VOL. 4, NO. 1, FEBRUARY 2009 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

EFFECT OF CHEMICAL ADMIXTURE ON CORROSION RESISTANCE OF REINFORCED STEEL RODS IN CONCRETE

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ABSTRACT

Water reducing admixture is widely used in concretes with less water-cement ratio, to improve some properties like strength and workability. In addition, this admixture has effect on corrosion resistance of embedded re-bars in concrete. In this work, the corrosion rate of mild steel rod, CTD (Cold Twisted Deformed) rod and TMT (Thermo Mechanically Treated) rod were observed by adding water reducing admixture in M25 concrete mix. By varying the percentage of admixture, the study was carried out for a period of 14 months. The corrosion rates were measured at different intervals by conducting electrochemical tests like ACI test, LPR test, and OCP test and by weight loss test (gravimetric method). In most of the time and cases, the corrosion rate was found to be less for 0.5% of water reducing admixture. Corrosion resistance of TMT rod is better than other rods like mild steel and CTD rods.

Keywords: chemical, admixture, concrete, steel rod, corrosion, resistance.

1. INTRODUCTION

Concrete is a composite material made of aggregates and porous cement paste, which is the reaction product of mixing water and cement. The structure and composition of cement paste determines the long term performance (durability) of concrete. Concrete is normally reinforced with steel rods. The reinforcing steel rods provide strength and ductility only through the bond strength and anchorage to the concrete [1, 2]. The effectiveness of bond and anchorage is reduced due to the deterioration of concrete, steel or both. The durability of concrete structure depends on the resistance of concrete against physical and chemical attack and its ability to protect the embedded reinforcement against corrosion.

Corrosion in general is the destruction or deterioration of a material because of the reaction with its environment [3]. Large number of existing structures is being damaged with time by reinforcement corrosion due to environmental exposure and changes. Reinforcement corrosion is a dangerous activity that takes place in the re-bars of the concrete structures, leads to delamination because of the expansive action of corrosion product [4].

Corrosion control of steel reinforced concrete can be done by various methods like steel surface treatment, use of admixture in concrete, surface coating on concrete and cathodic protection. Among all the said methods, mixing admixture with concrete is very effective and cheaper, when comparing to other methods [5].

Admixtures which are used primarily for structural property improvement can be by minerals like fly ash, blast furnace slag, silica fume, methyl cellulose, carbon fibres or by solid particle dispersions such as latex [6]. Preparing dense and impermeable concrete by reducing water-cement ratio can prevent the reinforcement corrosion [7, 14, 15, 16, and 17]. Adding mineral admixtures like silica fume with Blast furnace slag with concrete improved the compressive strength, capillary efficiency and corrosion current density, but the slump of the concrete is decreased [9,10,13]. Amino Alcohol based organic inhibitors reduce the corrosion rate of reinforcing steel in concrete with 2 g/l of NaCl and 4% of inhibitors [11]. Multifunctional Organic Inhibitors consisting Amines and Fatty acids, significantly reduces Chloride ingress regardless of concrete quality. The addition of multifunctional organic inhibitors is very effective in mitigating sulphate attack than silica fume addition in concrete [12]. Now-a-days chemical admixtures like water reducing compounds are added to concrete in the mixing stage itself, so that concrete with less water content can be obtained with increased workability and durability. Though so many experiments were done to study the strength properties and corrosion resistance behavior of concrete by adding mineral admixtures like fly ash and blast furnace slag etc., the corrosion resistance of concrete with rebars by adding chemical admixtures in fresh concrete, other than nitrates has not been reported so far [23, 24].

The objective of this study was to investigate the corrosion resistance of reinforced M25 concrete mix with various percentage of chemical admixture i.e. water reducing admixture. The standard specification of using chemical admixture in concrete is followed as per ASTM, C 494/C 494 M-05 [21]. Corrosion rate on mild steel rod, CTD rod and TMT rod were measured by electro-chemical tests called ACI test, LPR test, OCP tests, and by weight loss test (destructive test).150x150x150 mm cubes were cast with 0%, 0.5%, 0.75%, 1% and 1.25% in triplicate for all the tests and the average of corrosion rate were plotted against time. The effect of addition of chemical admixture on corrosion resistance of rebars is compared. Corrosion rate is indirectly proportional to the resistively offered by the concrete to the applied current. Which, intern depends on the property of concrete [22].

2. EXPERIMENTAL PROGRAMME

2.1 Materials

Table-1. Properties of materials used.

S. No.	Material	Properties	Remarks
1	Cement	Specific Gravity- 3.06	43 grade-O.P.C.
2	Fine aggregate	Specific Gravity- 2.67 Fineness modulus- 2.52	Cauvery river sand, Tamil Nadu, India
3	Coarse aggregate	Specific Gravity- 2.78 Fineness modulus- 7.28 Bulk density- 1523 kg/m^3	Local Quarry, Trichy, Tamil Nadu, India
4	Water	Potable- as per IS 456-2000	Cauvery river water, Tamil Nadu, India
5	Water reducing admixture- Conplast SP430	Brown colour liquid Specific gravity-z.22 @ 30°C Chloride content- Nil Sulphonated napthalene polymer	Obtained from a chemical supplying company, Bangalore, India.
6	Reinforcement MS,TMT &CTD rod	10mm Dia,76mm long, Mild Steel, Thermo mechanically treated, Cold twisted deformed Rebars- Fe 415	Obtained from a steel producing company, Trichy, Tamil Nadu, India.

2.2 Concrete mix design

As per ACI 211-1-91, M25 concrete mix was designed with the water cement ratio of 0.43. The proportion of ingredients by weight of cement is 1: 2.31: 2.57: 0.43. After 28 days of curing, the actual strength of M25 grade concrete obtained was 34.27 N/mm^2 for this mix proportion

2.3 Preparatory work for steel rods

As per ASTM G1-03 [18], the rods were cleaned by a pickling solution for the removal of unwanted deposits or rust over the surface of the rods. The pickling solution comprises 500 ml concentrated hydrochloric acid, 500 ml distilled water and 3.5 gm of hexamethylene tetramine (Hexamine). After cleaning weights of rods (initial weight) were taken in an electronic balance with four decimal accuracy because the weight of the corrosion product comes in milligrams.

The rods meant for electrochemical tests are connected by copper wires at one end. For firm fixing, rods are drilled at 1cm from one end and the copper-mild steel connection up to the drill of 1 cm was sealed with epoxy material for avoiding galvanic corrosion between mild steel rod and copper wire. Then the rods are suspended vertically inside the cube mould so as to have 1" cover at the top and bottom. The admixture added concrete was poured and compacted well. All the cubes are kept at room temperature for 24 hrs and then demoulded for placing them in water for curing. After 28 days of curing, the cubes are subjected to alternate wetting and drying so as to get accelerated corrosion. The cubes were ponded with 3% (by mass of water) sodium chloride (NaCl) solution. Electrochemical tests of ACI, LPR, OCP and the gravimetric test of weight loss were conducted periodically for every three months. Cubes with rods and without wires were cast separately for weight loss test. Since the initiation of corrosion over rebar was slow, readings were taken only after six months of casting (5 months after curing).

2.4. METHODOLOGY

2.4.1 AC Impedance test

AC Impedance technique is an electrochemical, non-destructive technique to quantify the corrosion of steel re-bars embedded in concrete [8]. Impedance 'Z' is the ratio of A.C. Voltage (ΔE) to A.C. current (ΔI). In this technique an alternating voltage (ΔE) of 20 mV is applied to the rebar and the resultant current (ΔI) and phase angle (ϕ) are measured for various frequencies. The general electrical circuit system is shown in Figure-1.

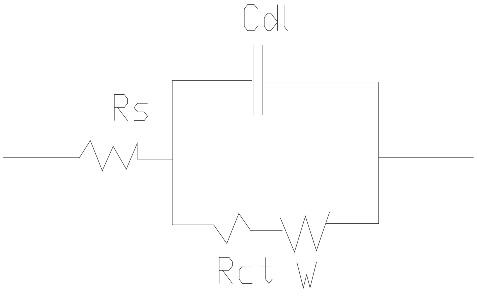

Figure-1. Electrical circuit.

Where,

R_s-Solution resistance; R_p-Polarization resistance

C_{dl} - Double layer capacitance; W- Warberg's Impedance

The response to A.C. input is a complex impedance that has both real (resistive) and imaginary (capacitive or inductive) component Z' and Z" as shown in Figure-2.

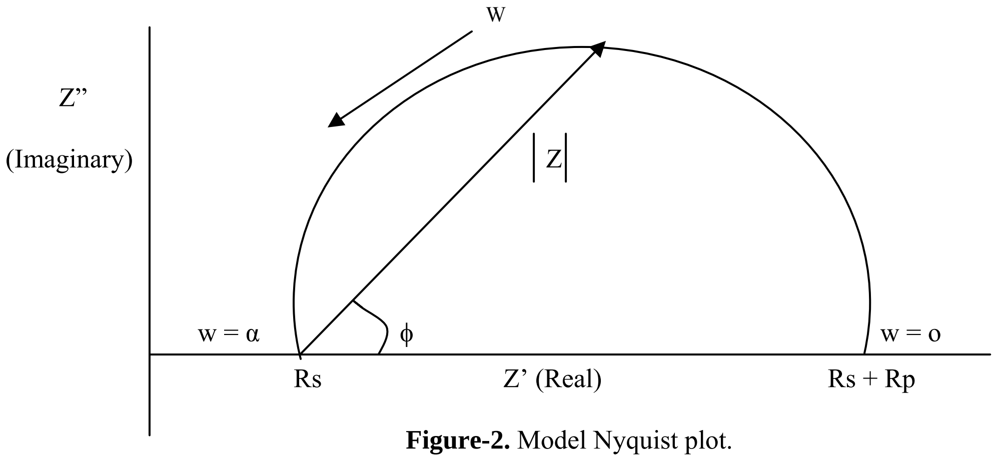

Figure-2. Model Nyquist plot.

From studying the variation of the impedance with frequency an equivalent electrical circuit can be determined which would give the same response as the corrosion system being studied.

The real part in X axis and imaginary part in Y axis in the 'Nyquist plot' as in Figure-2 are obtained, with the diameter equal to R_p. The semi circle is an offset from the origin by a value R_s (solution resistance), which is the ohmic resistance of the concrete cover zone between the reference cell and the reinforcing barring being measured. On the Nyquist plot the impedance can be represented as a vector of length $|Z|$.

In this electrochemical, 3-electrodes system, the embedded rebar acts as working electrode, stainless steel plate acts as counter electrode and the saturated calomel electrode (silver- silver nitrate) acts as reference electrode. Concrete surrounding the rebar is the electrolyte and all the things are kept wet for effective conduction of current between them. The three electrodes are connected to the electro-chemical analyzer CHI604C.

Figure-3. Experimental setup for AC Impedance test.

Nyquist plot is directly recorded for the frequencies from 0.01 Hz to 100 KHz by using the software provided with the electro chemical analyzer, when A.C. current is applied to the specimen. The experimental set up is shown in Figure-3. From the plot, Rp (polarization resistance) value is obtained (Difference of (R_s + R_p) and R_p values), then the corrosion rate (I_{corr}) is calculated by the formula [8].

$I_{corr} = B/R_p$ micro amps /cm^2

Where, B = constant from anodic and cathodic Tafel slopes (26 mV for actively corroding steel rod).
Then finally the corrosion rate in terms of mm / year was obtained by multiplying the I_{corr} value with the factor

K = 11.7 (mm/yr)/(mA/cm^2) [8]. One of the Nyquist plot is shown in Figure-4.

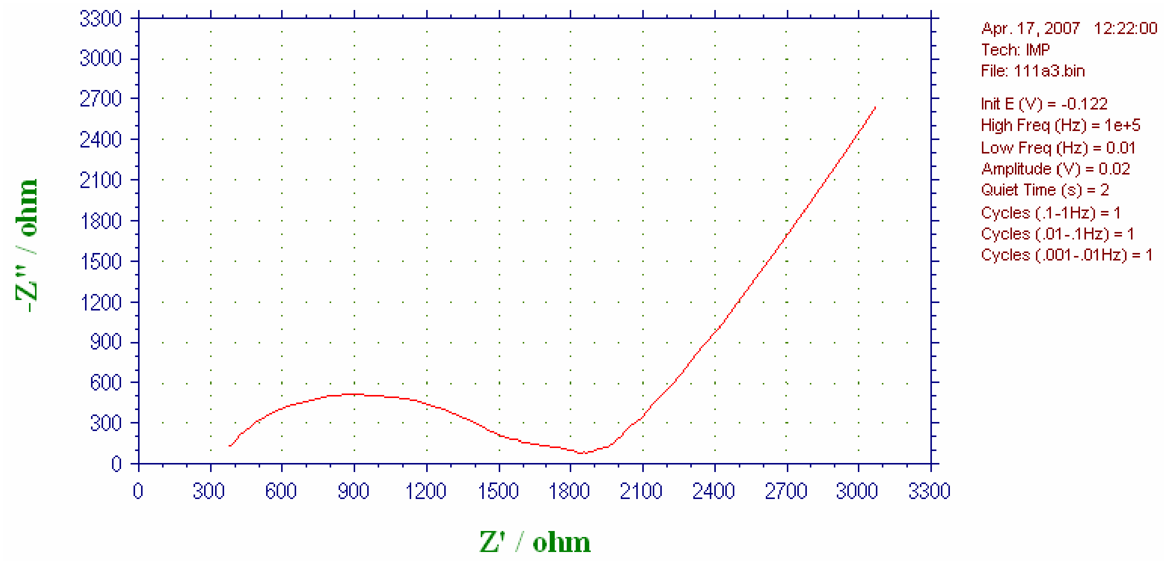

Figure-4. Nyquist plot.

2.4.2 Linear polarization resistance (LPR) test

Linear polarization resistance technique is the rapid, non intrusive technique of LPR plays major roll in finding the rate of corrosion of rebars embedded in concrete [25]. In LPR measurements, the rebar is perturbed by a small amount from its equilibrium potential. The term linear polarization refers to the linear regions of the polarization curve, in which slight changes in applied current to corroding rod in an ionic solution cause corresponding changes in the potential of the rod (Stern *et al.*). Figure-5 showed that for a simple corroding system, polarization curve as holds good for a few millivolts and obeys the quasi-linear relationship. The slope of this relationship is called 'Polarization Resistance'.

$$R_p = \Delta E/\Delta I$$

This slope is related to the instantaneous corrosion rate thro' the stern Geary equation

$$I_{corr} = \beta_a\beta_c/(2.3\ R_p\ (\beta_a - \beta_c)) = \quad B/\ R_p$$

Where

β_a = Anodic Tafel slope, β_c = Cathodic Tafel slope,
R_p = Polarization Resistance, B = Stern-Geary Constant.

The value B is a constant containing the anodic and cathodic Tafel slopes, i.e., the slopes of the polarization curves. Usually B = 26 mV for actively corroding steel in concrete (Stern *et al.*). Electrochemical analyzer CHI604C is the instrument used to measure the R_p value, which is working based on '3LP' method. The term '3LP' represents the "Three Electrode Linear Polarization". The embedded rod is the working electrode. A stainless steel plate is used as counter electrode to apply cathodic current to the working electrode. The third electrode saturated calomel electrode is used as the reference electrode to monitor the corresponding changes in potential of the steel-concrete interface. By knowing the area of steel rebar embedded in concrete the current applied is converted into corrosion current density.

The experimental set up is same like the AC Impedance test. The potential is scanned from initial 'E' to final 'E', at a scan rate of 0.1667 mv/s. The current potential curve is obtained, and the slope of that curve represents the polarization resistance (R_p) value. Figure-6 shows the typical slope of a current potential curve. Then the corrosion rate is calculated by I_{corr} = B/R_p (micro Amps/cm$^{2)}$ and the corresponding corrosion rate is calculated in mm/yr by multiplying I_{corr} value with a factor 'K' which is equal to 11.7 (mm/yr) / (mA/cm^2).

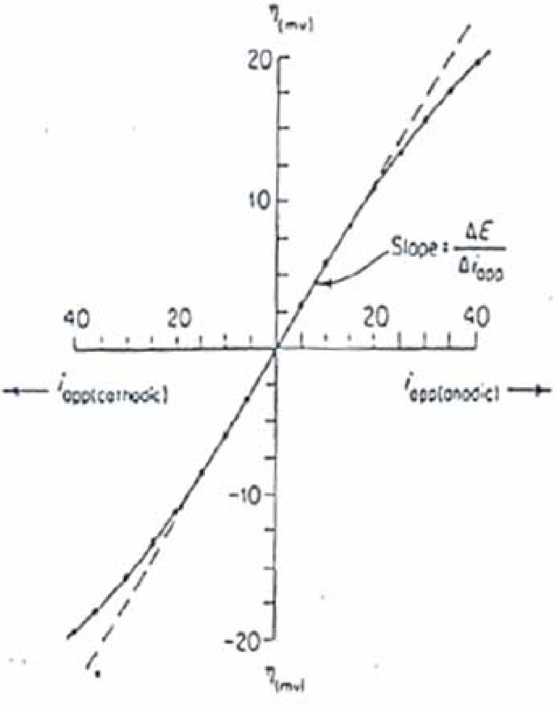

Figure-5. Tafel plot.

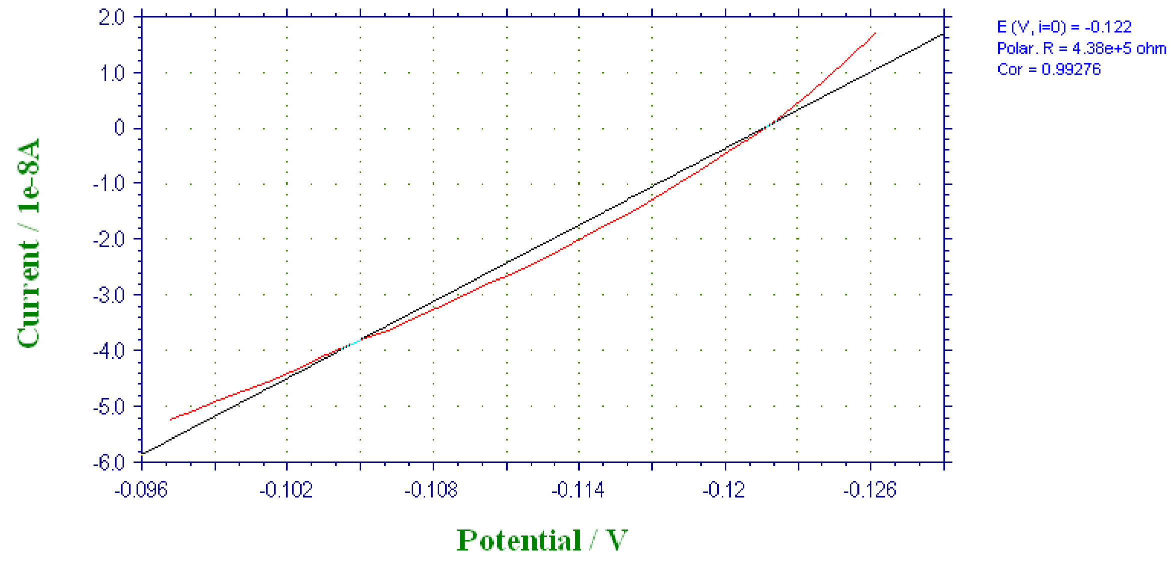

Figure-6. Tafel plot with R_p value.

2.4.3 Open circuit potential technique

Open circuit potential is the potential of an electrode measured with respect to a reference electrode or another electrode when current is not flowing into it or from it. The tendency of any metal to react with an environment is indicated by the potential it develops with the environment [20]. In reinforced concrete structures, concrete acts as an electrolyte and the reinforcement will develop a potential depending upon the properties of concrete environment.

Saturated Calomel Electrode, used as reference electrode was connected to the common terminal of the volt meter, whereas the working electrode i.e. rebars are connected to the +ve terminal [24]. According to this method if the potential of steel rebar becomes more negative than -275 mV Vs saturated calomel electrode, the probability of corrosion is 90% [22]. It is the most commonly applied electrochemical technique for diagnosing the corrosion risk of reinforced concrete structures.

The same experimental setup used for ACI test and LPR test is used for this test also. The OCP values obtained from this test are used as inputs to the other electrochemical tests like ACI and LPR tests.

2.4.4 Weight loss test (Gravimetric technique)

This Destructive technique involves weighing of re-bars before and after embedding into the concrete. Cleaning the rebar by a pickling solution and evaluation of rate of corrosion are done as per ASTM G1-03 [19]. Periodically the concrete cubes are broken open and the rods are taken out for weighing. Before weighing, the rods are cleared with the picking solution, so that there must not be any sticky concrete particles over the surface of re-bars. Picking solution consists of 500 ml hydrochloric acid + 500 ml distilled water + 3.5 grams of hexamethylene tetramine. The rods are weighed with a electronic balance of 4 decimal accuracy and the final weights are compared with the initial weights of rods before embedment. The loss of weight due to corrosion is calculated and from the weight loss, the corrosion rate is calculated by the formula [8].

Corrosion rate = KW/ ATD (mm/yr)

Where
K = A constant = 8.76 x 10^4; W = Weight loss in gm
T = Exposure time in hours; A = Surface area in cm^2
and D = Density of the rod (7.85 gm/cm^3).

3. RESULTS AND DISCUSSIONS

3.1 AC Impedance measurement test

3.1.1 MS rod

Figure-7 shows that in the 5th month, corrosion rate of M.S. rod in control concrete is higher than all the specimens in concrete mixed with admixtures. The corrosion rate increases for concrete without admixture when the duration increases. For concrete with admixtures, irrespective of their percentage the corrosion rate decreases with time.

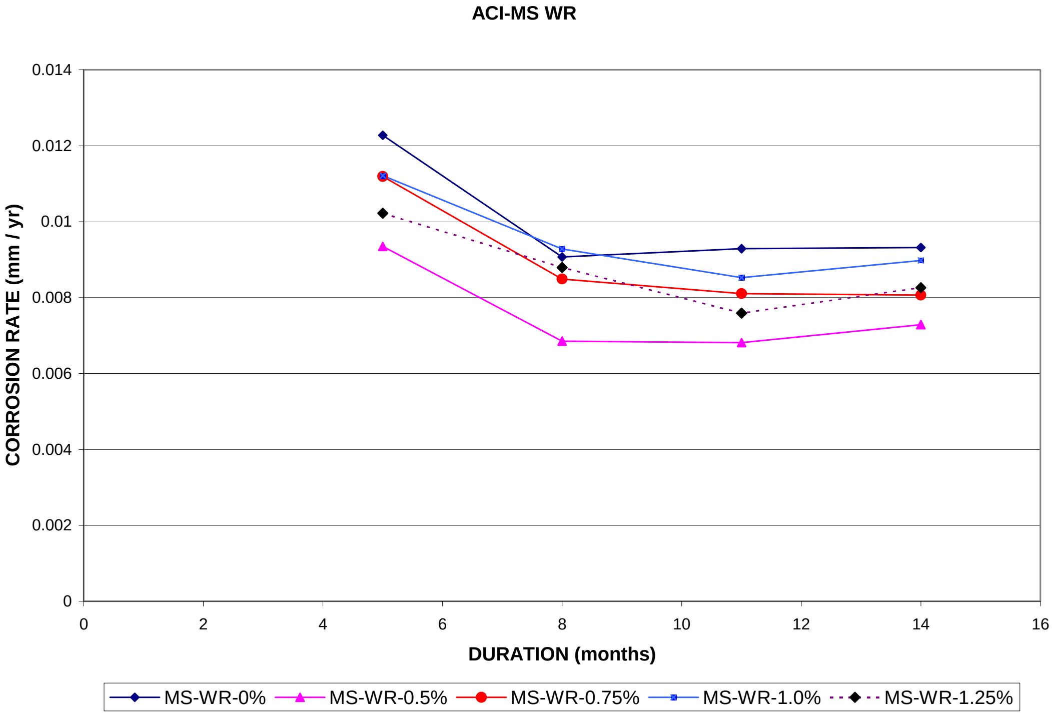

Figure-7. ACI test results-MS bar.

Each reading in the table is the average of three reading taken from three different cubes, which are cast in triplicate for the same admixture percentage. At all the periods of measurement, MS rod embedded in concrete with 5% of admixture shows less corrosion rate than concrete without admixture and all other admixed concretes. At the 14th month, corrosion rate of MS bar embedded concretes with different percentage of admixtures are given in Table-4.

After 11th month, in all percentages of admixture added concrete, the MS rod shows increased corrosion rate. Hence it is inferred that up to 11th month of duration, The passive film formed over the surface of rod is active and after that the film started deteriorating. But for rod in control concrete, the passive film got decayed even in the 8th month itself.

3.1.2 CTD rod

The corrosion rate of CTD rods with respect to admixture additions is shown in Figure-8. From this figure it is depicted that here also the corrosion rate of CTD rod in concrete without admixture started increasing from the 8th month onwards, whereas the same condition is established for all the percentage of admixture added concrete only after 11th month.

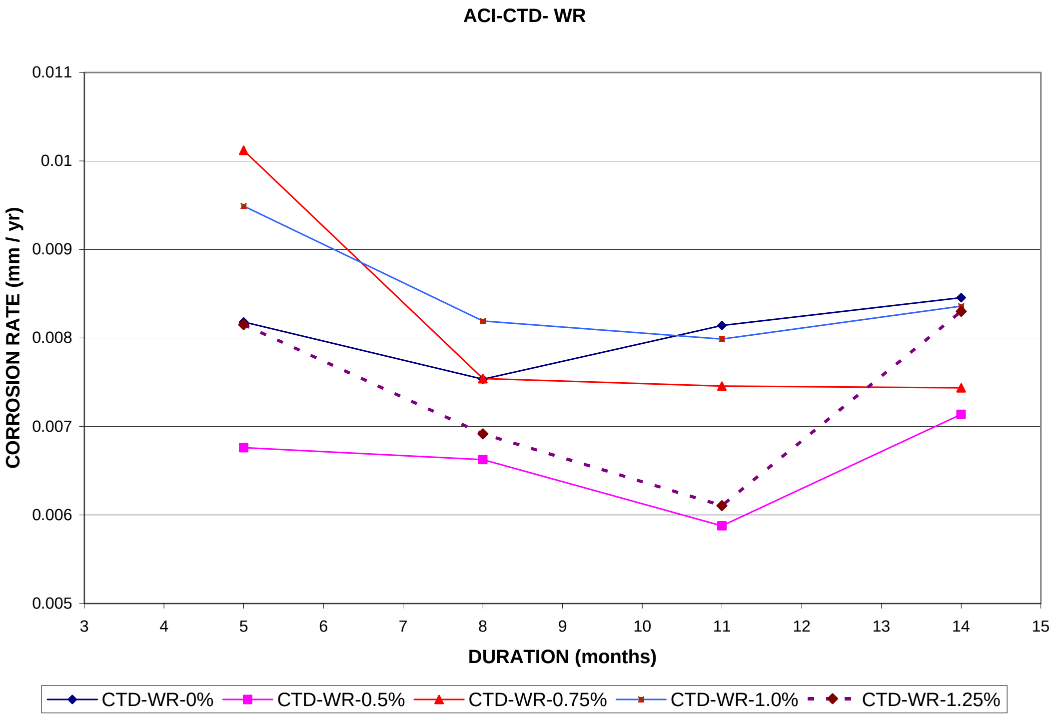

Figure-8. ACI test results-CTD bar.

3.1.3 TMT rod

The corrosion rate of TMT rods with respect to admixture additions is shown in Figure-9. From this figure it is depicted that here also the corrosion rate increases for all cases because of the breakdown of passive film only after 11th month except for 0.75% admixed concrete. At 14th month, corrosion rate of TMT rod embedded in concrete without admixture shows higher corrosion rate than the other rods of admixed concrete. In all the times corrosion rate of TMT bar in concrete admixed with 0.5% is observed less with respect to all the other cases.

3.2 L.P.R measurements

3.2.1 MS rod

The corrosion rate of MS rods using LPR technique, with respect to admixture additions is shown in Figure-10. From this figure it is depicted that MS Rod embedded in concrete with 0%, 0.5% and 1% of admixture started giving increased corrosion rate after 8th month, where as 1.25% admixed concrete, maintain the passive film stability up to 11th month, then the corrosion rate started increasing because of the decay of passive film after 11th month. Rod embedded in concrete with 0.75% depicts the declined nature of corrosion from the beginning. At 14th month of testing, rods with 1.0% admixture showed more corrosion than all other cases.

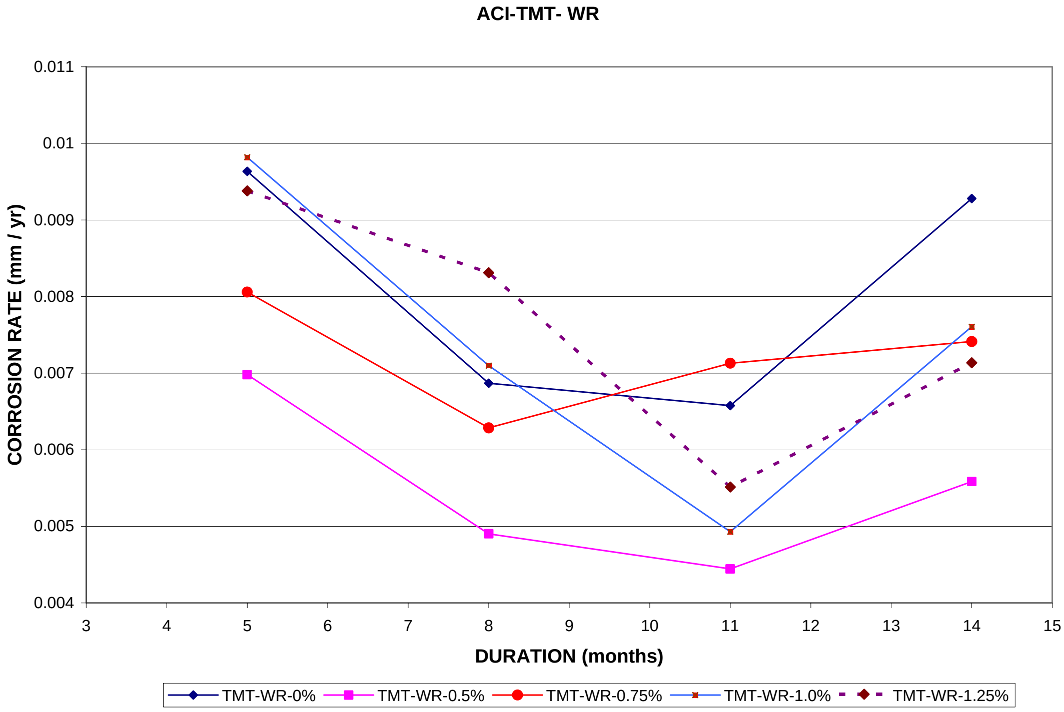

Figure-9. ACI test results-TMT bar.

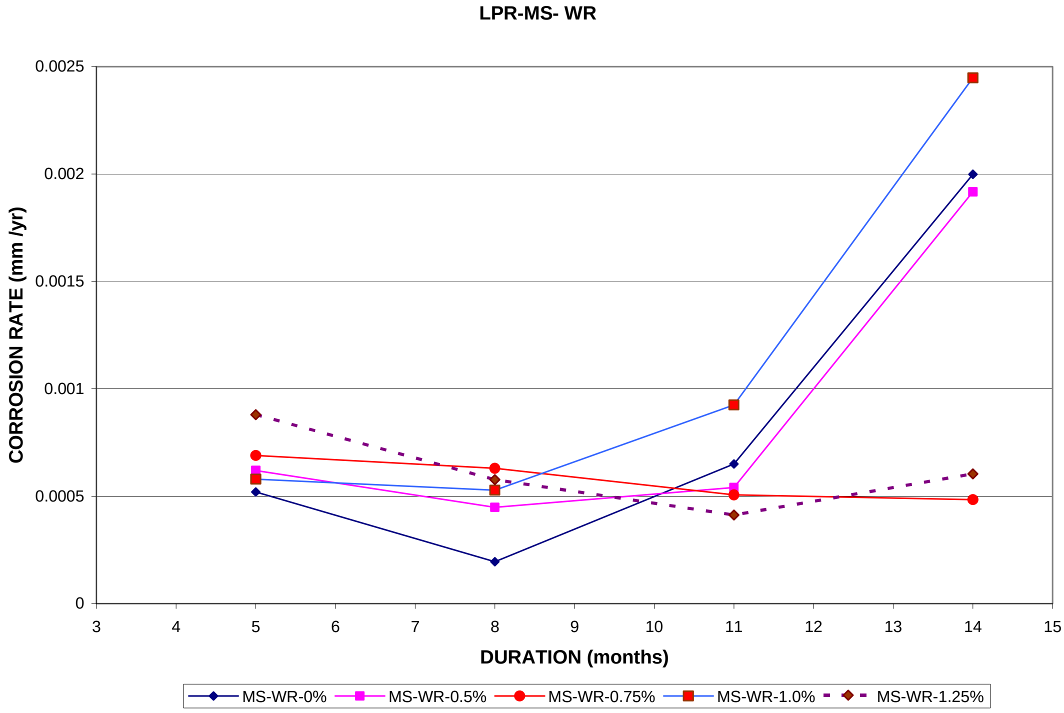

Figure-10. LPR test results-MS bar.

3.2.2. TMT rod

The corrosion rate of TMT rods with respect to admixture additions is shown in Figure-11. From the figure it is depicted that up to 8th month the passive film over the rod was stabilizing in this case also. But after 8th month in concrete admixed with 0%, 0.5% and 1%, it started decaying. Consequently the corrosion rate increases for the cases of 0%, 0.5% and 1.0%, where as rod embedded in concrete with 0.75% shows very good corrosion resistive character for TMT bars. Quantitatively in 1.0% admixed concrete, corrosion rate of TMT bar was more than the control concrete whereas, 0.75% concrete gave less corrosion than the control concrete.

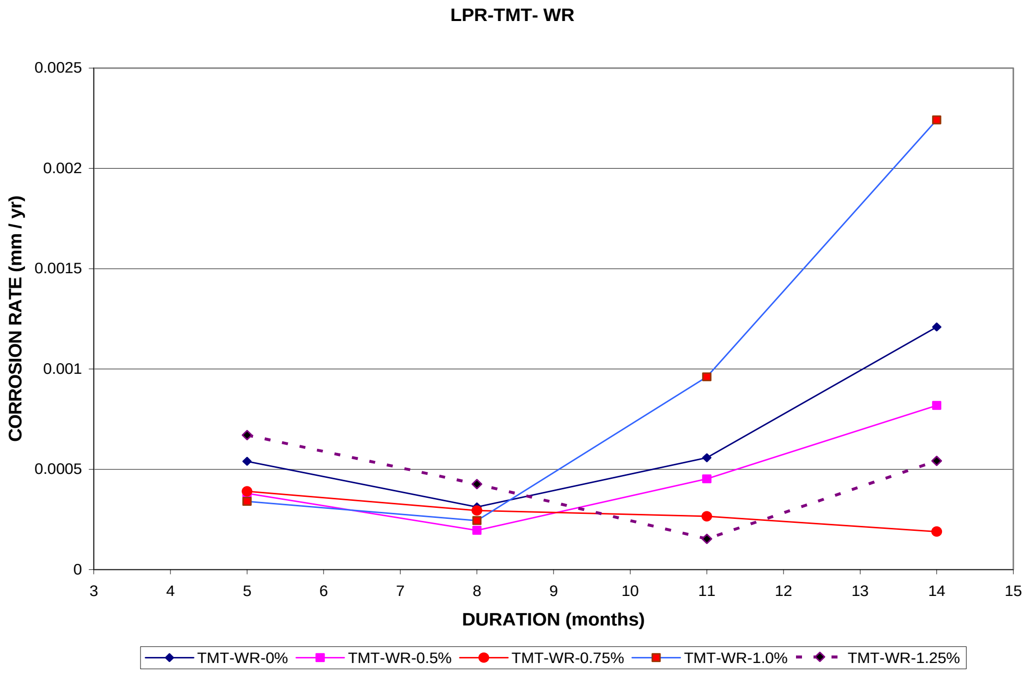

Figure-11. LPR test results-TMT bar.

3.2.3. CTD rod

The corrosion rate of CTD rods with respect to admixture additions is shown in Figure-12. From the figure it is depicted that except 1.25% of admixed concrete, the corrosion rate of CTD bar showed increase of corrosion rate after 11th month, where as other percentage of admixed concrete and control concrete, except 0.75% show increase of corrosion rate even from the 8th month itself. Among all the percentage of admixture, the rate of corrosion of rod in 0.75% admixed concrete shows the declination from the beginning. Corrosion rate in 1.0% of admixture added concrete depicts higher corrosion rate than that of control concrete, in 14th month.

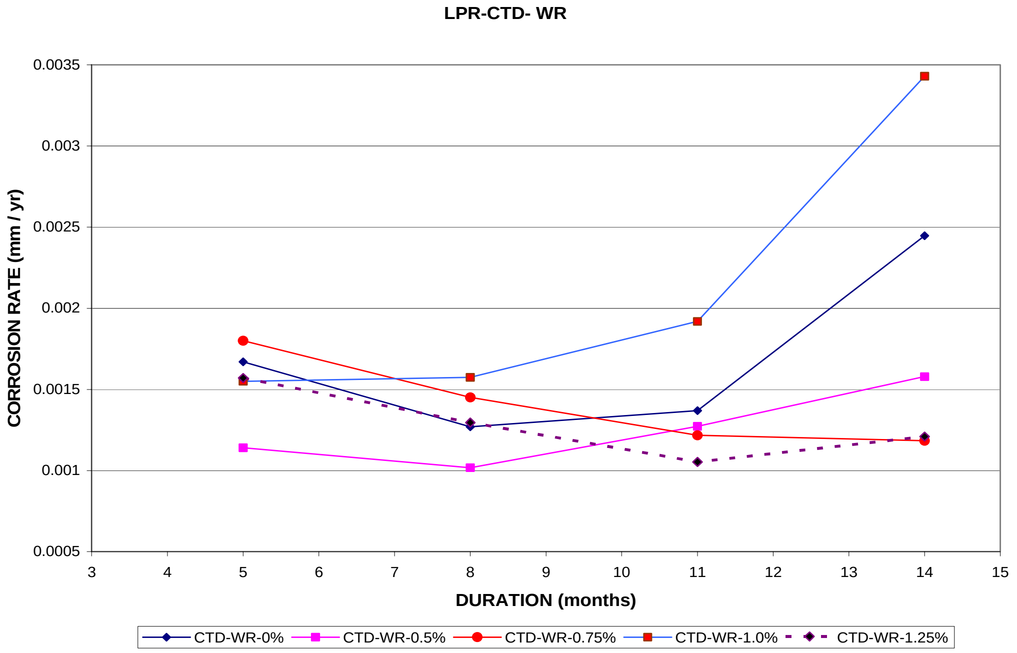

Figure-12. LPR test results – CTD bar.

3.3 OCP measurements

3.3.1 MS rod

The corrosion rate of MS rods with respect to admixture additions is shown in Figure-13. From the figure it is depicted that as per ASTM C876, - 270mV Vs saturated calomel electrode (SCE) has been taken as threshold potential for the active condition of rebar. Figure-13 relates the potential (in volts) – time (in months) behavior of concrete with different admixture proportions. OCP measurements were taken and observed for a period of 14 months from the date of curing. When the duration increases i.e., after 8th month itself, OCP values of normal concrete, 0.5% and 1.0% admixture added concrete changes its trend to anodic region, where as 0.75% and 1.25% admixture added concrete shows their change of path to anodic region in the 11th month only. Because of alternate wetting and drying, to accelerate the corrosion process, the concrete shows further propagation of corrosion. In 14th month only, the concretes having 0% and 1% of admixture entered the threshold value of 90% probability-corrosion zone. The potential value of concrete with 0.5% admixture is uncertain as it has the potential value of –0.2V. As per the results, concrete with 0.75% and 1.25% of admixture shows better corrosion resistance than control concrete, where as concrete with 1% admixture gives more corrosion probability than control concrete.

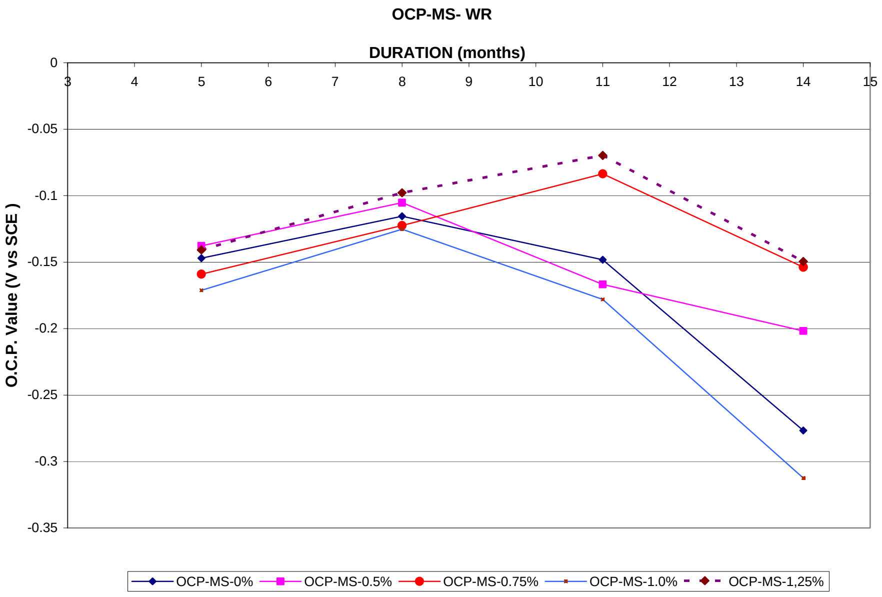

Figure-13. OCP test results- MS bar.

3.3.2 TMT rod

The corrosion rate of TMT rods with respect to admixture additions is shown in Figure-14. From the figure it is depicted that the concretes added with different percentages of admixture changed their trend to anodic region in the 8th month duration. Corrosion resistance of concrete with 1% admixture is poor and 0.75% and 1.25% admixture concrete proved better in their corrosion resistive activity. Even after 14th month, no case was entering into the zone of 90% corrosion probability.

3.3.3 CTD rod

The corrosion rate of CTD rods with respect to admixture additions is shown in Figure-15. From the figure it is depicted that the concrete with 1% admixture showed the worst nature of resisting corrosion. That case only entered the 90% probability of corrosion zone in the 14th month of observation. Concrete with 1.25% performed better against the corrosion resistive activity.

3.4 Weight Loss measurements

Figure-16 shows that the protective activity of passive film was destroyed after the 8th month for all the percentage of admixture added concrete, and even for control concrete. The corrosion rate of MS rod added with the admixture of 0.5 % only showed less, when compared to control concrete all the times. At the 14th month, rod embedded in control concrete took the lead and rate of corrosion is more than that of all the other types except the rod with 1.25% of admixed concrete. Figures 17 and 18 show that the same trend of MS rod for the TMT rod, as well as CTD bars embedded in concrete with water reducing admixture of different proportions.

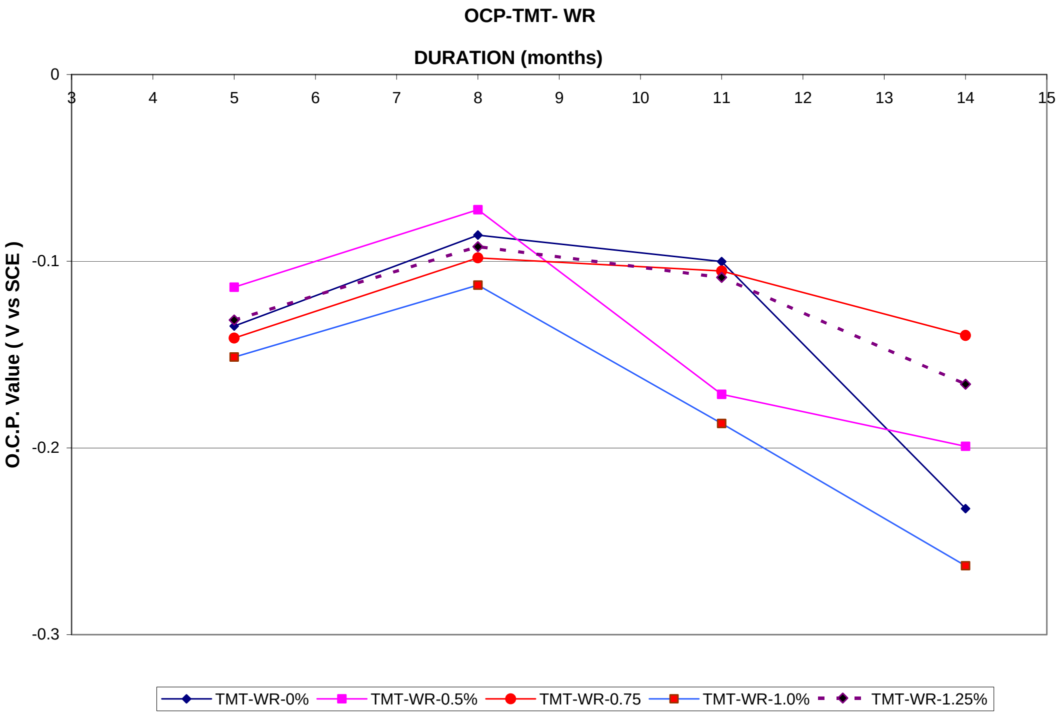

Figure-14. OCP test results-TMT bar.

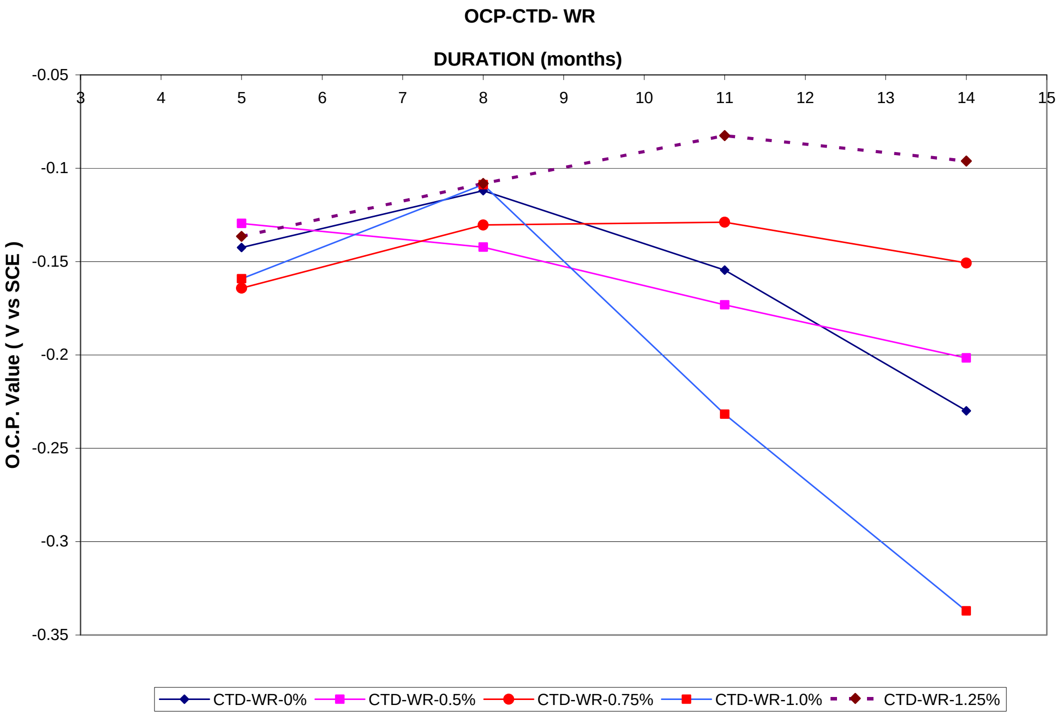

Figure-15. OCP test results-CTD bar.

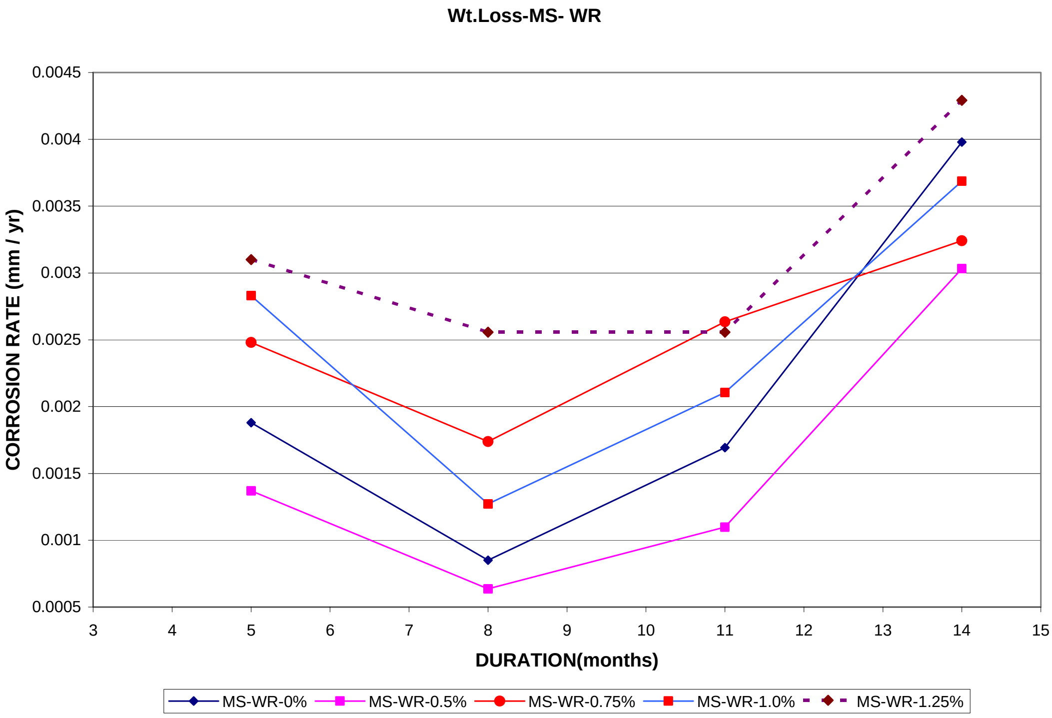

Figure-16. Weight loss measurements-MS bar.

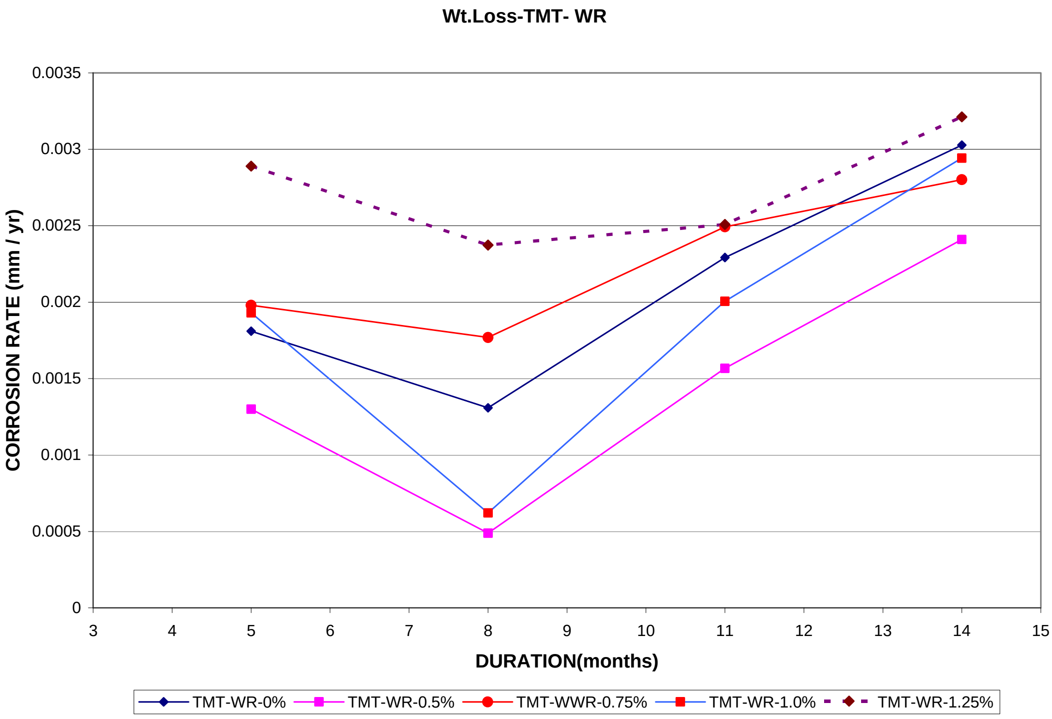

Figure-17. Weight loss measurements-TMT bar.

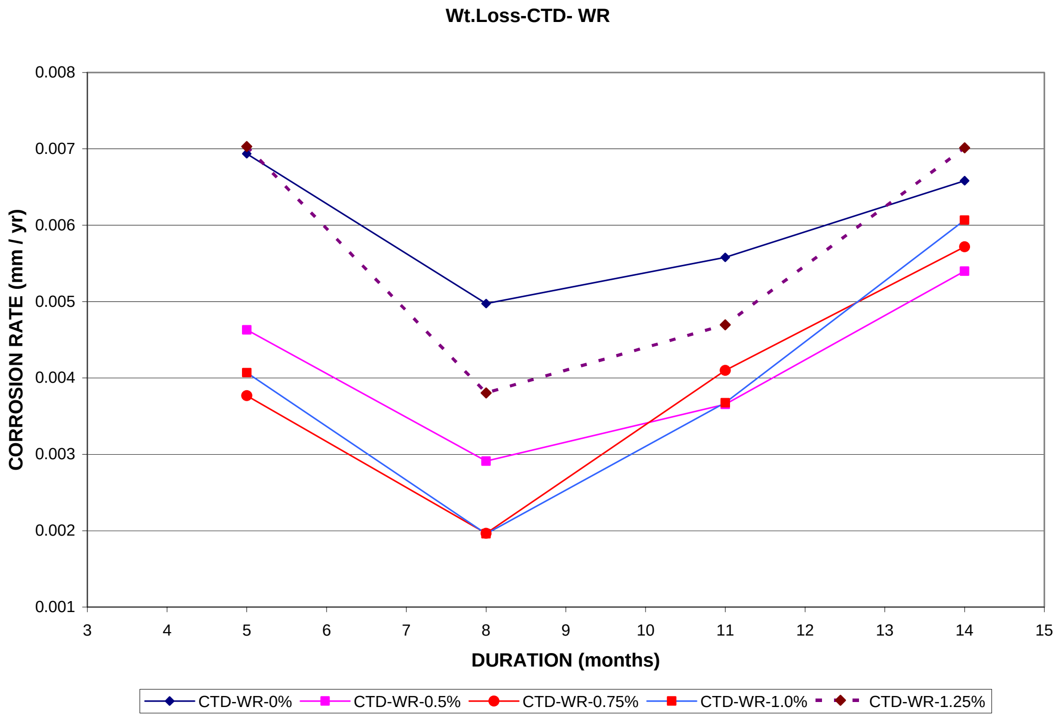

Figure-18. Weight loss measurements- CTD bar.

4. CONCLUSIONS

Based on the experimental study, the following conclusions are made:

- Initiation of corrosion in rebars was delayed due to the addition of chemical admixture. Because of the continuous formation of passive film over the metal due to the chemical reactions took place with the metal surface and the admixture added concrete environment, the corrosion effect was reduced up to 8th or 11th month of casting and curing of cubes.
- According to the results obtained from ACI measurement test, rods in concrete added with 0.5% - water reducing admixture gave better corrosion resistive character.
- As per LPR measurements tests, corrosion rate of MS, TMT and CTD bars embedded in concrete with 0.75% gave better performance to resist corrosion, as the trend of corrosion rate constantly decreasing with time.
- Data obtained from OCP test reveals better corrosion resistance was offered by 0.75% admixed concrete to all the rods, especially to TMT rods.
- The destructive test of weight loss measurements exposed, the rods embedded with 0.5% of water reducing admixture was always better in all the times and cases to resist corrosion.
- Corrosion rate of TMT bars are always less when compared with MS and CTD bars.
- From the overall data collected, it may be concluded that TMT rod embedded with concrete admixed with 0.5 % of water reducing admixture is better against the corrosion effect, than the control concrete.

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