 5000 = 9250$ ID.
- The cost of the reducing in compressive strength = 99750 ID.

- The total cost for casting 1 m³ from (0.5B_{SB} + 0.5B_{SS}) mix = 250000 + 18500 + 9250 + 99750 = 377500 ID.
- The price of 1m³ concrete after the service life (ID) = 0.
- No. of years of the building's Service Life = 63 years.
- The cost of the work to cast 1m³ concrete (ID) = 180000 ID.
- The cost of Durability = 75000 ID.
- The benefit (%) = 10.

$$1- \text{A.R.C.V for each mix} = \frac{377500 - 0}{63} \approx 6000 \text{ ID.}$$

$$2- \text{Benefit over the av. of E.C} = \frac{(377500 - 0) * 10\%}{2} \approx 19000 \text{ ID.}$$

4. Economical cost for (0.2B_{SBR} + 0.8B_{PD}) mix

- The cost of materials to cast 1m³ concrete = 250000 ID.
- The cost of Potassium Dichromate inhibitor for casting 1m³ concrete = 5.92 kg * 40000 = 237000 ID.
- The cost of Styrene Butadiene Rubber inhibitor for casting 1m³ concrete = 42500 ID.
- The cost of the reducing in compressive strength = 67500 ID.
- The total cost for casting 1 m³ from (0.2B_{SBR} + 0.8B_{PD}) mix = 250000 + 237000 + 42000 + 67500 = 596500 ID.
- The price of 1m³ concrete after the service life (ID) = 0
- No. of years of the building's Service Life = 65 years.
- The cost of the work to cast 1m³ concrete (ID) = 180000 ID.

- The cost of Durability = 75000 ID.
- The benefit (%) = 10.

$$1- \text{A.R.C.V for each mix} = \frac{596500 - 0}{65} \approx 9250 \text{ ID.}$$

$$2- \text{Benefit over the av. of E.C} = \frac{(596500 - 0) * 10\%}{2} \approx 30000 \text{ ID.}$$

The summary of economical cost values are shown in Table (4.11). The results of economical calculation indicated that $(0.5\mathbf{B}_{SB} + 0.5\mathbf{B}_{SS})$ mix is optimum mix, though, that $(0.2\mathbf{B}_{SBR} + 0.8\mathbf{B}_{PD})$ mix has better corrosion inhibition efficiency.

Table (4.11) Economical cost of concrete mixes which have given the best inhibition.

Details \ Mixes	Reference mix	$0.5\mathbf{B}_{EA} + 0.5\mathbf{B}_{CN}$	$0.5\mathbf{B}_{SB} + 0.5\mathbf{B}_{SS}$	$0.2\mathbf{B}_{SBR} + 0.8\mathbf{B}_{PD}$
The cost of the work to cast 1m^3 concrete (ID)	180000	180000	180000	180000
The cost of Durability (ID)	125000	75000	75000	75000
Annual Reduction for Capitalism Value for each mix (ID)	25000	14750	6000	9250
Benefit over the average of the Exploitation Cost (ID)	12500	42000	19000	30000
The summation (ID)	342500	311750	280000	294250

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

Based on the results of this work, the following conclusions are obtained:

1. The mixes which contain inhibiting admixtures presented a negative action on mechanical properties tests of concrete like, compressive strength test, splitting tensile strength test and absorption test.
2. Lowest compressive strength is occurred by $(0.5\mathbf{B}_{PD} + 0.5\mathbf{B}_{SBR})$ mix with a reduction about 30%, 33.3% and 34.3% at ages 28, 60 and 90 days respectively. However, $(0.2\mathbf{B}_{SBR} + 0.8\mathbf{B}_{PD})$ has got less reduction in compressive strength with respect to all other mixes with lowering about 11.3%, 15% and 16.4% at 28, 60 and 90 days, sequently.
3. For mixes which contain (CN + EA) admixtures, the reduction in compressive strength is higher at later ages than early ages where the reduction at 90 days age was 16.4% for $(0.2\mathbf{B}_{EA} + 0.8\mathbf{B}_{CN})$ mix, 17.9% for $(0.5\mathbf{B}_{EA} + 0.5\mathbf{B}_{CN})$ mix and 22.4% for $(0.8\mathbf{B}_{EA} + 0.2\mathbf{B}_{CN})$ mix.
4. For mixes which contain (SB + SS) admixtures, the reduction in splitting tensile strength was reduced with increasing of Sodium Silicate dosage upon Sodium Benzoate admixture.

5. All mixes, except $(0.8\mathbf{B}_{EA} + 0.2\mathbf{B}_{CN})$ mix, revealed an increase in the absorption in comparison with reference mixes. Where, $(0.8\mathbf{B}_{EA} + 0.2\mathbf{B}_{CN})$ mix had lower absorption, that's equal to reference mix.
6. There is an obvious fluctuation in the results of polarization resistance. That may be due to the limited period of the study. For this reason, it has been made fitting trend lines for the obtained results.
7. For precracked specimens, after three months of exposure to 3.5% NaCl solution, the $(0.5\mathbf{B}_{CN} + 0.5\mathbf{B}_{EA})$ mix has the best inhibition (about 82%) for (CN + EA) admixtures. Where as, for (SB + SS) admixtures, the perfect reduction in corrosion rate has got in $(0.5\mathbf{B}_{SB} + 0.5\mathbf{B}_{SS})$ mix with efficiency about 84%. The mix which contains $(0.8\mathbf{B}_{PD} + 0.2\mathbf{B}_{SBR})$ admixtures has produced best inhibition for corrosion about 85%.
8. For non-precracked specimens, after three months of exposure to 3.5% NaCl solution, the studied inhibiting admixtures have opposite action on corrosion process (increased the corrosion rate).
9. Electrical resistance of concrete, for most mixes, has decreased with time of exposure to sodium chloride solution.
10. Though these synergic inhibitors are decreasing the mechanical properties of the concrete, but they are considered as better economically along the service life of a structure by comparison with reference (without any inhibitor) concrete. The optimum economical mix is $(0.5\mathbf{B}_{SB} + 0.5\mathbf{B}_{SS})$.

5.2 Recommendations for Future Works

In addition to the results obtained from the present work, future investigation could be continued along the following lines:

1. Using these synergic admixtures with different application like applying them on the surface of hardened concrete (as migrating corrosion inhibitors) to know their influence on the mechanical properties of concrete.
2. Studying the effectiveness of these inhibitors against corrosion of steel reinforcement when adding sodium chloride internally rather than externally, for example, mixing sodium chloride salt with the mixing water during batching to accelerate the corrosion process.
3. An investigation is required to know the role of these inhibitors when using sulfate resistant cement rather than ordinary cement in concrete.
4. A research work is necessary to determine the action of these inhibitors under macro cracks conditions instead of micro cracks environments, in addition of studying the influence of crack width on their efficiency.
5. A study is recommended to show these inhibitors effectiveness in carbonated concrete.
6. A further study is required to investigate the activity of these admixtures on stopping the corrosion process at corroded reinforcing bars.

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