Technical Report
Reduction of Corrosion Process in Steel Bars Using Inhibitors

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Deterioration of steel bars due to corrosion is worldwide problem causing billions of dollars in repair and replacement and costing drastic failures in many infrastructures. If this is combined with harsh environment and aggressive chemicals, it becomes extremely difficult to avoid and protect. However, there are many recent innovations in the market producing commercial inhibitors and claiming these would protect steel bars against deterioration. Three commercial inhibitors are used in this study; they were Calcium Nitrate Inhibitor (CNI), anodic corrosion inhibitor (ACI), and RHEOCRETE 222+ corrosion inhibitor. Corrosion cell of four beams was constructed with three beams of different corrosion inhibitor admixtures and the forth beam was a control beam with no addition of admixture. Four steel bars were located in each beam with different locations from the brine solution. Data was collected after wet and dry cycles. The corrosion rate in each rebar was accelerated using impeded current of 5 volts supplied from an external power supply. The wetting/drying regime with salt solutions represents extremely harsh conditions and rapid chloride penetration was achieved. The corrosion was monitored for more than 6 months. The performance of admixtures against corrosion was highest for RHEOCRETE 222+ than others. Same findings were achieved from the corrosion mass loss which was calculated theoretically using Faraday law. Visual observation of the broken samples also confirmed these findings.

1. INTRODUCTION

Steel bars are usually protected in alkaline incubator combined with other protections such as coating, cover against exposure, and/or using inhibitors to mitigate their deterioration trend when exposed to harsh environment. The harsh environment would include elevated temperature, relative high humidity, and exposure to chemicals such as carbonation, chloride and other acidity agents that reduce their alkalinity to the extent that ions start to release and initiate anode and cathode which starts

the corrosion process. Reinforced concrete is used worldwide extensively as a construction material due to its superior compatibility between its constituting materials. The use of steel and concrete together improves properties of both components physically, mechanically and chemically. Steel reinforcements usage makes it possible for engineers to construct wide spans buildings and with different shapes. The failure of concrete structures in the Arabian Gulf area is more pronounced due to the carried over chloride ion air-borne salts or high chloride in soil. Chloride destroys protective oxide layer on steel rebar and the corrosion initiates. As corrosion progresses, copious oxide build and cause expansion resulting in disbandment of rebar and ultimately failure of the structure.

The rust volume will be two to four times greater than the volume of the parent steel, resulting in large stresses that ultimately crack and spall the concrete cover. The initiation time of corrosion depends on quality and thickness of the concrete cover and the permeability of concrete. It is important to know the initial Chloride content since they are present in the concrete mix ingredients from cement, aggregates, and water. They can also diffuse from outside of the structure [1, 2, 3, and 4]. Corrosion inhibitors can be added during mixing the fresh concrete or can be applied on the surface of hardened concrete structures [5]. Several advantages for using corrosion inhibiting admixtures are: All steel bars in structure are equally protected since the admixture is distributed uniformly throughout the concrete and there is no need for specialized skill because the task consists only adding the correct amount of admixture [6].

Number of studies has been conducted on the corrosion of steel in concretes made with cement containing mineral admixtures. The concrete with 10% SF + 20% BFS had the highest compressive strength, and that the concrete samples with 10% SF + 40% BFS and 0.35 water–binder ratios had the lowest corrosion density [7]. The effect of different corrosion inhibiting admixtures on concrete properties was investigated. The effect of four different corrosion inhibiting admixtures was evaluated: calcium nitrite-based inhibitor, amino and ester-based organic inhibitor, amino alcohol-based inhibitor and migrating corrosion inhibitor. The properties of fresh concrete (density, workability and air content) and of the hardened concrete (compressive strength, bending tensile strength, splitting tensile strength and Young's modulus) were evaluated. Earlier results showed that [5]:

1.   "Calcium nitrite-based corrosion inhibitor increases the early age compressive strength. The effect on the ultimate strength was observed to be dependent on the amount of inhibitor added to the concrete. Calcium nitrite-based corrosion inhibitor increases marginally the air content and the workability of fresh concrete.

2.   Amino and ester-based organic inhibitor causes a decrease in compressive strength by 10–20%. The air content was slightly increased.

3.   Amino alcohol-based inhibitor seems to decrease the compressive strength, while the workability tends to be increased. The air content might be slightly increased.

4.   Migrating corrosion inhibitor decreases the early age concrete strength, while the ultimate compressive strength seems to be improved. However, in combination with blast furnace slag cement, a decrease of ultimate compressive strength might be obtained" [5].

The main reason leading to the acceleration corrosion of steel bar in concrete is the wetting-drying cycles, which can increase corrosion potential difference between the anode and cathode of steel bar and the decrease of concrete resistance [8]. Steel bar in concrete can be corroded under

environment of chloride attack. The rust which has a characteristic of expansion and   porosity of the steel concrete interface offer a space of diffusing of the expansive rust. The diffusion of the rust transforms the porous steel-concrete interface into the dense mixed layer composed of concrete and rust. The development of the corrosion layer leads to mechanical effect on corrosion cracking and electrochemical effect on retardation of oxygen and water transportation. The dense corrosion layer resists rust diffusion and produces expansive force which finally forms corrosion cracking. The dense corrosion layer retards transporting oxygen and water to the surface of the steel bar and then the corrosion rate slows down [9]. The corrosion current density of steel bar in concrete can be measured in active corrosion process under a designed artificially controlled climate environment. The corrosion rate decreases at first then followed by a steady state finally after concrete cover cracking caused by corrosion [10]. Recently, an artificial climate environment has been used to accelerate reinforcing bar corrosion in concrete. This method is becoming important in assessing the durability of concrete structures because of the similarity in surface characteristics of the corroded steel bar under natural and artificial climate environments. In this study, two groups of reinforced concrete beams were degraded as a result of the corrosion of steel bars. One group of beams was subjected to the galvanostatic method, while the other group was corroded using the artificial climate environment. Comparative studies including the corroded characteristics of steel bar surface, the mechanical behavior of the corroded bar, and the load-bearing capacity were conducted. The comparisons between the two groups of beams were based on the identical width of corrosion cracking. Obvious differences were found from the comparisons [11].

2. MATERIALS AND METHOD

Three commercial corrosion inhibitors (admixtures) were used during the construction of each beam. They are: Calcium Nitrite Inhibitor (CNI), anodic Corrosion Inhibitor (ACI), and RHEOCRETE 222+. Super plasticizer was added to maintain approximate 100 mm slump for the four mixes. Beam 1 is a control beam (reference beam) for comparing the corrosion propagation in other beams, and to compare the performance of each inhibitor with respect to the other inhibitors. Three 100 x100 mm cubes were made for each of the mixes in order to record the 14 and 28 days compressive strength.

Lollipop configuration has been utilized in which all steel bars have been fixed vertically in four beam samples.

The length of each steel bar is 200 mm and embedded in the concrete leaving 10mm cover from the base. Four steel bars have been used in each beam and located at various distances from the edge of each beam. The first steel bar was located at 10 mm from the edge of the beam, the second bar was at 10 mm, the third bar at 30 mm and the last bar was located at 40 mm inside the beam. This represents four scenarios of exposure relative to concrete cover that is protecting each bar from direct external exposure. The lollipop arrangement is shown in Figure 1.

Beams were fixed on a ceramic plate and glued to each other by epoxy in order to prevent water leakage. All beams are attached to a power supply of 5V allowing a current to travel along the

steel rebars in order to accelerate the corrosion process. Steel mesh is inserted in the exposed face of the beams to close the electric circuit.

The cell is filled with 5% salty water (NaCl) where wet and dry cycles are applied to simulate the real life problems of tidal zones in marine structures. The current was measured for all the beams and for each rebar separately twice a day for 6 months.
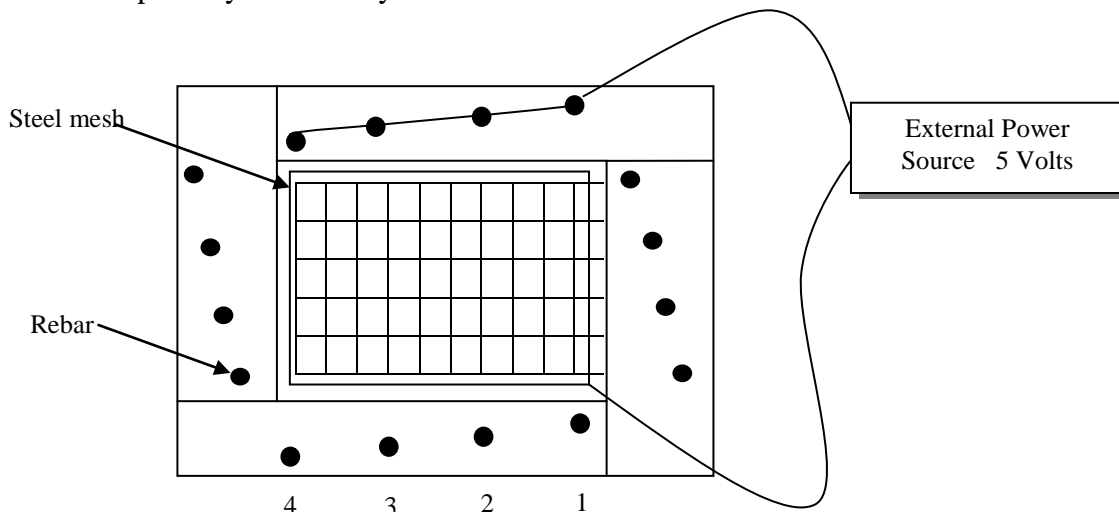
Figure 1. Lollipop diagram

3. RESULTS AND DISCUSSIONS

Samples of concrete cubes were taken from the four mixes and workability was kept the same for all samples and yielded 100 mm slump values. The 14 days and 28 days compressive strength for each mix is shown in Table 1[12].

Table 1. Compressive strengths [ref.12]

Compressive strength (MPa)	Mix 1	Mix 2	Mix 3	Mix 4
14 days Cube 1	56.2	61.2	44.0	52.1
28 days Cube 2	59.7	60.2	62.7	54.1
Cube 3	45.4	55.2	48.9	48.7

Mix 1 showed the highest compressive strength for the 14 days and Mix 3 showed the lowest strength. The 28 days strength is almost the same for all mixes. This shows that Mix 3 has the lowest 14 days strength and the highest 28 days strength. This relative large variation is a negative effect of adding CNI which reduced the early strength. The addition of CNI reduces the compressive strength comparing with the control mixture.

3.1. Effectiveness of corrosion inhibitors

Two periods of study was taken. The first active period was to monitor the current changes for more than two months on daily wetting and drying cycles. The corrosion cell was then dried and left for two months on drying basis without any measurements to observe if the changes of current with time in the second active period will behave similarly to active period one or not, or will the beams built up chloride on the rebars so that the corrosion current will change accordingly. This period can be described as a passive period if the beams current return back to its original state or not. This period was kept at room temperature. The second active period was repeated for the daily wetting and drying cycles with current measurements for more than six weeks.

Rebar one in all of the four beams are the closest to the inner surface while rebar four is the nearest to the outer surface of the cell. Therefore, rebar one is expected to have the highest corrosion rate with respect to rebar 2, 3, and 4. This is due to the fact that the penetration time of chlorine ions through concrete to reach the rebar is the minimum and rebar 4 has the lowest corrosion rate because of the higher distance from the salt solution to penetrate through the concrete beam as shown in Figure 2 for beam 4.
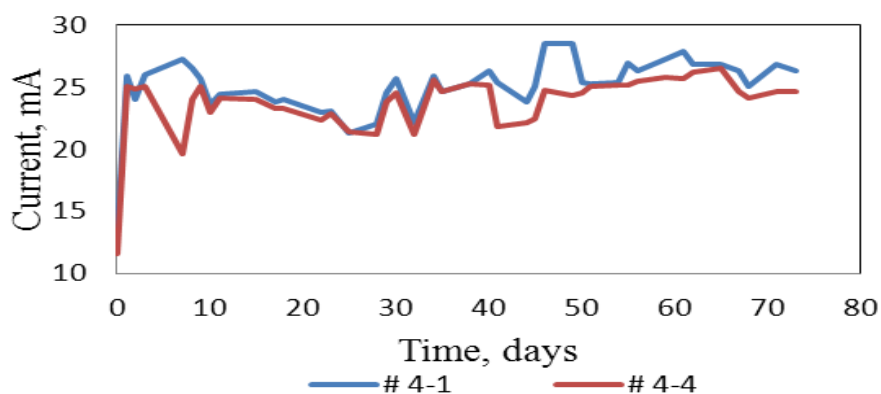
Figure 2. Current changes with time for different steel bar location in Beam #4

From this figure, it is clearly shown that the deviation of current for rebar 1 in beam 4 is much higher than for rebar 4.
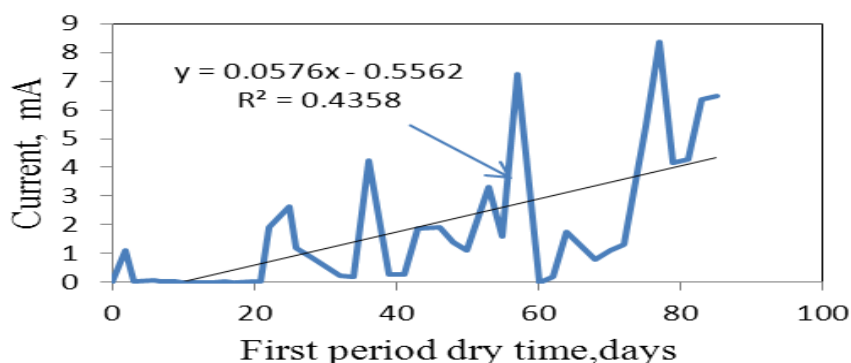

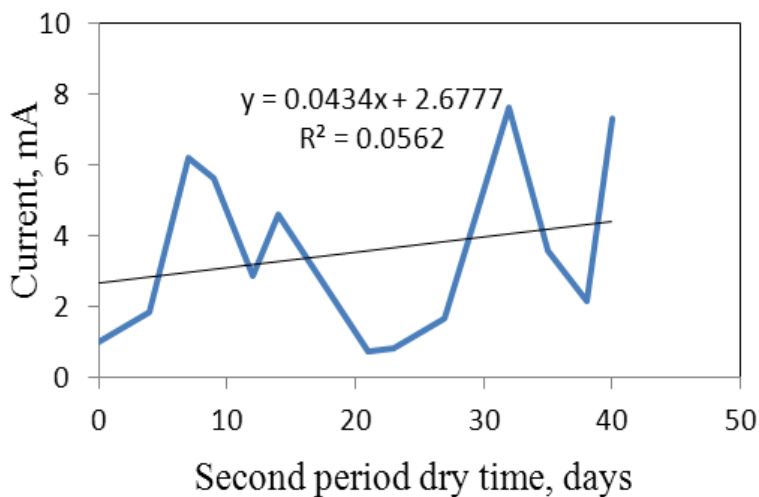**Figure 3A.** Change of current with time for beam 1 for the first period

Figure 3B. Change of current with time for beam 1 for the second period
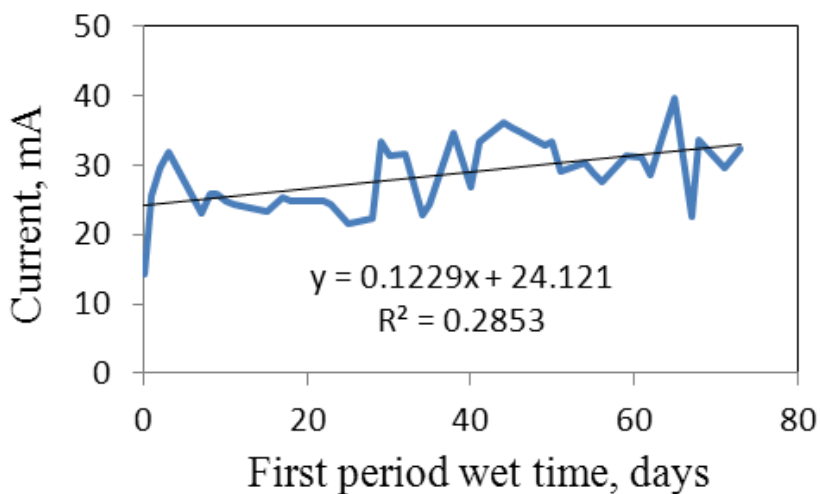

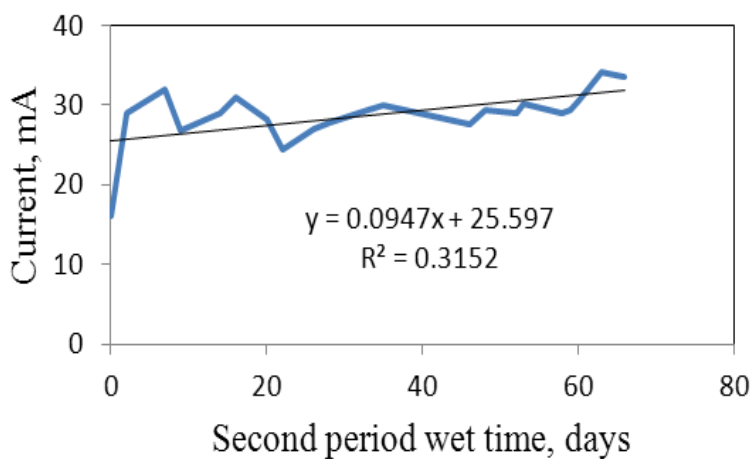**Figure 3C.** Change of current with time for beam 1 on wet basis for the first period

Figure 3D. Change of current with time for beam 1 on wet basis for the second period
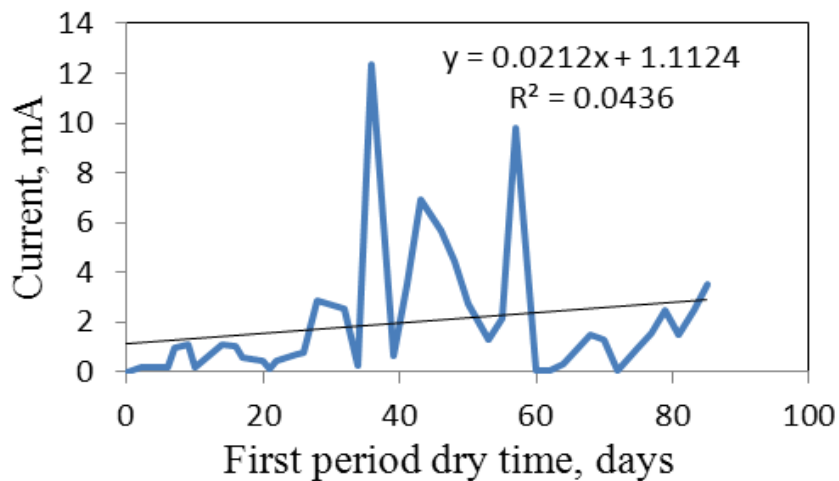
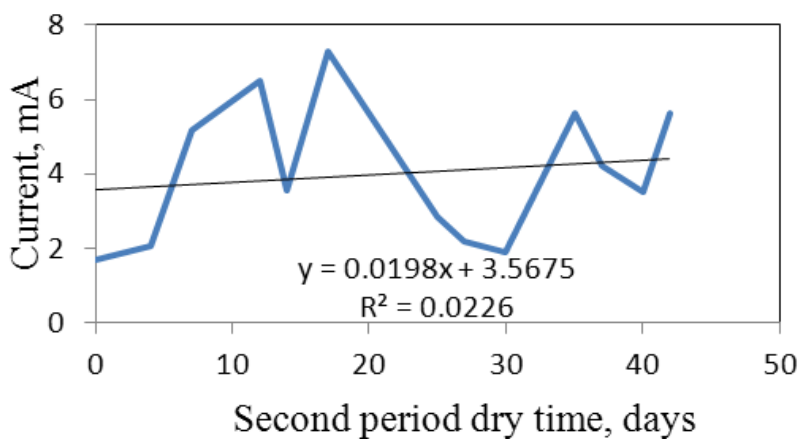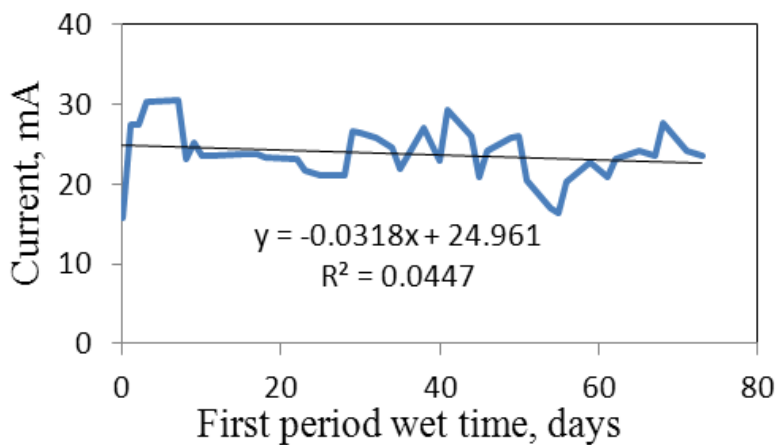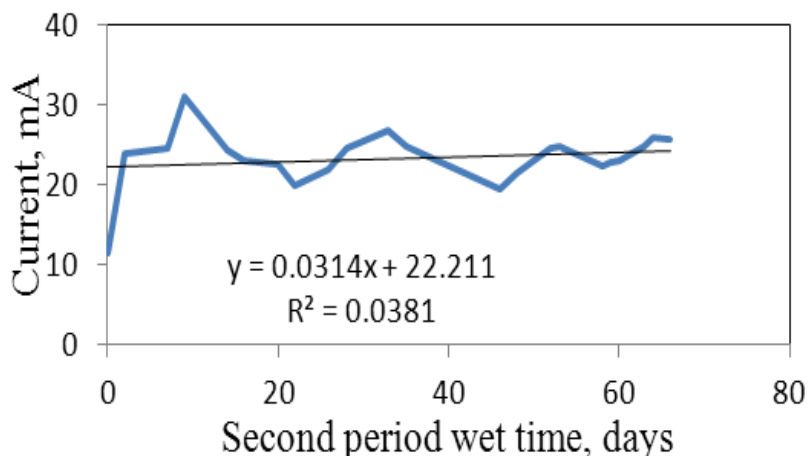**Figure 4A.** Change of current with time for beam 2 for the first period

Figure 4B. Change of current with time for beam 2 for the second period

Figure 4C. Change of current with time for beam 2 on wet basis for the first period

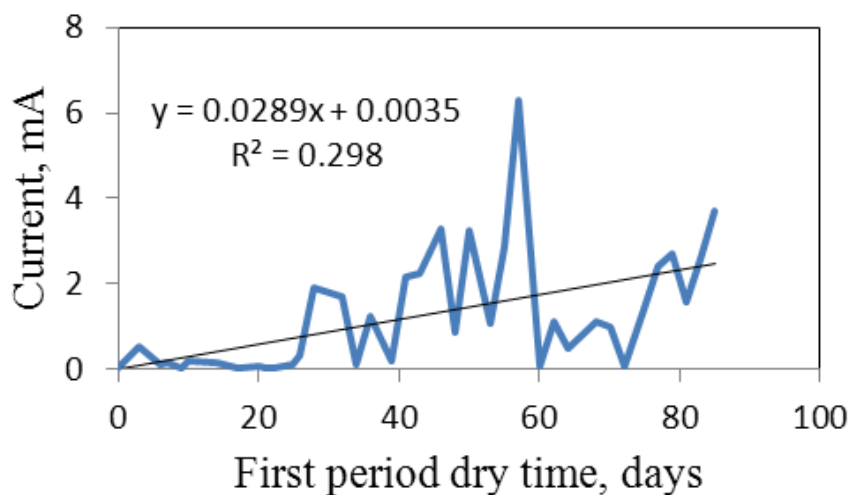**Figure 4D.** Change of current with time for beam 2 on wet basis for the second period

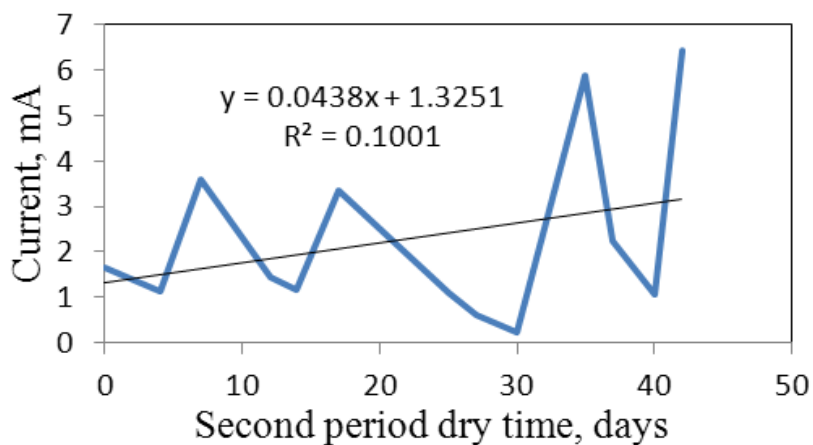**Figure 5A.** Change of current with time for beam 3 for the first period

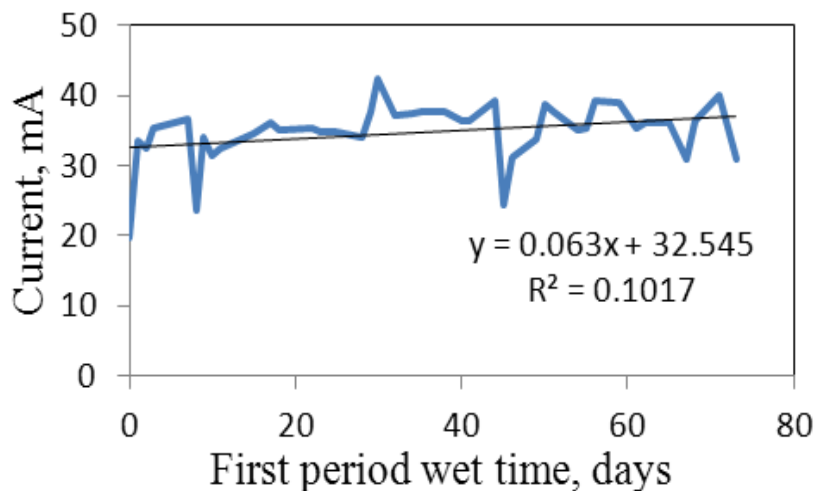**Figure 5B.** Change of current with time for beam 3 for the second period

Figure 5C. Change of current with time for beam 3 on wet basis for the first period
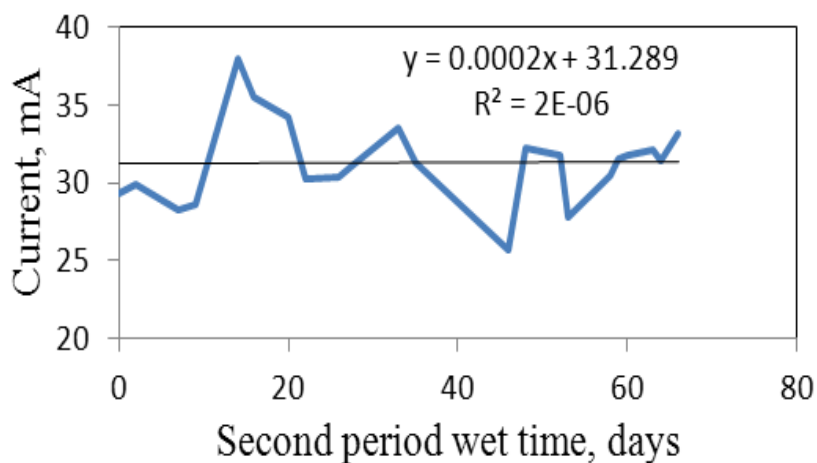

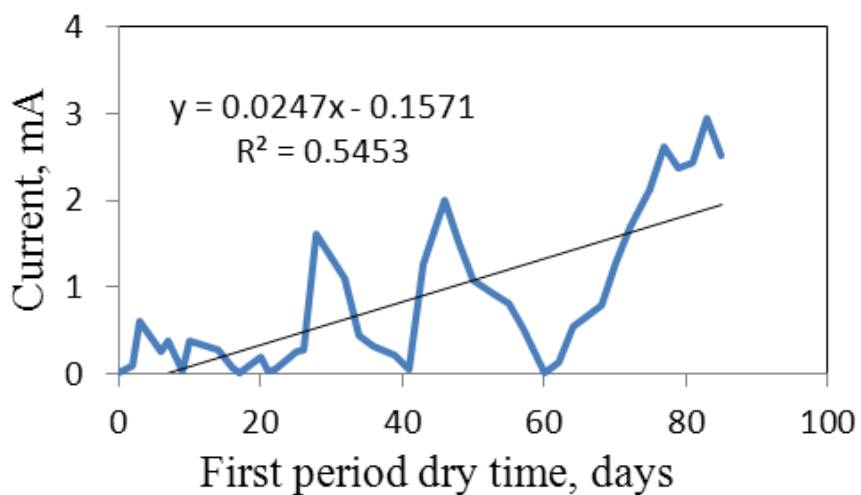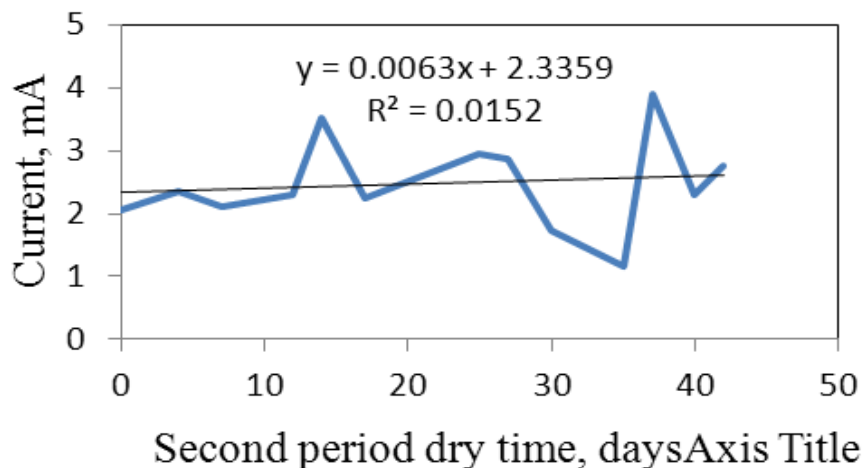**Figure 5D.** Change of current with time for beam 3 on wet basis for the second period
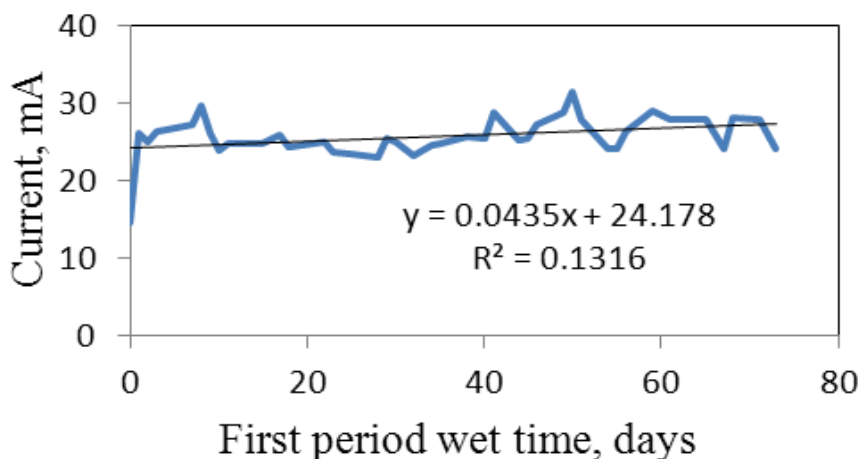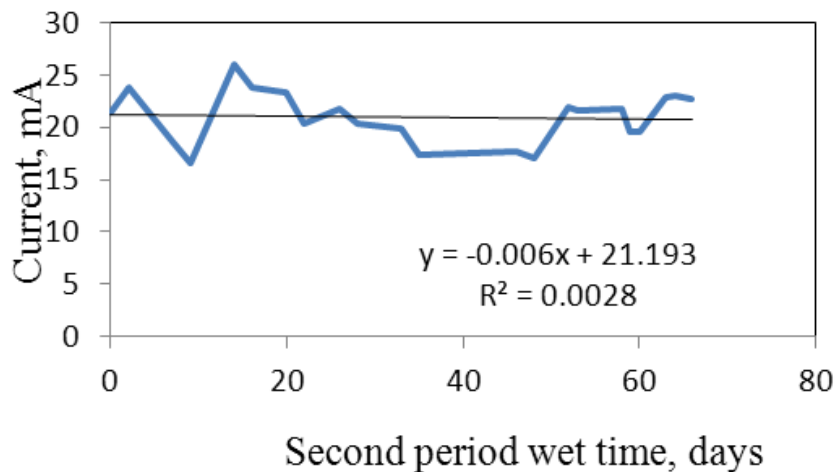

Figure 6A. Change of current with time for beam 4 for the first period

Figure 6B. Change of current with time for beam 4 for the second period

Figure 6C. Change of current with time for beam 4 on wet basis for the first period

Figure 6D. Change of current with time for beam 4 on wet basis for the second period

This means higher corrosion rate for rebar 1. Visual observation showed also more salt coverage for bar 1 comparing with other bars in the entire concrete beam. The control beam 1 showed the lowest resistance to steel corrosion and this is because it is constructed without the addition of any inhibition admixture.

The current measurements of the four beams in the first and second period of work for drying and wetting cycles are shown in Figures 3, 4, 5, and 6 (A, B, C, and D) for beams 1, 2, 3, and 4 respectively. This can attributed to the slope of the best straight lines that can be gained by the plot of current with time for the wetting and drying basis measurements for the first and the second period.

Table 2. The slope of the best straight lines of the current change with time in beams 1, 2, 3, and 4

Beam No.	First drying period	Second drying period	First wetting period	Second wetting period
Beam 1	0.057	0.043	0.1222	0.094
Beam 2	0.021	0.019	- 0.031	0.031
Beam 3	0.028	0.043	0.063	0.000
Beam 4	0.024	0.006	0.043	- 0.006

Table 2 shows clearly that beam 4 has the lowest slope for the first and second period of measurements on wetting and drying basis. This beam represents the concrete with the added (RHEOCRETE 222+) admixture. The control beam 1 has the highest slopes because there is no admixture added. Although high fluctuating was appeared in measuring the current change with time in the first drying period of beam 1(Figure 3 A & B), but it showed much higher in the second drying period. This can be attributed to the amount of salt solution that penetrated to the beam and when dried it remain active in activation the rate of corrosion and it started to increase more sharply for the second drying period. Beams 2 and 3 were studied deeply to evaluate the performance of admixture in each beam. Beam 2 didn't show current change for the first wetting period but it increased sharply in the second wetting period. This can be again attributed to the salt built up on the steel bars inside this beam. The drying slope showed lower than beam 3. For beam 3, there was no current change with time in the second wetting period. It means that the beam reached stable condition when the current change was lowest.

The same scenario was observed for Figures 4 A and B & 5 A and B for beams 2 and 3 respectively. Lower fluctuating can be observed for beam 4. Beam 4 looks to be more stable relating to current change with time. This can be regarded as a result of lower penetration of salt solution to the beam. For wetting cycles Figure 3, 4, and 5, C & D the beam No. 4 seems to have more stable in reading for both periods. The mass of rust produced per unit surface area of the bar due to applied current over a given time can be determined theoretically using the following expression based on Faraday's law [16, 17]:

$$M\ theoritical = \frac{W.I\ app.T}{F}$$

Where:

$M\ theoritical$: Theoretical mass of rust per unit surface area of the bar (g.cm^{-2})

W: Equivalent weight of steel taken as the ratio of atomic weight of iron to the valency of iron
   (27.925 g)

$I\ app$: Applied current density (Amp.cm^{-2})

T: Duration of induced corrosion (sec)

F: Faraday's constant (96487 Amp-sec).

The theoretical mass of rust is shown in Figure 7-12 for the first and second period, and all the contact time. The changes in the theoretical mass loss with time for the four beams can be summarized in the Table 3.
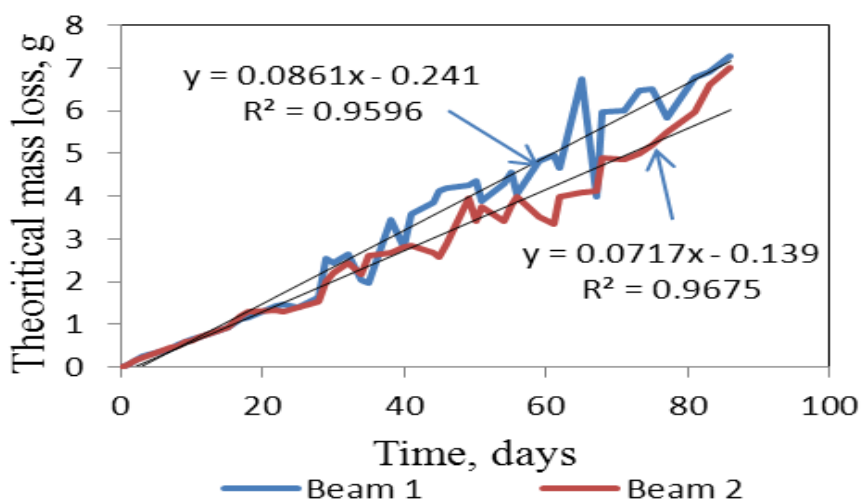

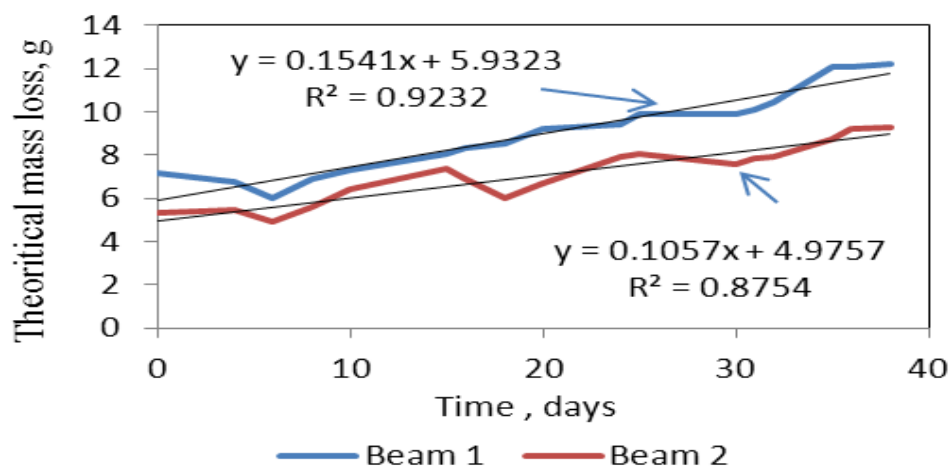**Figure 7.** Theoretical mass loss of bars in beams 1 and 2 with time for the first period

Figure 8. Theoretical mass loss of bars in beams 1 and 2 with time for the second period
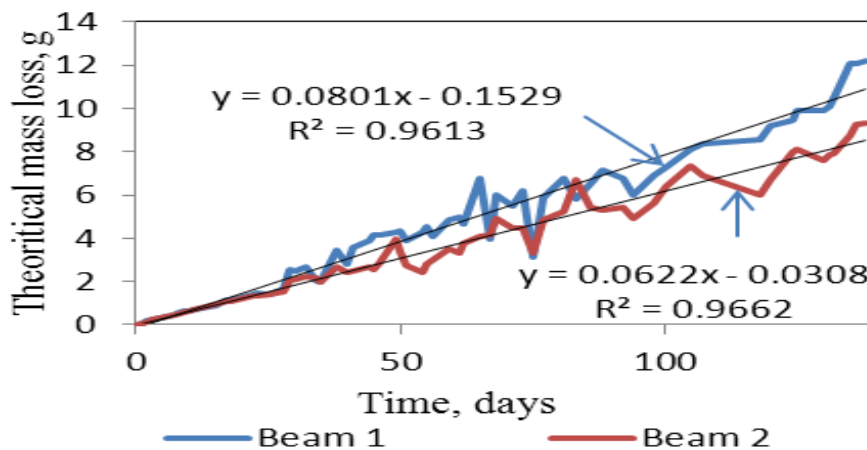
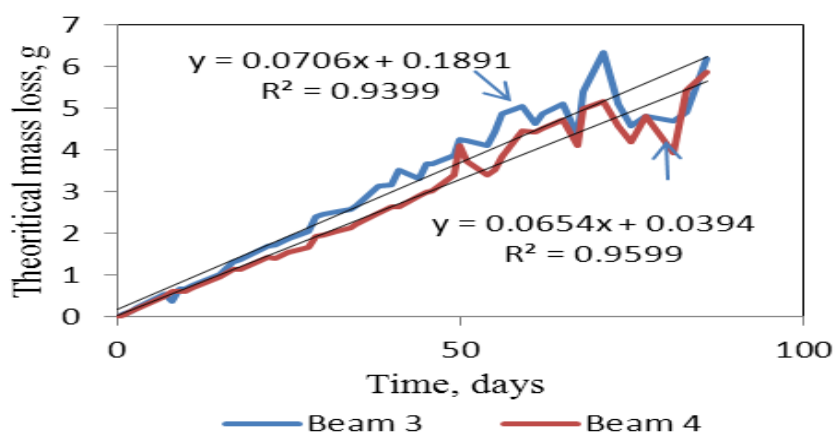**Figure 9.** Theoretical mass loss of bars in beams 1 and 2 with time.

Figure 10. Theoretical mass loss of bars in beams 3 and 4 with time for the first period
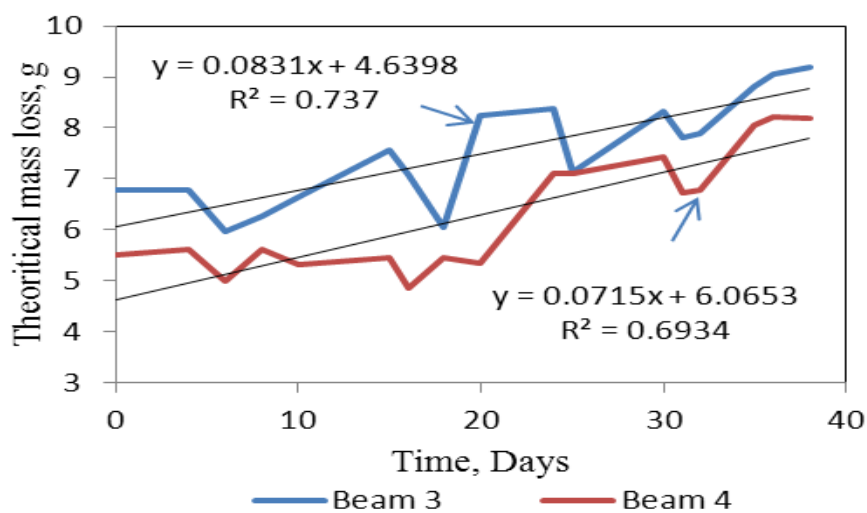
Figure 11. Theoretical mass loss of bars in beams 3 and 4 with time for the second period
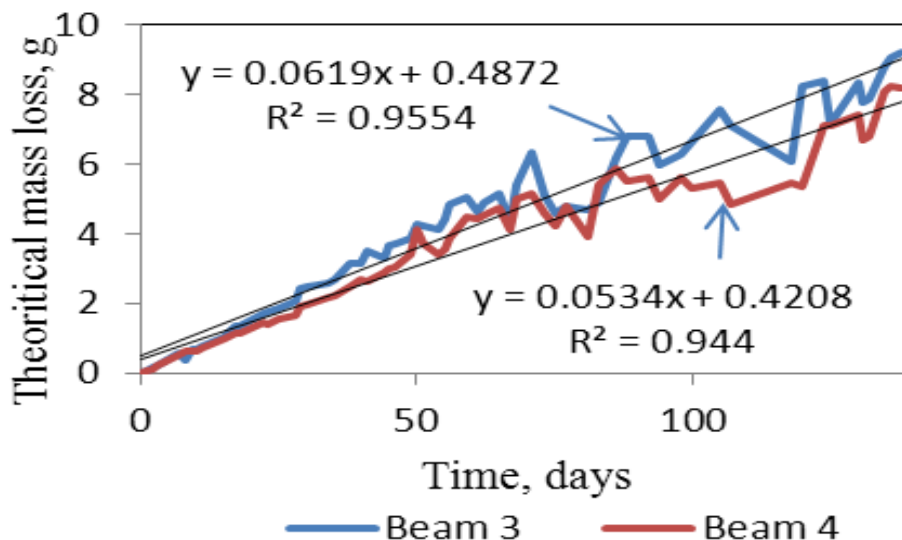
Figure 12. Theoretical mass loss with time in beams 3 and 4.

Table 3. Best fit line slope of changing the theoretical mass of rust with time for beams 1, 2, 3, and 4 for the first and second period as well as whole contact time

Beam No.	First drying period	Second drying period	Complete study
Beam 1	0.086	0.154	0.080
Beam 2	0.071	0.105	0.062
Beam 3	0.070	0.083	0.061
Beam 4	0.065	0.071	0.053

It is clear that beam 1 has the highest corrosion rate followed by beam 2 (with admixture of anodic corrosion inhibitor ACI) then beam 3 (with admixture of calcium nitrite inhibitor CNI) and finally Beam 4 (with admixture of type RHEOCRETE 222+). The performance of admixtures for corrosion rate reduction was as follow:

RHEOCRETE 222+ admixtures > Calcium Nitrate admixtures > Anodic Corrosion admixtures

The steel bars were removed from the corrosion cell, cleaned, dried and weighted. The actual mass of rust per unit surface area could be determined by gravimetric test in accordance with ASTM G1 [19] on rebars extracted from the concrete by breaking the specimens after the accelerated corrosion test is completed:

$$Mac = (Wi - Wf)$$

Where: Mac is actual mass of rust of the bar (g); Wi is initial weight of the bar before corrosion (g);

Wf is weight after corrosion (g) for a given duration of induced corrosion (T)

The actual mass loss was compared with theoretical mass loss at the conclusion of this work which is taken from Figures 9 and 12 for beams 1, 2, 3, and 4 are shown in Table 4.

Table 4. Comparison between actual and theoretical mass loss in steel bars in Beams 1, 2, 3, and 4

	Beam 1	Beam 2	Beam 3	Beam 4
Actual mass loss, gm	10.6226	8.6313	7.571	6.2689
Theoretical mass loss, gm	12.21	9.298	9.20	8.2

The difference between actual and theoretical mass loss can be attributed to measurement error or to the way of treatment of the corroded steel bars. The final visual observation of the corrosion cell showed that Beam 4 (with admixture of type RHEOCRETE 222+) has the lowest salt built up on steel bars followed by beam 3 (Calcium Nitrate admixture CNI) and beam 2 (with admixture of anodic corrosion inhibitor ACI). The beam 1 (control beams) showed the highest salt built up. These observations are shown in Figure 13(A, B, C, D, and E).

(A) Concrete cell   (B) Beam 1

(C) Beam 2   (D) Beam 3   (E) Beam 4

Figure 13. Corrosion Cell after 6 months of accelerated corrosion in harsh environment

The RHEOCRETE 222+ admixture is a combination of amines and esters in a water medium. The ester component acts by lining the pores of the cement matrix, slowing the rate at which chlorides and moisture enter the concrete. The amines adsorb onto the reinforcing steel to provide an additional barrier to corrosion by forming a protective film. This film slows the corrosion process once it begins by preventing chlorides from reacting with the reinforcing steel, and by depriving the corrosion process of moisture [23].

4. CONCLUSIONS

The rate of corrosion of rebars in concrete cell in an accelerated exposure varies not only from beam to beam but also within the same beam in different rebar with respect to their location from the salt solution. Rebar 1 in all of the four beams experienced the highest amount of corrosion because no corrosion inhibitor was added and then comes rebar 2, 3, and 4, respectively. This conclusion comes from collecting of current with time on wet and dry cycles, the theoretical mass loss and actual measurements of mass loss in each beam. Results suggest that the wetting/drying regime was very aggressive and the inhibitor in most case was only partially effective.

The continuous movement of chloride solution through the concrete may have also contributed to the instability of corrosion current measurements. After cycles the blocks were allowed to dry for two months in an attempt to model the drying that might occur after the application of a hydrophobic coating to the concrete surface. Corrosion rates in blocks containing inhibitor were found to drop significantly during this drying period while control block showed insignificant change.

References

1. P. Marlova, M. Fernanda & C. Denise, *Int. Journal of Construction and Building Materials*, 23 (2009)1189–1195.
2. J. Junsomboona, & J. Jakmuneea, *Journal of Talanta* 76 (2008)365–368.
3. G. Batis, P. Pantazopoulou, A. Routoulas, *Journal of Cement & Concrete Composites*, 25(2003)371–377.
4. A. Scott Civjan, J. M. LaFave, J. Trybulski, D. Lovett , J. Lima, & D.W. Pfeifer, *Journal of Cement & Concrete Composites*, .27(2005)688–703.
5. G. De Schutter & L. Luo, *Journal of Construction and Building Materials*, 18 (2004)483–489.
6. D. Paul, G. C. Frantz, & J.E. Stephens, Final Report, December 2000.
7. Ibrahim Tu¨rkmena, & Mehmet Gavgalıb, *Journal of Materials Letters*, 57 (2003)3222–3233.

8. Li Guo; Y. Ying Shu; Li, Fu-Min, *Journal of China University of Mining and Technology*, 215, 3 (2005), 197-202.
9. Y. Yuan, and Ji Yongsheng,   *International Journal of Structural Engineering*, 1, 2 (2010) 199-206.
10. Y. Yuan and Ji. Yongsheng , J. Jiang, *Material and Structures*, 42 (2009) 1443-1450
11. Y. Yuan, Ji. Yon sheng, and P. S. Surendra, *ACI Structural Journal*, 104, 3(2007), 344-347.
12. A. Al Tamimi and E. Al Zubaidy, IMS/ 4th international conference on the applications of traditional and high performance materials in Harsh environment, AUS, March 24-25, 2010.
13. Ma, B. Peng, Sixth CANMET/ACI Conference on Fly Ash, Silica Fume, Slag and Natural pozzolans in concrete. Supplementary Papers. Bangkok, Thailand: May 31–June 5, 1998.
14. P. Montes, T. Bremner, & D.H. Lister, *Cement & Concrete Composites 26* (2004), 243-253.
15. A.U. Malik, I. Andijani, F. Ozair, 9th Middle East corrosion conference & exhibition. Bahrain: Feb 12-14, 2001.
16. S. Ahmed, *The Arabian Journal of science and Engineering* 34, 2C (2009) 95-104
17. F.P. Ijsseling, *British Corrosion Journal*, 21(2)(1986), 95–101.
18. ASTM G1, "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens", *American Society for Testing and Materials*, PA, 2000.
19. S.A. Austin, R. Lyons, and M. J. Ing, *Corrosion*, 60(2)(2004), 203–212.
20. S.A. Azher , *MS thesis* submitted to King Fahd University of Petroleum & Minerals, Saudi Arabia, January 2005.
21. B.H. Al-Gohi, MS thesis submitted to King Fahd University of Petroleum & Minerals, Saudi Arabia, May 2008.
22. G. Batis, E. Rakanta, "Effects of Migrating Corrosion Inhibitors on Reinforced Lightweight and Common Mortars
23. BASF's Rheocrete 222+ Rated Most Effective in UAE Study of Corrosion Inhibitors, March 31,2010,   http://www.basf-cc.com.eg/en/products/Admixture_for_Concrete/Pages/default.aspx