

Effect of Using Corrosion Inhibitors on Concrete Properties and Their Activity

تأثير استخدام مثبطات التآكل على خواص الخرسانة ومدى فاعليتها

Lecture.Dr. Falah K. Matlob
Ph.D in Chemical Engineering

Abeer Mohammed Abdul Amir
M.Sc. in Civil Engineering

Nada Flah Hassan

B.Sc. in Civil Engineering College of Engineering - Babylon University

Abstract :

In this investigation, the effect of using sodium benzoate, potassium dichromate as corrosion inhibitors in concentrations (1%, 2% and 3% by weight of cement) is studied on concrete properties; compressive strength, splitting tensile strength, flexural strength and absorption. Also the activity of these admixtures in their three concentrations were studied to reduce the corrosion rate where the three electrode polarization resistance is used to measure the corrosion rate and by measuring the electrical resistance of concrete. The reinforced concrete samples were immersed partially in 3.5% NaCl solution for three months. Half of these samples were loaded with 10% of the design load after 6 weeks of immersing to make micro cracks in the concrete body. The test results indicate that the use of sodium benzoate, potassium dichromate in 2% concrete, 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 specimens got an increase in compressive strength about 7% and 11% at 90 days respectively, 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 test with 38% and 42% respectively and inhibitor efficiency about 98% for each one.

Keywords: :Corrosion of Steel in Concrete ,Corrosion Inhibitors, Corrosion of reinforced concrete.

الخلاصة :

وفي هذا البحث تم دراسة استخدام كل من بنزوات الصوديوم ودايكرومات البوتاسيوم كمثبطات انودية بالنسب (١%، ٢%، و ٣% من وزن الاسمنت) ومدى تأثيرها على خواص الخرسانة : كمقاومة الانضغاط، مقاومة شد الانشطار، مقاومة الانتشاء و الامتصاص مع دراسة قابليتها على منع أو تأخير حصول التآكل لحديد التسليح في الخرسانة المسلحة من خلال فحص مقاومة الاستقطاب بطريقة الأقطاب الثلاثة للحديد ومعرفة نسب التآكل وفحص المقاومة الكهربائية للخرسانة . تم وضع النماذج الخرسانية المسلحة فقط في محلول مائي حاوي على أملاح كلوريد الصوديوم NaCl بتركيز ٣.٥ % (مقارب لتركيز ماء البحر) لمدة ثلاثة أشهر. نصف عدد هذه النماذج تم تعريضه إلى ١٠% من الحمل الأقصى لكل خلطة بعد ستة أسابيع من الغمر في المحلول الملحي لغرض عمل تشققات شعرية في النماذج الخرسانية المسلحة لتسريع عملية التآكل. نتائج الفحوص جاءت بالاستنتاجات التالية : استخدام بنزوات الصوديوم ودايكرومات البوتاسيوم بتركيز ٢% من وزن الاسمنت سبب انخفاض في مقاومة الانضغاط بعمر ٢٨ يوم بمقدار ١٥% و ٤% على التوالي ، لكن في الاعمار المتأخرة كانت هناك زيادة في مقاومة الانضغاط حوالي ٧% و ١١% بعمر ٩٠ يوم على التوالي. وأعطى هذان المضافان تحسن وزيادة في كل من الخواص التالية: مقاومة شد الانشطار بمقدار ١٧% لبنزوات الصوديوم و ٢١% لدايكرومات البوتاسيوم، زيادة في مقاومة الانتشاء بمقدار ١٨% و ٢٠% على التوالي، كذلك سببت هذه المضافات انخفاض كبير في خاصية الامتصاص بمقدار ٣٨% و ٤٢% على التوالي وكانت كفاءة المثبط ٩٨% لكل منهما .

1. Introduction

Corrosion can be defined as: the destruction or deterioration of materials due to reaction with its environment. Reinforced concrete is a versatile, economical and successful construction material. It can be molded to a variety of shapes and finishes. Usually it is durable and string, performing well throughout its service life typically exceeds 50 years. Some times, it does not perform adequately as a result of poor design, poor construction, inadequate materials selection, a more severe environment than anticipated or a combination of these factors (John P. B.1997)

Reinforced concrete superstructures along the coast can corrode due to marine atmospheric exposure if not properly designed. Marine atmospheric can be defined as that atmosphere within 300m (1000 ft) of ocean or tidal water, tidal water: is any body of surface water having a chloride content of 500ppm or greater (**Corrosion Guidelines,2003**).

The cost of repairing or replacing deteriorated structures has become a major liability for highway agencies, estimated to be more than \$20 billion and to be increasing at \$500 million per year that's in united state (**Paul Teng T.,2000**).

Reinforcing steel embedded in concrete shows a high amount of resistance to corrosion because the cement paste in good quality concrete provides an alkaline environment with pH (12.5-13.5) that protects the steel from corrosion by passivating or protective ferric oxide film that forms on the surface steel bar when it is embedded in concrete. This passive film is only a few nanometers thick and is stable in the highly alkaline concrete (pH approx. 11-13.5) (**John P. B.1997**).

The protective action of the passive film is immune to mechanical damage of the steel surface, it can, however, be destroyed by carbonation of concrete or by the presence of chloride ions. The reinforcing steel is depassivated when the pH falls below 10 for any reason then the corrosion may occur (**Paul Teng T.,2000**).

Then carbonation or chloride ions can penetrate through the concrete pores to the oxide layer on the rebar breaking down the passive layer and leaving the steel bar vulnerable against aggressive agents; in the presence of moisture and oxygen the corrosion will occur (**Corrosion Guidelines,2003**).

1.1 The Corrosion Process

Once the passive layer breaks down then areas of rust will start appearing on the steel surface. The chemical reactions are the same whether corrosion occurs by chloride attack or carbonation. When steel in concrete corrodes, it dissolves in the pore water and gives up electrons:

The anodic reaction: $\text{Fe} \rightarrow \text{Fe}^{+2} + 2\text{e}^- \dots\dots\dots (1)$

The two electrons (2e^-) created in the anodic reaction must be consumed elsewhere on the steel surface to preserve electrical neutrality. In other words, it is not possible for large amounts of electrical charge to build up at one place on the steel; another chemical reaction must consume the electrons. This is a reaction that consumes water and oxygen (**Perez N., 2004**):

The cathode reaction : $2\text{e}^- + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow 2\text{OH}^- \dots\dots (2)$

Hydroxyl ions (2OH^-) are generated in the cathodic reaction; These ions increase the local alkalinity and will therefore strengthen the passive layer, warding off the effects of carbonation and chloride ions at the cathode) (**John P. B.1997**). If the iron is just to dissolve in the pore water (the ferrous ion Fe^{+2} in equation 2.3 is soluble) cracking and spalling of the concrete can not be seen. Several more stages must occur for rust to form. This can be expressed in several ways; one of which is shown below where ferrous hydroxide becomes ferric hydroxide and then hydrated ferric oxide or rust (**Perez N., 2004**):

$\text{Fe}^{+2} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2 \dots\dots\dots (3)$

Ferrous hydroxide

$4\text{Fe}(\text{OH})_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4 \text{Fe}(\text{OH})_3 \dots\dots (4)$

Ferric hydroxide

$2\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2\text{H}_2\text{O} \dots\dots\dots (5)$

Hydrated ferric oxide (rust)

Most problems with corrosion of steel in concrete are not due to loss of steel but growth of the oxide that has a volume of about twice to six time that of the steel it replaces when fully dense

(Bertolini, L. et al, 2004). When it becomes hydrated it swells even more and becomes porous. This means that the volume increases at the steel/concrete interface in two to several times. This leads to the cracking and spalling of the concrete cover that we observe as the usual consequence of corrosion of steel in concrete and the red/brown brittle, flaky rust on the bar and the rust stains seen at cracks in the concrete (John P. B.1997).

1.2 Chloride Attack

The passivity provided by the alkaline conditions can be destroyed by the presence of chloride ions, even through a high level of alkalinity remains in the concrete. The chloride ion can locally depassivate the metal and promote active metal dissolution (Bertolini, L. et al, 2004).

Chloride reacts with the calcium aluminates (C3A) and calcium aluminoferrite (C4AF) in the concrete to form insoluble calcium chloroaluminates and calcium chloroferrites in which the chloride is bond in non-active form; however, the reaction is never complete and some active soluble chloride always remains in equilibrium in the aqueous phase in the concrete. At the low concentration levels of chloride in the aqueous phase, the rate of corrosion is very small, but higher concentration increases the risks of corrosion (Persson M, 2000). Thus the amount of chloride in the concrete and, in turn, the amount of free chloride in the aqueous phase (which is partly a function of cement content and also of the cement type) will influence the risk of corrosion.

While the concrete remains in uncarbonated state the level of free chloride in the aqueous phase remains low (perhaps 10% of the total Cl). However, the influence of severe carbonation is to break down the hydrated cement phase and, in the case of chloroaluminates, the effect is to release chloride. Thus more free chloride is available in carbonated concrete than in uncarbonated materials (ACI Committee201 2R-92).

The level of chloride ions required to initiate corrosion in concrete corresponds to 0.1% soluble chloride ion by weight of cement. This is equivalent to between 0.6 -0.8 Kg of chloride per m³ of concrete (Bavarian B., 2000).

There is a ‘chloride threshold ‘ for corrosion given in terms of the chloride /hydroxyl ratio. When the chloride concentration exceeds 0.6 of the hydroxyl concentration, corrosion is observed. This approximates to a concentration of 0.4% chloride by weight of cement cast into concrete [(John P. B.1997), (Persson M, 2000)] see table 1 and 2.

Table 1 Chloride concentration in reinforced concrete (Corrosion Guidelines,2003)

Cl⁻ concentration Kg/m³	Assumed condition
0 to 0.7	Passive (non- corroding)
0.9 to 1.8	Corrosion initiation
> 1.8	Active corrosion

Table 2 Chloride limits for new construction (ACI Committee 222 R -96).

Category	Chloride limit for new construction as a percentage of concrete mass	
	Acid –soluble ASTM C1152	Water –soluble ASTM C1218
Prestressed concrete	0.08	0.06
Reinforced concrete in wet condition	0.10	0.08
Reinforced concrete in dry condition	0.20	0.15

1. 3Corrosion Inhibitors

Corrosion inhibitors technology has been used around since 1960, but has only been available to the construction industry for the past ten years. Corrosion inhibitors are chemical admixtures when added to concrete mix in very small concentration can be able to prevent or delay the corrosion that happens in reinforcement bars (د. حسين باقر، ١٩٨٩).

Corrosion inhibitors are generally used as admixtures in concrete for construction, but they can also be used for repairs by being admixed into concrete for paths, sprayed or painted onto the surface of the concrete or applied by saturation treatment (**Roberge P.R.,٢٠٠0**).

There is accomplished behavior for inhibitor molecules to penetrate the concrete through cracks and pores and then react with the cement and reinforcement steel to restore with successfully the passivating film to the steel and extend the useful life of the concrete structure (**John P. B.1997**).

Corrosion inhibitors are organic or inorganic. Inorganic inhibitors like, potassium dichromate, zinc and lead chromate, sodium benzoate, calcium hypophosphite, and calcium nitrite and organic inhibitors like, sodium cinematic, ethanolamine (**Bregman J.I.,1963**).

In general, they are classified based on their protection mechanism that are added to a water source or other fluids or gases in small amounts to stop or delay corrosion of metals exposed to corrosive environment, they can protect by affecting the anodic reaction or the cathodic reaction or both reaction (mixed) [(**John P. B.1997**), (**Fontana M.G.,1978**)].

Inhibitors have been classified in many ways ,including by composition ,mechanism of action or form (**Persson M, 2000**).

According to the mechanism of action inhibitors fall into several classes, passivation, precipitators, vapor phase, cathodic, anodic, neutralizing and absorbents (**Landroum R.J.,1989**).

Organic inhibitors are adsorbed layer formers, which strongly adsorb to the metal surface and interfere with the anodic and cathodic reaction in the area of adsorption. The chemical structure of the inhibitor molecule plays a significant role and often determines whether or not compounds will effectively inhibit a specific system in this study (**Fontana M.G.,1978**).

They also may :

- Increase the anodic or cathodic polarization behavior;
- Reduce the movement or diffusion of ions to the metallic surface, and;
- Increase the electrical resistance of the metallic surface (**Kepler J.L.et al,2000**).

There are three major concerns regarding the use of corrosion inhibitors. The first one is the long-term stability and performance of the inhibitor. The second is the inhibitor's effect on corrosion propagation after corrosion initiation. The third is the inhibitor's effect on concrete's physical properties over the service life of the structure (**Persson M, 2000**).

Berke N.S.,1989 studied the corrosion inhibiting properties of calcium nitrite ,and he states that calcium nitrite is successfully being used because it provides corrosion inhibition in the presence of chloride ; it is not detrimental to concrete properties ; and it is available in sufficient quantities for commercial use in concrete .

. **Hope B.B. and Thompson S.V,1995** found during an investigation on the effectiveness of corrosion inhibitors that, all samples of concrete containing NaCl which were soaked in saturated $\text{Ca}(\text{NO}_2)_2$ solution undergo severe mortar deterioration. The mortar cracked and bulged without corrosion of reinforcing steel due to the use of corrosion inhibitors.

Limaye R.G.et al,2000 studied the ability of new generation of corrosion inhibitors (CPCI a Concrete-surface applied Penetrating Corrosion-Inhibitor), which is based on bipolar mechanism and which can penetrate even dense concrete by virtue of its vapor pressure and affinity for the embedded steel in concrete. The inhibitor was used in both as an admixture in fresh concrete and as a coating on hardened concrete.

Limaye R.G.et al,2000 used two types of concrete mix ; weak and strong. The result was that the using of penetrating corrosion inhibitor as admixture to concrete did not impair any mechanical properties or physical properties like workability, water absorption, initial and final setting time and other properties did not show any change, also compressive strength and bond strength showed improvement at ambient temperature and even at higher temperature of 60°C .

The corrosion rate that was measured with half cell potential has an reduction in both weak and strong concrete. However, this effect is more pronounced in weak concrete as compared to stronger concrete grades.

Stephen R.S.,2004 investigated the use of penetrating corrosion inhibitors to extend the life of existing reinforced concrete bridge decks. The idea of simply applying inhibitors to the concrete surface is appealing. It is critical that the inhibitor not only penetrates the concrete but also reaches the reinforcing steel in sufficient concentrations to inhibit corrosion. They used the vacuum to remove residual moisture from the concrete followed by the application of pressure to inject an inhibitor into the concrete. This technique reduces the corrosion rate by hindering the anodic reaction, the cathodic reaction, or both. The two corrosion inhibitors evaluated were TPS-II and Ferrogard 903.

On September 2002 TPS-II was applied to the bridge decks surface with using the compression sprayer (2 spans were treated and one span remained without treatment as control span).

Measurements included half-cell potential (versus copper- copper sulfate reference electrode [CSE]), corrosion rate (by measuring the polarization resistance), and degree of delamination. Testes were made before and following treatment, after 28 days and 190 days. After one year the study found that the treated spans had a more positive values of half – cell potential than the control span that means the corrosion rates were reduced and the corrosion inhibitor has a good effect to coat the rebar surface with protective layer.

2. Experimental Work

2.1 Materials

Ordinary Portland cement type I locally available was used in this study conforming to the Iraqi specification IQS No.5/1984 (**IOS 5 :1984, for Portland Cement**).

The physical properties and chemical composition of this cement are given in Tables 3 & 4. respectively as tested in cement test laboratory/ Babylon University.

Graded sand was used in this study. It was washed and left in laboratory to dry and brought from Al-Akhader - Karbala. Table 5 shows the sieve analysis ,Mud % , SO₃ % and fineness modulus according to IQS 45 :1984specification (**IQS 45 :1984, for Aggregate**).

Graded gravel that used in this study. It was brought from Al-Nibae -Baghdad with maximum aggregate size 20 mm. It was washed and left in laboratory to dry and table 6 shows the sieve analysis, Mud % , SO₃ % and limits according to specification for IQS 45:1984 (**IQS 45 :1984, for Aggregate**). Tap water was used throughout this work for both making and curing the specimens.

Table 3 Physical characteristics of cement

Physical properties	Test results	Limit of Iraqi specification IQS No.5/1984
• Setting Time, min ,Initial Final	105 220	>= 45 min <= 600 min
Fineness (Blain Method) in cm²/g	2880	>=2300
Compressive strength in MPa : at 3 days 7 days	18.0 27.0	>= 15 >= 23

Table 4 Chemical composition and main compounds of ordinary Portland cement

Oxide	Content %	Limits according to IQS No.5/1984
SiO ₂	20.82	-----
CaO	62.45	-----
MgO	1.53	<= 5%
Fe ₂ O ₃	3.60	-----
Al ₂ O ₃	5.46	-----
SO ₃	2.41	<= 2.5% if C ₃ A < 5% <= 2.8% if C ₃ A > 5%
Free lime	1.23	-----
Loss of Ignition	3.05	<= 4%
Insoluble Residue	1.10	<= 1.5%
L . S . F	0.88	0.66 – 1.02
Main compounds (Bogue's equation)		% by wt. of cement
C ₃ S		42.29
C ₂ S		27.78
C ₃ A		8.38
C ₄ AF		10.95

Table 5 Sieve analysis and some properties of fine aggregate

Sieve size (mm)	% Passing	Limit of Iraqi Specification No.45/1984 (zone 1)
10	100	100
5	95	90– 100
2.36	80	60 – 95
1.18	67	30 – 70
0.6	51	34 – 75
0.3	21	5 – 20
0.15	4	0 – 10
0.075	0	<=5%
SO3 % = 0.14 , Limit of Iraqi Specification for SO3 %<= 0.5		
Mud % = 0 , F.M= 2.8		

Table 6 Sieve analysis for coarse aggregate

Sieve size (mm)	% Passing	Limit of Iraqi Specification No.45/1984 ,5-20 mm
37.5	100 %	100 %
20	100 %	95 – 100 %
10	35 %	30 – 60 %
5	5 %	0 – 10 %
2.36	0 %	----
SO3 % = 0.08 , Limit of Iraqi Specification for SO3 %<= 0.1, Mud % = 0		

2.2 Corrosion Inhibitors:

Two type of anodic, inorganic corrosion inhibitors were used :

2.2.1 Sodium Benzoate (SB) (C₆H₅COONa)

The trade name is 71300 Natriumbenzoat, with purity >97%, soft powder material with white color

(SB) has approximate density of (572.2) kg /m³, it was used in three concentrations (1%, 2% and 3% by weight of cement), it was added to mixing water with stirring until diffusing completely then added to the concrete mix. After hardening, the concrete specimens will show on their surfaces a white thin layer which was easy to peel with hand or water as shown in figure 1 .

2.2.2 Potassium Dichromate (PD) (K₂Cr₂O₇)

The trade mark of potassium dichromate is REACHIM, with purity 99.8%. (PD) grains look like sugar grains in size and shape with orange color

(PD) has approximate density of (1281)kg/m³, it was also used in three concentrations (1% ,2% and 3% by weight of cement), it was added to water mix and stirred until diffusing completely, then added to the concrete mix. After hardening the concrete specimens have a green color due to adding this admixture.

2.3 Steel Reinforcement

The steel reinforcement that was used in this work were wires of 0.5 cm in diameter. These wires were cleaned with wetted grinding paper (rough then smooth) then immersed in cleaner liquid (flash liquid) to remove any rust or deposits on their surface. See table 7 and Figure 2.

Table 7 Steel reinforcement wires dimensions

Diameter of wire (mm)	Cross section area (mm²)	Length of embedded Wire in concrete (mm)	Surface area of imbedded wire in concrete (mm²)
5	19.64	180	2830.53



Fig. 1 The white layer on the surface of the concrete specimens due to the using of sodium benzoate admixture .



Fig. 2 Steel reinforced wires before and after cleaning

2.4 Concrete Mixes

Concrete mixes were designed in accordance with the American mix design method (ACI 211) to have a compressive strength 25 MPa at age of 28 days .Ordinary Portland cement concrete mix with cement : sand : gravel ratio of 1 : 1.8 : 2.5 and water / cement ratio of 0.48 was prepared for casting specimens. The materials were mixed by using an electrically driven batch mixer.

Seven types of concrete mixes were prepared throughout this study :

1. Reference concrete mix without any admixture (two mixes).
2. Three concrete mixes containing sodium benzoate (SB) in three concentrations(1%,2% and 3% by weight of cement).
3. Three concrete mixes containing potassium dichromate(PD) in three concentrations(1%, 2% and3% by weight of cement).

Table 8 illustrates the proportion of concrete mixtures and some properties of fresh and hardened concrete.

2.5 The Mold of Reinforced Concrete Specimen

The details of reinforced concrete specimens with dimensions are shown in Fig.3 . The reinforced concrete specimens were taken out of the curing tap water after 80-85 days instead of 28 days because the delay in preparing the machine that was used to measure the polarization resistance and getting a concrete with low porosity and good hydration. After recording the first electrical resistance and polarization data for each specimens, the specimens were immersed partially in aggressive solution (3.5% NaCl solution for three months, through this period the recording of data were continued.

The three bars of reinforced concrete samples arranged as equal leg triangular with 9 cm leg length as shown in Figure 6.

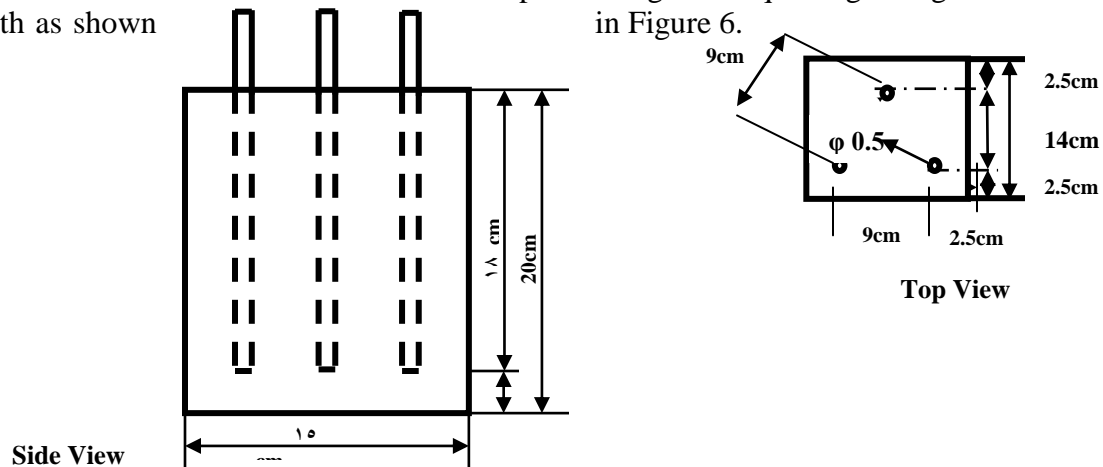


Fig. 3 Details of reinforced concrete specimen

Table 8 Illustrates the proportion of concrete mixtures and some properties of fresh and hardened concretes .

Type of mix			Slump in mm In 30-40C°	wet density kg/m ³
Symbol of mix	Type of admixture	% of adding		
N (Reference)	No adding	Nil	80	2410
SB 1	Sodium benzoate	1% by weight of cement	80	2400
SB 2	Sodium benzoate	2% by weight of cement	78	2385
SB 3	Sodium benzoate	3% by weight of cement	75	2380
PD 1	Potassium dichromate	1% by weight of cement	78	2400
PD 2	Potassium dichromate	2% by weight of cement	77	2375
PD 3	Potassium dichromate	3% by weight of cement	74	2475

2.6 Concrete Testing

2.6.1 Compressive Strength Test

The concrete compressive strength was measured with 150 mm cube, the Cubes were removed from the curing water at age of 28, 60 and 90 days. The reported values were the average of three specimens for each age (B.S. 1881: Part 116, 1989).

2.6.2 Splitting Tensile Strength Test

The concrete splitting tensile strength was measured with 100 *200 mm cylinders according to ASTM C 496-86 (ASTM, Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens 1989)

The cylinders were removed from the curing water at age of 28 days. Splitting tensile strength can be calculated by using the following equation : $St = 2P / \pi DL$ (6)

Where : St : splitting tensile strength (N/mm²). P : applied load (N).

D : diameter of cylinder (mm).

L : length of cylinder (mm)

(د. مؤيد نوري الخلف ، هناء عبد يوسف ١٩٨٤)

The reported values were the average measured on three specimens for each mix.

2.6.3 Flexural Strength Test

Test of flexural strength was carried out on (100*100*400 mm) simply supported prisms with a clear span of 300 mm. The prisms were tested according to arrangement two - point load. The test was performed according to B.S.1881- part 118 – 1989 (B.S. 1881, Part 118, 1989).

The average of three prism specimens was adopted and the specimens were tested at age of 28 days.

Flexural strength can be calculated from the following equation : $fs = PL/bd^2$...(7)

Where : fs : flexural strength (N/mm²).

P : applied load (N).

L : effective length (mm).

b : width of prism (mm).

d : depth of prism (mm).

(د. مؤيد نوري الخلف ، هناء عبد يوسف ١٩٨٤)

2.6.4 Absorption Test

The concrete absorption was measured on 100 mm cube specimens after 28 days of curing in tap water, these specimens were dried in 105±5°C for 72 hours until the weight be constant then the specimens immersed in water for 24 hours (د. مؤيد نوري الخلف ، هناء عبد يوسف ١٩٨٤).

The average result of three specimens was adopted.

The percentage of total absorption was calculated with the following equation :

$$Absorption (\%) = (W2 - W1) / W1 * 100 \quad \text{.....(8)}$$

Where :

$W1$: the average weight of dry specimens (g).

$W2$: the average weight of wet specimens

(g).

2.7 Electrochemical Tests

2.7.1 Electrical Resistance Test for Reinforced Concrete Specimens

(140*150*200 mm) concrete prisms reinforced with three 5 mm diameter longitudinal wires were cast for this test.

The electrical resistance for the reinforced concrete specimens was measured with using Ohmmeter machine (MX 553 – Metcix) digital multimeter by measuring the electrical resistance between each two wires (Jamil H.E et al ,2004)

The average of three readings was recorded and the reading was in KΩ (Kilo Ohm) units. The results of the electrical resistance before and after partial immersing of specimens in [3.5% NaCl solution] for three months were measured as shown in figure 4.

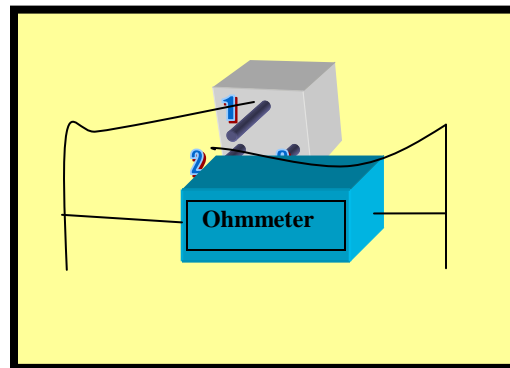


Fig. 4 Diagram of Electrical Resistance Test Circuit.

2.7.2 Polarization Resistance of Steel Reinforcement Wires

2.7.2.1 Instrumentation

The setup used for polarization measurement (Three electrode method) according to ASTM STP 908 (ASTM Special Technical Publication 908, 1984) shown in Fig. 5 includes the following parts:

1. Power supply (EIS CO. Low voltage power supply) D.C Voltage max. 250 v, D.C Amps. max. 4 Amper.
2. Current measuring instrument (MX 553 – Metcix) digital multimeter.
3. Voltage measuring instrument (MX 553 – Metcix) digital multimeter.

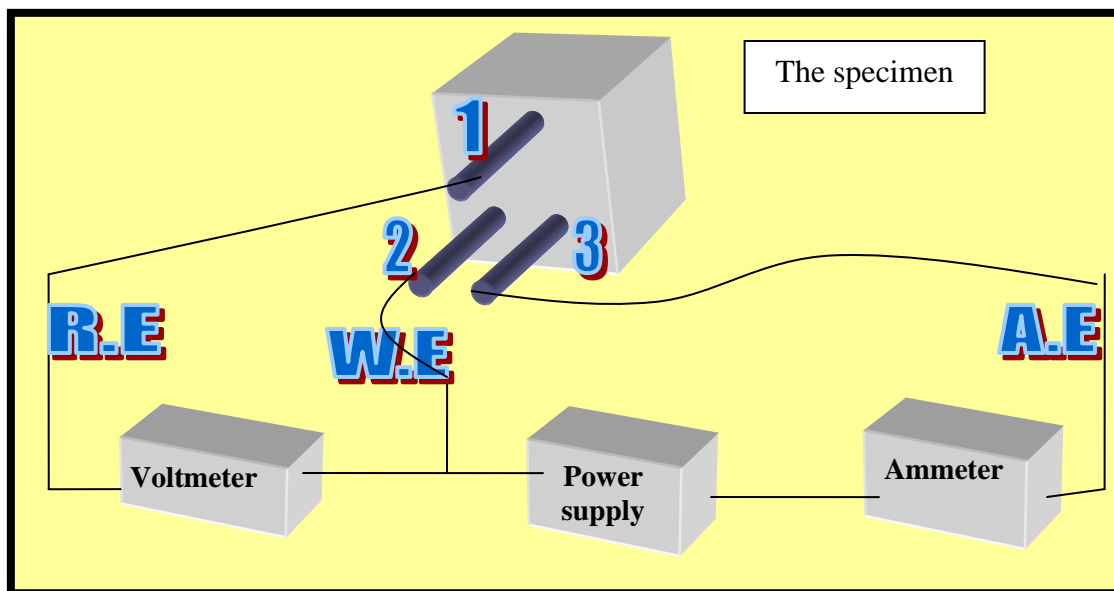


Fig. 5 Diagram of Polarization Resistance Test Circuit.

3. Results and Discussion

3.1 Compressive Strength Test

For sodium benzoate admixture in concrete. (1% by weight of cement) there is no reduction in compressive strength in ages 28, 60 and 90 days, and the specimens have given results higher

than the reference mix (C25) by approximate 12%, 15% and 14% for ages 28 ,60 and 90 days respectively.

The using of sodium benzoate as corrosion inhibitor in concrete. 2% and 3% by weight of cement affect compressive strength at early ages (28 days) with a considerable reduction 15% for 2% addition ,and 11.5% for 3% addition, but in the later ages the specimens have got an increase in compressive strength by about 7% and 17% at age 90 days respectively and that means this admixture may be works as a retardar as shown in Fig. 6.

For potassium dichromate admixture with concrete. of (1% and 2% by weight of cement) compressive strength has got a considerable reduction of 8% and 4% respectively at ages 28 days and obtained a development in compressive strength at ages 60 and 90 days, with an increase 49% and 11% at age of 90 days respectively . That's may be due to this admixture works as a retardar, it retards the action of C3S or C3A who get the compressive strength at the early ages of the concrete.

For 3% addition of potassium dichromate by weight of cement has improved the compressive strength of 15.4%, 15% and 14% for ages 28 ,60 and 90 days respectively as shown in figure 7. These results agree with Limaye & Angal (**Limaye R.G.et al,2000**) who used two types of corrosion inhibitors in two types of concrete: strong and weak; they state that “the using of penetrating corrosion inhibitor as admixture to concrete did not impair any mechanical or physical properties also compressive strength and bond strength showed improvement at ambient temperature and even at higher temperature of 60°C”.

3.2 Splitting Tensile Strength Test

The concrete with sodium benzoate admixture revealed an increase in splitting tensile strength by about 10%, 16.6% and 17% for concrete specimens with 1%, 2% and 3% of admixture by weight of cement respectively.

The concrete with potassium dichromate admixture gave an increase in splitting tensile strength by about 15%, 21% and 30% for concrete specimens with 1%, 2% and 3% of admixture by weight of cement respectively.

Results showed an increase in splitting tensile strength with the increase of the percentage adding for the two corrosion inhibitors which used in this study as shown in Fig.8 ; and this agrees with Berke (**Berke N.S.,1989**) who states that: corrosion inhibitor provides corrosion inhibition in the presence of chloride and improves the concrete properties with increasing the percentage of adding.

3.3 Flexural Strength Test

The concrete mixes with different admixtures in different concentrations recorded an increase in values of modulus of rupture as compared with the reference concrete mix as shown in figure9.

The concrete mixes with Sodium Benzoate admixture exhibited an increase in modulus of rupture by about 13%, 18% and 24% for mixes with conc. of 1%, 2% and 3% by weight of cement respectively.

The concrete mixes with Potassium Dichromate admixture recorded increase with 15%, 20% and 29% concentrations 1%, 2% and 3% by weight of cement respectively.

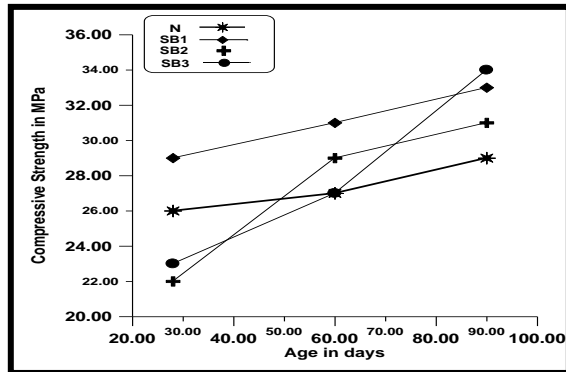


Fig. 6 Development of compressive strength with age for mixes with sodium benzoate

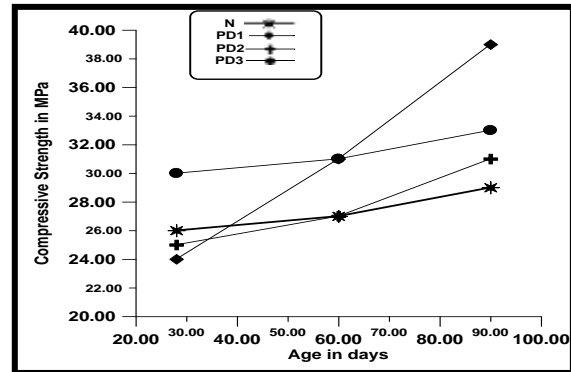


Fig. 7 Development of compressive strength with Age for mixes with potassium dichromate admixture

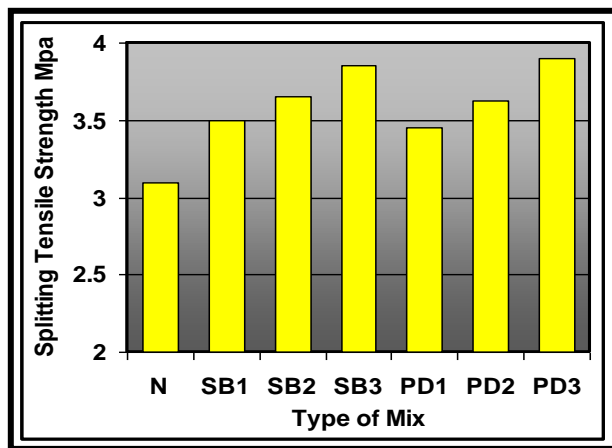


Fig8 Splitting tensile strength for concrete specimens with different admixtures

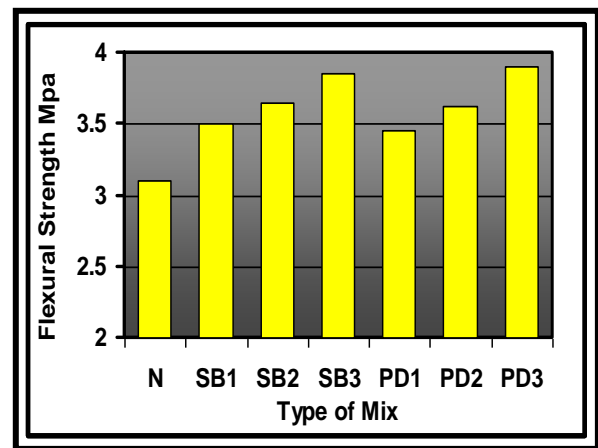


Fig 9 Flexural Strength for different concrete mixes

**3.4
Ab**

sorption Test

Concrete mixes with different admixtures in different concentrations showed a noticeable reduction in water absorption. This reduction increases with increasing of the concentrations for all admixtures. This finding conforms with properties of corrosion inhibitors which prevent or delay the corrosion of steel reinforcement without any effect or with a little effect on concrete properties with decreasing the absorption and porosity of concrete mix (**Qian S. and Cusson D.,2004**). See table 10 and Figure 10.

3.5 Concrete Electrical Resistance Test

The results of electrical resistance test for reinforced concrete samples with pre cracks in (k.ohm) are shown in Figures 11and 12. When the concrete produced with a good quality, its electrical resistance will be high. The micro cracks in concrete mass that open a way for water and salts to go through increase the conductivity and decrease the electrical resistance for concrete.

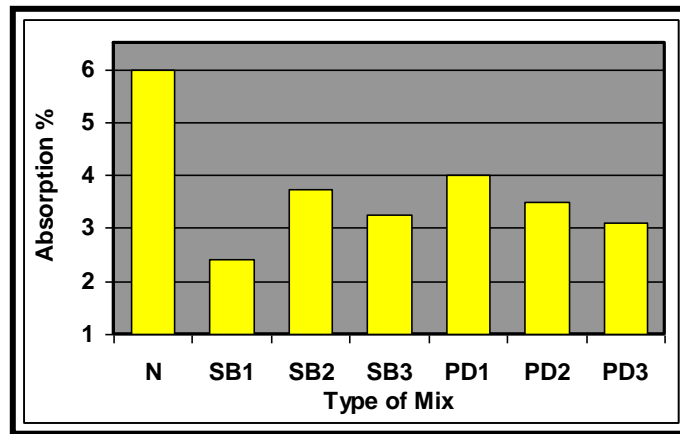


Fig. 10 Absorption for different concrete mixes

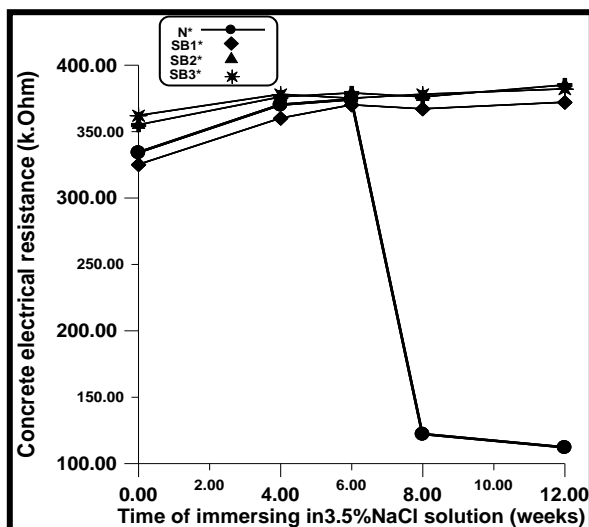


Fig. 11 Electrical resistance for reinforced concrete samples with sodium benzoate admixture without pre cracking

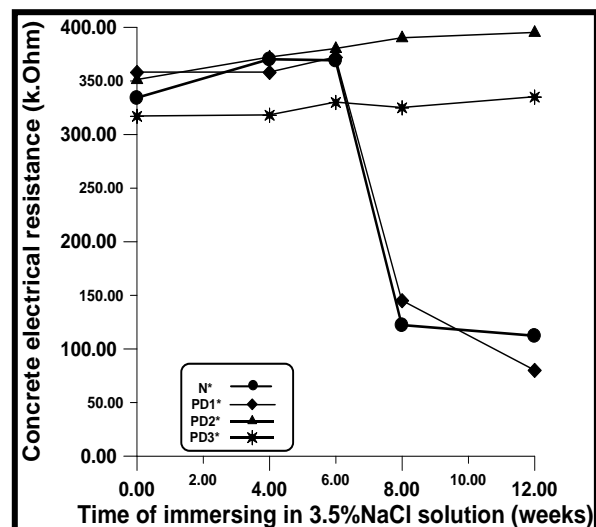


Fig. 12 Electrical resistance for reinforced concrete specimens with potassium dichromate with pre cracking after 6 weeks of immersing

3.6 Corrosion Rates of pre cracking Reinforced Concrete Samples.

3.6.1 Sodium Benzoate Inhibitor (SB)

The sodium benzoate inhibitor decrease the corrosion rate in all concentration as shown in Figure (16). The corrosion rates are low in the three concentrations (1%, 2% and 3% by weight of cement) and they do not indicate any noticeable increase or decrease with time in (8 to 12 weeks).

The sodium benzoate inhibitor has good efficiency because it enhances the alkaline environments. The adhered layer that is produced on the steel bar due to the effect of sodium benzoate will protect in form further attack. The presence of oxygen can form a strong chemical bond ($C_6H_5COO Na$) with iron and this will reduce the active regions on the surface of the iron and facilitates the passivation of remaining regions (Anton D. B. and Norman E.H. ,1970)

3.6.2 Potassium Dichromate Inhibitor (PD)

The corrosion rate of sample (PD1*) increased after 12 weeks of immersion in salt solution. The chromate is an anodic inhibitor. It can, in case of incomplete protection, increase the corrosion rate intensity. There is a critical concentration below which the corrosion intensity steadily increases. When the inhibitor concentration is increased beyond the critical value, the corrosion intensity begins to drop, as in samples (PD2*) and (PD3*) see figure (17).

Hence, the inhibition efficiency of (PD2*) and (PD3*) samples are better than (PD1*) due to the higher dosage of the inhibitor. The presence of Cl^- increases the corrosion rate and needs more dosage of the inhibitor. The following explanation was stated by Rozenfeld (**Rozenfeld I. L.,1975**) and Anton (**Anton D. B. and Norman E.H. ,1970**): “ Anodic inhibitor which cause a large shift in the corrosion potential are called passivating inhibitors, they are also called dangerous inhibitors because, if used in sufficient concentrations they cause pitting corrosion and some times an increase in corrosion rate”. The corrosion rate is almost equal in sample (PD2*) through 6 weeks to 12 weeks .

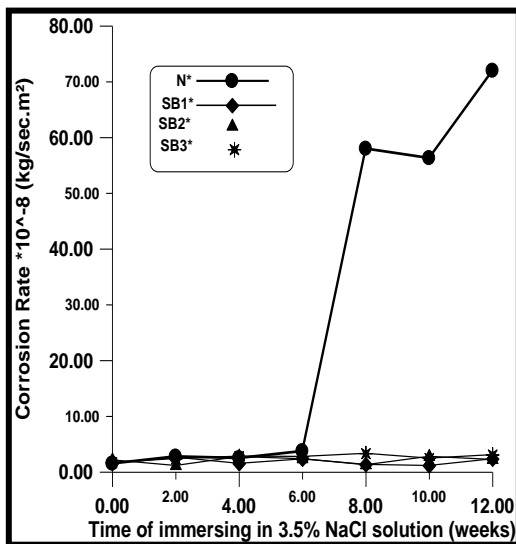


Fig. 13 Corrosion rate for reinforced concrete samples with sodium benzoate admixture with pre cracking after 6 weeks of immersing in 3.5%NaCl solution

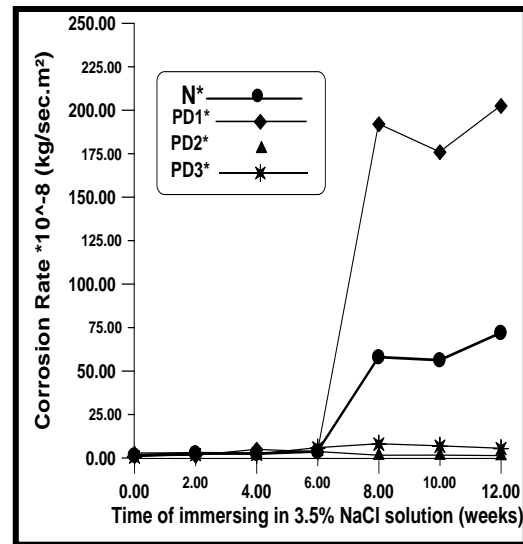


Fig 14 corrosion rate for reinforced concrete samples with potassium dichromate admixture with pre cracking after 6 weeks of immersing in 3.5% NaCl solution

3.7 Inhibitors Efficiency

The efficiency of the inhibitor is measured by :

$$\text{Inhibitor Efficiency (\%)} = 100 * (\text{CR}_{\text{uninhibited}} - \text{CR}_{\text{inhibited}}) / \text{CR}_{\text{uninhibited}}$$

where: $\text{CR}_{\text{uninhibited}}$ = corrosion rate of the uninhibited system

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

In general, the efficiency of an inhibitor increases with the increase in inhibitor concentration that was clear for mixes without pre cracking; the inhibitor efficiency for sodium benzoate increased from 44% for concrete mix with 1% dosage to 82% for concrete mix with 3% dosage of (SB) as shown in table 11. Where the mixes with potassium dichromate (PD) show some convergent in values of inhibitor efficiency that shown in table 4.3 but, all of these values are less than sodium benzoate inhibitor's efficiency.

3.8 Classification Degree of Corrosion Current

Corrosion can be classify as the following degree (**John P. B.1997**).

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

Low corrosion : $I_{corr} (0.1 - 0.25) \mu A / cm^2$

Moderate corrosion : $I_{corr} (0.25 - 0.75) \mu A / cm^2$

High corrosion : $I_{corr} (0.75 - 1) \mu A / cm^2$

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

Classification degree of corrosion current at the end of the 12 weeks of partial immersing in 3.5% NaCl solution shows in table 12

Table 11 Inhibitors efficiency for concrete samples with and without pre cracking after 12 weeks of immersion in salt solution

<i>Type of mix</i>		<i>Type of admixture and % of adding</i>	<i>Inhibitors Efficiency %</i>
<i>Symbol of the mix</i>	<i>Making pre cracking after 6 weeks of immersion (*)</i>		
SB1		<i>Sodium benzoate</i>	44%
SB1	*	<i>1% by weight of cement</i>	97%
SB2		<i>Sodium benzoate</i>	77%
SB2	*	<i>2% by weight of cement</i>	97%
SB3		<i>Sodium benzoate</i>	82%
SB3	*	<i>3% by weight of cement</i>	96%
PD1		<i>Potassium dichromate</i>	78%
PD1	*	<i>1% by weight of cement</i>	(-) adverse effect
PD2		<i>Potassium dichromate</i>	77%
PD2	*	<i>2% by weight of cement</i>	98%
PD3		<i>Potassium dichromate</i>	62%
PD3	*	<i>3% by weight of cement</i>	92%

Table 12 Classification degree of corrosion current

Symbol Of sample	Making pre cracking after 6 weeks of immersing in 3.5% NaCl solution *	I corr. ($\mu A/cm^2$)	Classification Degree
N	*	0.248	low
N		0.025	Passive
SB1	*	0.009	passive
SB1		0.0143	Passive
SB2	*	0.0076	Passive
SB2		0.0058	Passive
SB3	*	0.0106	Passive
SB3		0.0045	Passive
PD1	*	0.699	Moderate
PD1		0.0056	Passive
PD2	*	0.0047	Passive
PD2		0.0059	Passive
PD3	*	0.0193	Passive
PD3		0.0097	Passive

4. Conclusions and Recommendations

4.1 Conclusions

If the concrete is produced in compressive strength 25 MPa with high cement content (390 kg), low water / cement ratio, good compacting, good curing and high thickness of concrete cover, the steel reinforcement will have a good protection (pH 12- 13.5 and low permeability) against corrosion even in aggressive environment.

Through the use of two anodic, inorganic corrosion inhibitors and SBR admixtures it can be observed that:

- 1. If some kinds of anodic corrosion inhibitors (like potassium dichromate are used in low dosages,** they will act as corrosion accelerators not as corrosion inhibitors therefore they are known as dangerous inhibitors.
- 2.** Corrosion inhibitors work better in concrete with micro cracks than in concrete without micro cracks.
- 3.** The sodium benzoate admixture in dosages 2% and 3% by weight of cement has no significant effects on concrete properties it only has an effect on compressive strength at (28 days), but that effect diminishes at later ages (60 and 90 days). Also this admixture is active to protect the steel reinforcement wires against corrosion after initiating cracking for 90 days of immersing in 3.5% NaCl solution. The inhibitor efficiency is 97% and 96% respectively.
- 4.** The potassium dichromate admixture in dosage of 1% by weight of cement acts as corrosion accelerator and not as corrosion inhibitor.
- 5.** The potassium dichromate admixture in dosage of 2% and 3% by weight of cement has no detrimental effects on concrete properties. It just has an effect on compressive strength in the age (28 days), but that effect diminishes at the later ages (60 and 90 days) with increasing ; in compressive strength of 12% for dosage 2% and 14% for dosage 3% at age of 90 days, in splitting tensile strength of 21% and 30% respectively, in flexural strength of 19% and 29% respectively, with a reduction of 42% and 48% respectively in absorption. Also this admixture is active to protect the steel reinforced wires against corrosion for 90 days of partial immersing in 3.5% NaCl solution with inhibitor efficiency of 98% and 92% respectively.

5. References

- John P. B. **“Corrosion of Steel in Concrete”** ,Understanding, Investigation and Repair ,1997 , E & FN Spon an Imprint of Rutledge London & New York .
- California Department of Transportation ,Division of Engineering Services , Materials Engineering and Testing Services , Corrosion Technology Branch **“Corrosion Guidelines”**, Version 1.0 , September 2003 .
- Paul Teng T. **“ Materials and Methods for Corrosion Control of Reinforced and Prestressed concrete structures in New Construction”**,U.S. Dep. Of Transportation , Federal Highway Administration . August, 2000.
- Perez N.,**”Electrochemistry and Corrosion Science”**, Department of Mechanical Engineering, University of Puerto Rico, Kluwer Academic Publishers,2004.
- Bertolini, L. , Elsener B. , Pedeferra P. and Polder R. **“Corrosion of Steel in Concrete”** , copyright 2004 , printed in Federal Republic of Germany .
- Persson M., **“Investigation of the impact of load – induced cracking of the initiation time on steel corrosion in concrete Master’s Thesis, Institution of Civil Engineering Luleå University of Technology, 2000 .**

- ACI Committee 201 2R-92, "Guide to Durable Concrete", Chapter 4, ACI Manual, chapter four, p.16-20
- Bavarian B. , "Corrosion Protection of Steel Rebar in Concrete Using Corrosion Inhibitors MCI 2021 and MCI 2022 " , College of Engineering and Computer Science , California State University , Northridge , March 2002.
- ACI Committee 222 R -96, "Corrosion of Metals in Concrete", ACI Manual.
- د. حسين باقر رحمة الله ، هندسة التآكل و حماية سطوح المعادن ، الجامعة التكنولوجية ، ١٩٨٩ .
- Virman Yash Paul "Effectiveness of Calcium Nitrite Admixture as a Corrosion Inhibitors " , Public Roads , Vol. 54 , No. 1 , 1990 , PP. 171-182.
- Virman Yash Paul and Clemena G.G. , "Corrosion Protection Concrete Bridges" Report No.FHWA-RD-98-088, Federal Highway Administration , Washington , D.C.1998.
- Roberge P.R. , "**Handbook of Corrosion Engineering**", MC Graw –Hill , 2000 , Chapter 10.
- Bregman J.I. , "**Corrosion Inhibitors**", Collier-Macmillan Canada, Toronto, Ontario, 1963.
- Fontana M.G. , "**Corrosion Engineering**", McGRAW-HILL international book company, 1978.
- Landroum R.J. , "Fundamentals of Designing for Corrosion Control : A Corrosion Aid for The Designer " , National Association of Corrosion Engineers , Houston , Texas , 1989, PP.352 .
- Kepler J.L., Darwin D. and Locke C.E. "Evaluation of Corrosion Protection Methods for Reinforced Concrete High way Structures . University of Kansas , Center for Research , INC ,Law Rence ,Kansas ,May 2000.
- Berke N.S. "Review of Corrosion Inhibitors in Concrete " , Materials Performance , Vol.28 , No.10 , Oct. 1989 ,PP.41-44.
- Hope B.B. and Thompson S.V. , "Damage to Concrete Induced by Calcium Nitrite " ACI Materials Journal , Sep –Oct. 1995, PP. 529-531.
- Limaye R.G., Angal R.D and Radke A.S. , "Experiment Studies on Penetrating – type Corrosion inhibitor in reinforced conceit", Indian Concrete Journal, Jan. 2000, PP. 22 – 26 .
- Stephen R.S. " Evaluation of Two Corrosion Inhibitors Using Two Surface Application Methods For Reinforced Concrete Structures " , Virginia Dep. of Transportation , University of Virginia , Des. 2004.
- Iraqi Organization of Standards, IOS 5 :1984, for Portland Cement.
- Iraqi Organization of Standards, IOS 45 :1984, for Aggregate.
- British Standard Institution, "Method for Determination of Compressive Strength of Concrete Cubes " , B.S. 1881: Part 116, 1989 , PP.4.
- American Society for Testing and Materials, C496-86, "Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens" , Annual Book of ASTM Standards, Vol. 04.02, 1989, PP. 259-262 .
- د. مؤيد نوري الخلف ، هناء عبد يوسف ، "تكنولوجيا الخرسانة " ، الجامعة التكنولوجية ، ١٩٨٤ .
- British Standard Institution, "Method for Determination of Flexural Strength, B.S. 1881, Part 118, 1989, PP. 3.
- Jamil H.E., Shriri A., Boulif R. ,Bastos C., Montemor M.F. and Ferreira M.G.S. , "Electrochemical Behavior of Amino Alcohol- Based Inhibitors Used to Control Corrosion of Reinforcing Steel", Science @ Direct, Electrochemical Acto , 2004, internet.
- ASTM Special Technical Publication 908, "**Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods**", Canada, 22-24 May 1984.

- Qian S. and Cusson D.,2004 “Electrochemical Evaluation of The Performance of Corrosion Inhibiting System in Concrete Bridges “ , Journal of Cement and Concrete Composites,Vol.26, No. 4, May -2004, P.P. 217-233, (NRC) National Research Council Canada , Ottawa , Ontario, Canada.
- Anton D. B. and Norman E.H. ,“**Nace Basic Corrosion Course**”, Scope and Language of Corrosion, Graduate Engineering Center, University of Missouri, National Association of Corrosion Engineering, St. Louis, 1970.
- Rozenfeld I. L. ,”**Corrosion Inhibitors**”, Institute of Physical Chemistry USSR Academy of Sciences, Mc GRAW-HILL International Book Company,1975.