

H24/3138

MONASH UNIVERSITY
THESIS ACCEPTED IN SATISFACTION OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

ON..... 7 December 2001

.....
for Sec. Research Graduate School Committee

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ADDENDUM

Part A :

The following discussion addressing the issues that were raised during thesis examination (written in "italics").

1a. The one chapter that I would criticise is that on diffusion. In many places the concentration-time curve is described (e.g. p. 196) as showing a plateau (the result we expect), whereas results such as Fig. 6.6 clearly show a peak concentration in the downstream compartment followed by a fall. This is eventually described and an explanation advanced, but the results do not show a plateau. The explanation advanced is that inhibitor leaks out - this idea should not be difficult to test, but no checks have been made. Is there any other way to explain this?

The diffusion cells were monitored over a long period (i.e. 450days) and in all the systems it was noticed that after an initial period (which was found to vary for each set of experiments) the concentration/time plot reached a maximum and then started showing a decrease (or a plateauing effect in some cases). This phenomenon was observed as a general feature. The explanation that "the rate of loss of inhibitor through evaporation from the downstream cell being higher than the rate of its arrival leading to a net decrease in the downstream concentration" is presented here as one possibility for the above anomaly. It was further observed that the rate of decrease in the downstream concentration after reaching the peak concentration is significantly higher in the case of DMEA (possibly due to its higher vapour pressure) as compared with that observed in the case of DICHAN and MCI (refer to Figures 6.4 and 6.5 on p.115), which supports the above statement.

When it was observed that the inhibitor concentration in the downstream compartment was decreasing with time (a few months after beginning the monitoring), several possibilities were considered. One of these was the loss of inhibitor from the cell and so an attempt was made to check the concentration in the original (upstream) compartment. Due to the high initial concentration in this compartment, several dilutions were necessary to reach concentration levels in the range of the electrode calibration. In this experiment, taking into account all the dilutions (which can lead to errors), a minute decrease in the original concentration (well within experimental errors) was found. This approach was ultimately abandoned since it was felt that the outcomes were inconclusive. Any future work which attempts such long term diffusion measurements should consider cell modification to ensure that losses due to volatility can not occur.

Other alternatives for the decline in concentration were considered. One of the effects that may explain the decrease of inhibitor molecules is the possible interaction of inhibitor with the concrete. Different inhibitor/concrete interactions are postulated such as inhibitor molecules adsorption onto the concrete pore walls with the non-polar molecular tails forming a hydrophobic barrier or the attachment of the permeating inhibitor solution to the ionic sites in concrete or chemical complexation of inhibitor molecules with the constituent cement phase. These interactions are likely to result in binding of the diffusing molecules to the concrete and reduce their effective ionic transport. This may cause partial or complete blocking of concrete pores thus reducing concrete permeability and hence the diffusivity. The suggestion of inhibitor/concrete interaction is somewhat supported by the consistent observation of the plateau/decline of the inhibitor concentration. Furthermore, its timing showed certain trends with respect to concrete membrane thickness, w/c ratio and inhibitor concentration as discussed in sections 6.4.1 to 6.4.3. It should also be noted that anecdotal evidence suggests that concrete resistivity increases with time when MCI type inhibitors are used in the field. This also supports some form of chemical interaction.

1b. One point of procedure puzzles me. For the analysis by ion-selective electrode the pH of the sample is adjusted to 12 with alkali (I would expect it in any case to be above 12 from contact with the concrete) then a buffer of ionic strength added. The sample is finally returned to the diffusion cell. If this is repeated several times, what are the levels of these chemicals in the test cell? Does it

have any influence on the test electrode or the diffusion process? Were tests made to check that this procedure does not affect the measurements?

While doing measurements on the downstream solution, a check of the pH of this solution was made each time. It was observed that during initial stages the pH of the test solution from the downstream cell was lower than 12 hence a few drops of sodium hydroxide were needed to bring the solution pH above 12. At the later stages, however, the pH was more or less maintained (possibly due to previous periodic addition of sodium hydroxide). This was always followed by the addition of a few drops of the ionic strength adjuster (comprising of 5M NaOH/0.05M disodium EDTA/10% methanol with colour indicator). With regards to the second part of your question, there are three issues to consider.

1. The electrode works by a gas sensing element, and is sensitive only to volatile amines, which can diffuse through the gas permeable membrane. All other anions, cations and dissolved species do not interfere with the working of the electrode. Chemicals added during monitoring are non-volatile/non-amine based and are unlikely to affect the potential measurement and hence concentration determination.

Additionally, the calibration plots showing a linear relation (plotted over a wide range of concentrations) between potential vs concentration of all inhibitors supports the fact that there may not be any adverse reaction between various inhibitors and the chemicals added during testing.

2. With regards to the effect of these chemicals on the diffusion process, it is assumed that the inhibitor transport is primarily driven by the concentration gradient. Hence the effect on the diffusion process, if any, should be minimal and within experimental error.

In the longer term, the assumption is that the driving force for diffusion of inhibitor is the large ΔC , which remains large even at the end of the test period.

3. Finally, the actual additions of sodium hydroxide and ionic strength adjuster are not significant when the dilutions into the ~300ml downstream cell is considered. It should be noted that in the later stages of measurements these additions were not necessary, although the checks of pH and ionic strength were always performed. In total, addition of approximately 0.2-0.5 ml would have been carried out in each case. When one considers the dilution factor this was thought to be within the experimental error.

2a. It is not altogether clear to me how the diffusion coefficient is evaluated from Fick's 1st law. It would be useful to know where and how the slope of the conc./time plot was determined. In Fig. 6.6.2 inhibitors seem to give the same slope (by eye) for different sample thickness.

The slope of each plot, considered in the calculation of diffusion coefficient, is determined by carrying out linear regression analysis of the (initial) linear or apparent linear part of the actual concentration/time plot. e.g. in the case MCI, the initial region of the concentration/time plot extending up to 270 days was considered for 30mm concrete membrane having 0.45 w/c ratio, whereas for a similar membrane having 0.6 w/c ratio, region up to only 220 days was considered. It must, however, be pointed out that the plots included in the thesis are not the inhibitor concentration (in terms of absolute values)/time plots but instead %inhibitor diffused/time plots, which would show concentration in the downstream cell as a ratio of the original upstream concentration. This was done mainly because of different starting (upstream) concentrations of commercial MCI (5wt%) and the individual amines (0.1M), which makes the comparison of diffusivity of different inhibitors, based on absolute values of their diffused concentrations emerging out into the downstream cell meaningless. Additionally, the lack of information on the amine component in commercial inhibitors like MCI makes the comparison more complex.

Once the slope was calculated, the diffusion coefficient was determined as per the Equation 6.2 (p. 113) using Fick's 1st law, which can be written as

$$D_{eff} = \frac{C_2}{(t-t_0)} \frac{Vl}{C_1 A}$$

or

$$D_{eff} = slope \frac{Vl}{C_1 A}$$

since V volume of the solution, A cross-sectional area of the concrete membrane, l thickness of the membrane and C_1 concentration in the upstream cell are known, D_{eff} diffusion coefficient can be calculated by substituting a value of the slope in the equation.

Regarding your observation about Figure 6.6 (b), we agree that the slopes of the graphs in the case of DMEA for concrete membranes having two different thicknesses (w/c 0.45) appear similar. (the calculated values of the slopes being: 8.00×10^{-5} in the case of 30mm concrete membrane and 9.00×10^{-5} in the case of 10mm concrete membrane). Nevertheless, the thickness of the membrane (or the path length l), in a 30mm membrane is three times higher than that observed in a 10mm membrane. Similarly, the volume of the compartments with a 30mm concrete membrane cell is smaller than that for a 10mm concrete membrane cell. When these facts are substituted in the above equation and assuming that C_1 and A remain practically constant, the net effect of the above two variables will clearly show more than two times increase in the diffusion coefficient in the case of a 30mm membrane.

2b. A procedure for analysis using Fick's 2nd law is given on p. 113-4, but no details. Similarly the analysis of results (p. 128) does not show how the iterative method was used. This should either be set out more fully or (given its lack of real success) taken out.

The key reason for performing the second law fits was to ascertain whether the diffusion was better fitted to non-steady state kinetics. Taywood Engineering have used this program successfully for chloride diffusion in concrete. As it turns out the fits were only marginally improved. Nevertheless I feel that the fitting attempts were important for completeness since the 1st order model clearly could not be used to fully explain the observed different behaviour (see p. 128). Interestingly the second law fits did suggest a possible model whereby the inhibitor diffusion occurs rapidly in the initial stages possibly through the vapour state and capillary action, as opposed to the longer time slower process of liquid phase diffusion (p. 128, 129).

3. One factor that has been overlooked in the design and the analysis of the tests on joint action of cathodic current and inhibitor. The work takes up a suggestion from other published papers that cations derived from the protonation of the amine inhibitors can be "electrically injected" into the concrete. The discussion fails to consider the relative quantities of cation and free amine under the conditions here. Amines are weak bases, which in the strongly alkaline conditions of the concrete will be virtually undissociated. The relative pK_b values of the amines should be checked and taken account of in the discussion. The alternative explanation (put forward in the thesis) that electrochemical chloride removal makes the inhibitor more effective, seems more likely to me. If injection were important it should be possible to show that inhibitor takes effect more rapidly with cathodic polarisation.

The premise that an electric field can be used to accelerate inhibitor diffusion was that the amine groups were quaternary charged species. Throughout the thesis it was accepted that in a high pH environment such as that in good concrete, neutral amine molecules were likely.

e.g. p.53 section 3.2.4 --- "Indeed, in a high pH environment such as that existing in concrete, it is unclear whether charged inhibitor ions or neutral inhibitor molecules predominate."

p. 73 section 4.3.5 --- "It may, however, be mentioned that in the high pH environment such as that existing in the saturated calcium hydroxide solution in the above experiments, it is unclear whether $(C_6H_5)_2NH_2^+$ or $(C_6H_5)_2NH$ molecules predominate considering a possibility of some interaction between the protonated inhibitor molecules and OH^- ions in the solution."

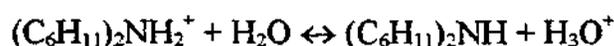
p.119 section 6.4.1 --- "DICHAN is an alkyl-substituted quaternary ammonium salt of the nitrite anion. Although steric factors and deprotonation of free alkyl-ammonium ions to simple substituted amine molecules by the alkaline pore water would be expected to inhibit binding of the cation,

In this part of the addendum, the issue of likely amine protonation is addressed in more detail. The discussion of dissociation of dicyclohexylamine nitrite DICHAN in concrete has been divided in two parts.

- a. pK_a/pK_b values for DICHAN and the likely amount of charged /protonated species
- b. the possibility of decrease in the pH of the concrete due to carbonation, admixed chloride and DICHAN

(a) Determination of protonated fraction:

The dissociation of DICHA in water can be represented as



The acidic dissociation constant i.e. pK_a for DICHA, deduced by referring to other amines/diamines, is between 10.5-11. (e.g. pK_a for other mono and diamines are between 10-11, pK_a values for ethylamine 10.63, diethylamine 10.93 and for cyclohexylamine 10.64 (Vogel, 3rd Edition)). If pK_a for DICHA is considered as 10.8, the percentage of neutral molecules and charged species can be calculated as follows:

$$\frac{[H_3O^+][(C_6H_{11})_2NH]}{[(C_6H_{11})_2NH_2^+]} = 10^{-10.8}$$

at pH = 10.8

$$\frac{10^{-10.8}[(C_6H_{11})_2NH]}{[(C_6H_{11})_2NH_2^+]} = 10^{-10.8}$$

$$\frac{[(C_6H_{11})_2NH]}{[(C_6H_{11})_2NH_2^+]} = \frac{10^{-10.8}}{10^{-10.8}}$$

$$\frac{[(C_6H_{11})_2NH]}{[(C_6H_{11})_2NH_2^+]} = 1$$

Therefore,

at pH = 10.8, $[(C_6H_{11})_2NH_2^+] : [(C_6H_{11})_2NH] \quad (50 : 50)$

Similarly,

at pH = 9, $[(C_6H_{11})_2NH_2^+] : [(C_6H_{11})_2NH] \quad (98.4 : 1.6)$

at pH = 12, $[(C_6H_{11})_2NH_2^+] : [(C_6H_{11})_2NH] \quad (6.0 : 94.0)$

at pH = 13, $[(C_6H_{11})_2NH_2^+] : [(C_6H_{11})_2NH] \quad (0.6 : 99.4)$

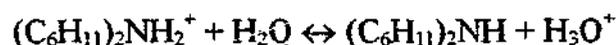
Hence for pH < 12, at least some of the amine molecules will be protonated and hence positively charged. What the pH for the present situation is likely to be will be discussed in (b).

(b) Factors influencing pH in concrete

The pH of fresh concrete is considered to be ≥ 13 . However, in the case of concrete specimens, which were kept in a fog room for 28 days with high admixed chloride content and high w/c 0.6 ratio, it is quite likely that the pH of concrete will have decreased due to

- i) carbonation
- ii) pitting corrosion with a local decrease in the pH

Further, the experiments carried out in simulated concrete pore water (saturated calcium hydroxide solution) (chapter 4 and 5) have indicated that there was indeed a decrease in the pH with time (8 days) in all solutions i.e. Ca(OH)_2 solution, $[\text{Ca(OH)}_2 + \text{NaCl}]$ control and $[\text{Ca(OH)}_2 + \text{NaCl} + \text{DICHAN}]$ solution. The actual pH values decreased from 12.6 to 10.5 in the case of Ca(OH)_2 solution, from 12.6 to 9.2 for the $[\text{Ca(OH)}_2 + \text{NaCl}]$ control solution and from 12.4 to less than 9.0 for the $[\text{Ca(OH)}_2 + \text{NaCl} + \text{DICHAN}]$ solution. A decrease in the pH on addition of DICHAN would shift the equilibrium of the following reaction to the left, which would result in an increase in the amount of the protonated species.



On comparing this situation with that in actual concrete, although newly made concrete would indeed have a pH of 13 or greater, the pH would decrease significantly with time due to the two points mentioned above. In the experiments that were conducted here, the concrete mix was chosen to be relatively 'poor' concrete having high w/c ratio, which would most likely accelerate these factors. In hindsight, simple pH measurements could have been made on control specimens to confirm these possibilities

We would like to cite here the published works of other researchers, where the cationic inhibitor injection studies have been performed (Asaro et al., 1990; Hettiarachchi and Gaynor, 1992) based on quaternary ammonium and phosphonium corrosion inhibitors. In this work a two compartment cell separated by a concrete membrane was prepared. The inhibiting ion was added to the anode compartment and the extent of inhibitor electromigration was determined by analysing the original inhibitor free compartment for the presence of the inhibitor ion after application of an electric field for a predetermined time. The presence of the inhibitor in the concrete was confirmed by crushing a sample of the matrix, extracting with boiling water and analysing the resulting solution for the inhibitor ion. The electrical-field assisted cation movement was further confirmed by comparing the results thus obtained with simple diffusion experiment under similar conditions without an applied electric field. Therefore there also appears to be some literature support for the presence of quaternary ammonium ions in concrete.

Given the above discussion together with the experimental evidence presented in the thesis, we can say that at least some (but by no means all) fraction of amine molecules will indeed be protonated thus justifying the original premise.

Regarding preference for the alternate explanation of electrochemical chloride removal making the inhibitor more effective, one can observe from Figure 8.8 on p. 184 that the specimens subjected to a combined treatment of inhibitors and electric field not only exhibit higher level of inhibition as compared with that displayed by control_{EM} (the specimen subjected to electric field alone), but the inhibition levels were maintained until the end of the test period (i.e. 300 days after the current was switched off). Whereas in the case of control_{EM} the protection level started to decrease after approximately 60 days, and it dropped further below the zero level around 250 days suggesting accelerated corrosion. Thus higher level of inhibition obtained in the case of specimens treated with both high current and inhibitor, may suggest the electrically assisted diffusion of the inhibitor molecules to the rebar and their subsequent chemisorption on to the charged surface forming a barrier film. In the case of cathodic polarisation, as mentioned in section 8.3.1, the results suggest that the magnitude of the applied current density may be insufficient to enhance the rate of inhibitor transport to the steel surface.

Besides the above explanation there may be a possibility of formation of local anodes on the rebar surface in chloride contaminated concrete. In the case of a mixed inhibitor e.g. DICHAN (cationic amine and anionic

nitrite), the nitrite anion may adsorb strongly onto metal surface and promote the subsequent adsorption of quaternary amine cation thus resulting in higher efficiency. However, this has not been postulated in the thesis and needs to be further investigated. It would be interesting to state here the results obtained by Asaro et al., (1990) where it was found that the larger the anion, higher the corrosion inhibition efficiency (in terms of a polarisation resistance R_p) for a given quaternary cation

$$\text{e.g. } R_p(\text{MoO}_4^{2-}) > R_p(\text{NO}_2^-) > R_p(\text{Br}^-)$$

It was believed that this trend is due to the higher polarisability of the larger anions, which adsorb strongly onto the metal surface promoting further cationic adsorption.

ERRATA

p. 31

Below Equation 2.6 delete $\Delta C/C$ in the sentence "It should be noted that this situation might be expected at longer times when an effective concentration gradient $\Delta C/C$ has been established." Read this sentence as "It should be noted that this situation might be expected at longer times when an effective concentration gradient has been established."

p. 32

Please read in Equation 2.7, "dC/dt" instead of "DC/dt"

p. 213

Treadaway, 1966 (ref)

I acknowledge that in this context, the original reference i.e. Berke, (1991) should have been given.

REFERENCES

Asaro, M. F., Gaynor, A. T., and Hettiarachchi, S., (1990), "Electrochemical Chloride Removal and Protection of Concrete Bridge Components (Injection of Synergistic Corrosion Inhibitors)", Strategic Highway Research Program Report, SHRP-S/FR-90-002 Contract C-102C, National Research Council, Washington, DC.

Berke, N. S., (1991), "Corrosion Inhibitors in Concrete", *Concr. International.*, **13**, No. 7, pp. 24-27.

Hettiarachchi, S. and Gaynor, A. T., (1992), "Corrosion Inhibitors for Rebar Corrosion Control", *Mater. Perform.*, **31**, No. 3, pp. 62-66.

Part B:

1. So far as diffusion is concerned what I really would have liked to see is to what extent she believes leakage influences the quantitative analysis of her data. For instance, with DMEA (Fig 6.5) the concentration falls as rapidly as it has risen. What does this mean in terms of the value of D ?

I believe that the inhibitor losses from diffusion cell were not very significant. As mentioned earlier when inhibitor concentration in the downstream compartment was found to decrease with time (a few months after beginning monitoring), an attempt was made to check the concentration in the original (upstream) compartment. In this experiment considering all the dilutions, a minute decrease in the original concentration was found, which could have been within the experimental error. We therefore conclude that

losses due to vaporisation from the cell were not significant and are unlikely to be the dominant factor influencing the plateau/ decreasing concentration behaviour.

However, even if we consider that the losses were in fact significant, then assuming the extreme case that the decrease in the concentration of DMEA after 300 days was purely due to vaporisation of inhibitor, the slope for the part of the graph after the maximum can be estimated. It is also assumed that this slope (dc/dt) when multiplied by time t i.e. $t(dc/dt)$, should give the amount inhibitor lost due to vapourisation at any given time t . The assumed value C_2^a , which is the diffused concentration in the downstream cell in the absence of losses, can be calculated as per the following equation

$$C_2^a = C_2^m + t(dc/dt)$$

where C_2^m is the measured concentration in the downstream cell.

Figure 1 represents the plot for C_2^a calculated as per the above equation versus time. Figure 2 depicts linear regression analysis for the initial linear part of the above curve i.e. considering the first four data points whereas Figure 3 shows analysis for the later age data points (steeper part of the curve before the maximum). Diffusion coefficient values estimated using the slopes from Figures 2 and 3 are $7 \times 10^{-12} \text{ m}^2/\text{s}$ (slope: 0.0003) and $14 \times 10^{-12} \text{ m}^2/\text{s}$ (slope: 0.0006) as against the original value (without considering losses) of $4.6 \times 10^{-12} \text{ m}^2/\text{s}$ (slope: 0.0002).

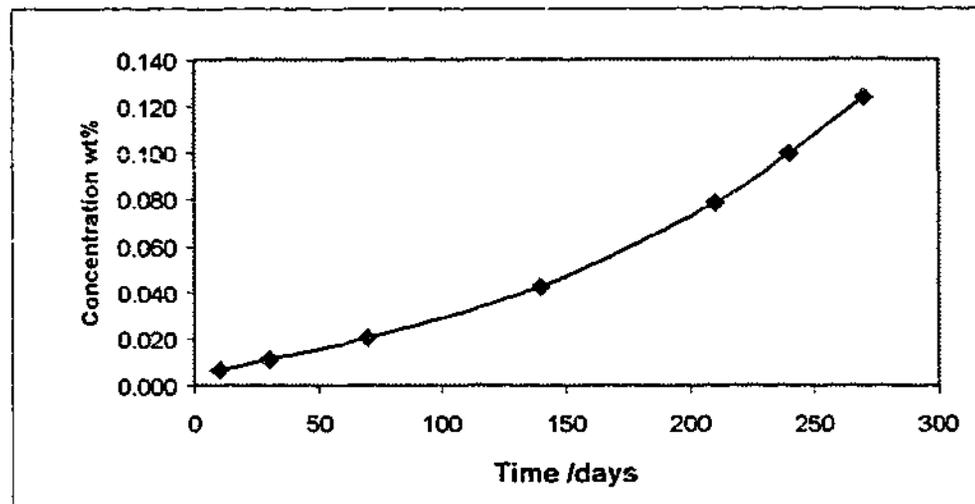


Figure 1: Concentration of DMEA (C_2^a) diffused through 30mm concrete membrane having w/c ratio 0.6

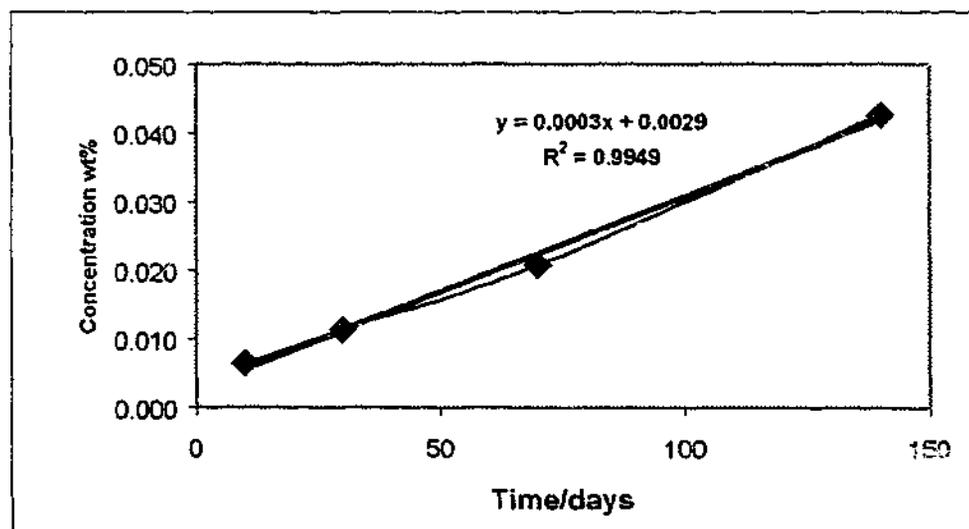


Figure 2: Linear regression analysis for the initial part of C_2^a vs t curve (Figure 1)

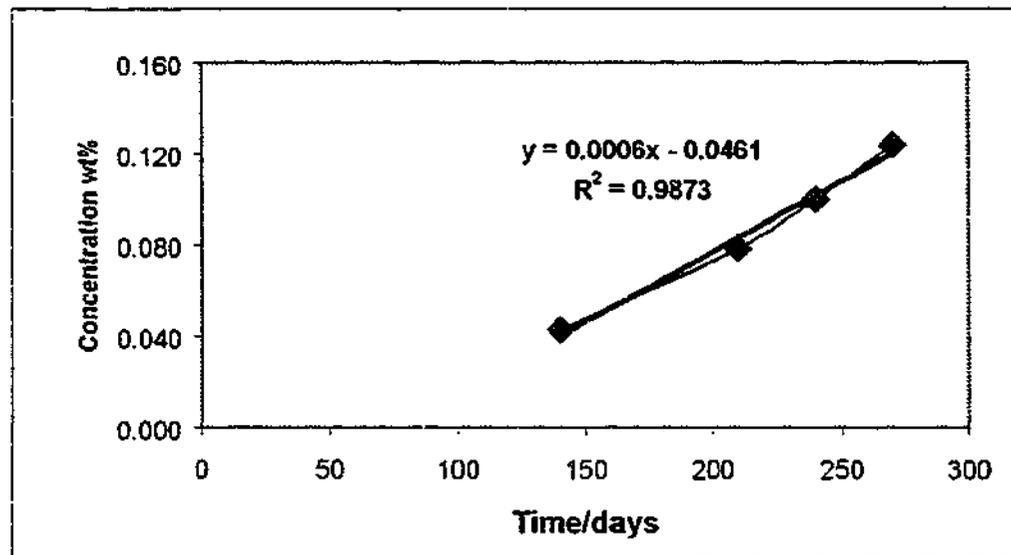


Figure 3: Linear regression analysis for the steeper part of C_2 vs t curve (Figure 1)

This shows that on considering the inhibitor losses from diffusion cell there is an increase in the diffusion coefficient value, however, the order of magnitude remains the same. Hence one can conclude that the penetration of these inhibitors through saturated concrete will be a slowish process and that this alone would not be sufficient to afford adequate protection in a reasonable time frame. Of course the inhibition data on concrete specimens which were treated with inhibitor alone show that the inhibitor does penetrate in a time considerably less than 1000 days, which is consistent with penetration through capillary action /vapour phase.

Further, on comparing the slope values obtained for DMEA in the case of concrete having w/c ratio 0.6, with those (for the same inhibitor) obtained with w/c 0.45 (in the case of both 10mm and 30mm concrete membrane), it was observed that the slopes in the case of w/c 0.45 were an order of magnitude lower than those obtained for w/c 0.60. This suggests that the diffused concentrations C_2 obtained in the case of w/c 0.45 were lower than those observed for w/c 0.6. This trend is actually consistent with lower porosity of concrete having w/c 0.45. If inhibitor losses were assumed to be the dominant factor influencing the downstream concentration C_2 , this being the property of the diffusion cell design, it would have been maintained in all cases irrespective of the concrete property such as w/c ratio, which is certainly not the case here.

2. Her explanation of how D is calculated does not seem to fit with the analysis she has presented. It is clear that concentration should not increase at all until the period $t(0)$ has passed. This seems to be ignored which would give entirely wrong values for D . Indeed for a value of $1 \text{ E-}12$ it would take about 1000 days for amine to penetrate a 10mm sample – so D must be far too small (taking $t = x^2/D$). D should probably be calculated from the steeper part of the curve just before the maximum. The question of how amine reaches the downstream cell before $t(0)$ should also be addressed.

It seems that there are two issues to be addressed here.

- a. The % diffused vs time plots do not pass through zero (origin); even at $t(0)$ some concentration of amine in the downstream cell (i.e. C_2) is detected by extrapolating data to $t=0$. Whereas from the value of $D= 1\text{E-}12$ it appears that it would take several days for amine to penetrate a 10mm sample.
- b. Calculation of D from the steeper part of the curve just before the maximum.

I will address each of these in turn below:

- a. The presence of inhibitor in downstream cell at $t(0)$ clearly suggests that the transport of these inhibitors through concrete membrane is not merely through ionic diffusion in the liquid phase but through other modes of transport such as vapour phase transport and by capillary action driven by the moisture gradient. This has also been suggested from the fits obtained using Fick's second law for non steady state conditions (section 6.4.4 in thesis) where it was clear that some inhibitor diffusion must have occurred near $t=0$ in order for the data to adequately fit at times $t>0$.

The likely reason for this is that concrete membranes were fog room cured and as fog room curing does not saturate concrete, it is assumed that the test specimens at commencement of the test were not saturated. Hence inhibitor penetration through the concrete membrane can take place by capillary action with moisture movement and/or transport by vapour phase (unsaturated pores). This has shortened the induction period and some concentration of amine (C_2) has been detected in the downstream cell at the commencement of the test period. In fact the issue of initial transport of inhibitor through the concrete membrane is very important as this may be the more dominant means of inhibitor penetration to the rebar in the field. A research programme to fully investigate this has recently begun in the group.

- b. Calculation of D from the steeper part of the curve just before the maximum has already been shown while explaining point 2 above. I would however, like to show representative linear regression analysis originally used (for calculating D values in the thesis) for DICHAN, DMEA and MCI in the case of 30mm concrete membrane having w/c ratio 0.60 (Figure 4). The slopes of the trendlines (and diffusion coefficient values) for these inhibitors are 0.0011 ($4.4 \times 10^{-12} \text{ m}^2/\text{s}$) for MCI, 0.0002 ($4.6 \times 10^{-12} \text{ m}^2/\text{s}$) for DMEA and $4E-5$ (0.4×10^{-12}) for DICHAN.

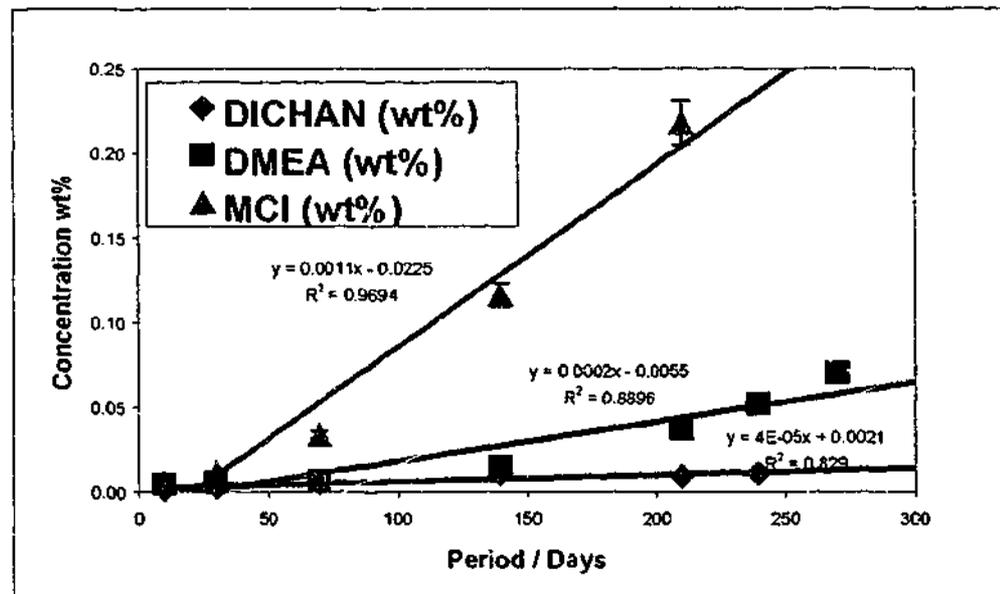


Figure 4 – Concentration of inhibitors diffused through 30mm concrete membrane having w/c ratio 0.6

If we consider only the steeper part of the curves, just before the maximum, by disregarding the early data points (as shown in Figure 5), the revised slope values will be 0.0013 for MCI and 0.0004 for DMEA (DICHAN has not been considered here because of very low downstream cell concentrations). The respective revised diffusion coefficients will be $5.2 \times 10^{-12} \text{ m}^2/\text{s}$ for MCI and $9.3 \times 10^{-12} \text{ m}^2/\text{s}$ for DMEA. A comparison of these values with the earlier values presented in the thesis do show an increase in the D_{eff} (especially for DMEA), however, the order of magnitude for both remains the same. These results are consistent with the results shown earlier.

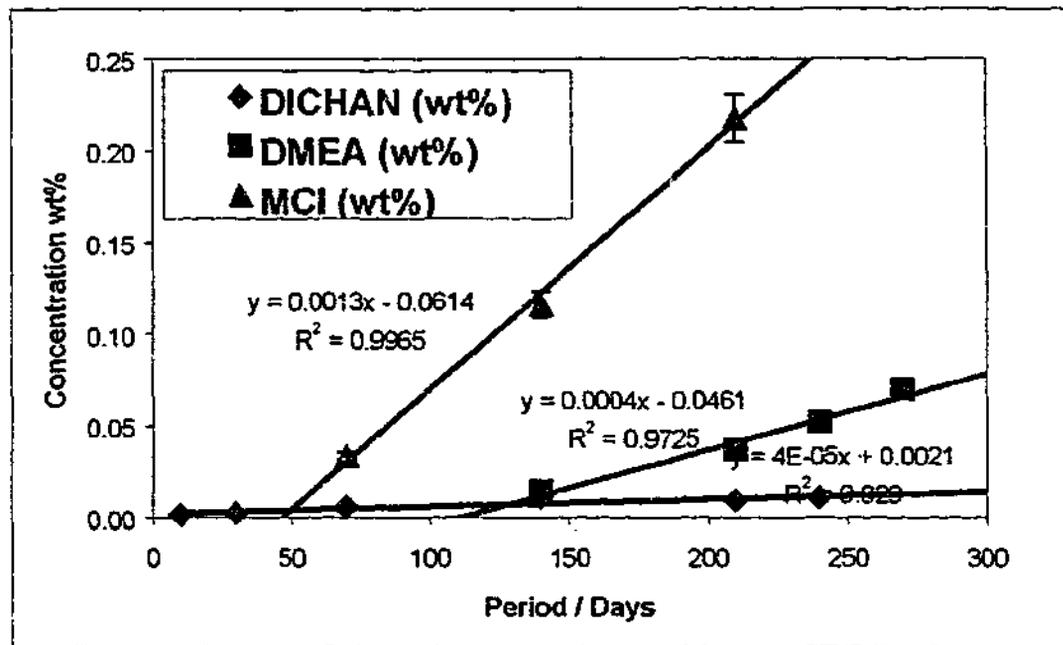


Figure 5 – Concentration of inhibitors diffused through 30mm concrete membrane having w/c ratio 0.6 (leaving early data points)

Therefore, I would like to conclude my response to your questions regarding the diffusion analysis by saying that, even considering losses due to volatility of inhibitor from the cell (which I do not believe can completely account for the observed trends) and if we consider the slope of the concentration versus time plots at later stages of the diffusion process (rather than the initial pseudolinear region) the diffusion coefficients calculated are still of the order of magnitude 10^{-11} to 10^{-12} m^2/s . This cannot account for the observations of inhibition in concrete specimens when MCI and DMEA are surface applied. Given the deviation of the data at early times it must be concluded that capillary action and vapour phase diffusion of the inhibitor in the concrete will be much more important than diffusion through the water filled pores of the concrete.

In summary, the process of inhibitor diffusion in concrete is considered to be dependent upon the level of saturation in concrete. In fully saturated concrete the transport of inhibitor takes place mainly by an extremely slow process of diffusion through the water filled pores of the concrete. Whereas, in partially saturated concrete one would expect that a combination of vapour phase diffusion through the partially filled concrete pores as well as capillary action would dominate; both processes being faster modes of transport as compared to solution diffusion.

**DIFFUSION AND PROTECTION MECHANISMS OF
MIGRATORY CORROSION INHIBITORS IN
REINFORCED CONCRETE**

by

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M.Sc., Ph.D. (Chemistry)

A thesis submitted to the Faculty of Engineering, Monash University
in fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Supervised by Dr. M. Forsyth and Professor B. W. Cherry

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December 2000

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SUMMARY

The aim of this research program was to develop an understanding of the mechanism of action of organic amine based migratory corrosion inhibitors for corrosion mitigation of reinforced concrete structures. The corrosion inhibition process in reinforced concrete was assumed to be a complex balance between two processes, namely the protection afforded by inhibitor at the steel surface and the transport of inhibitor molecules through the concrete pores. It was necessary, therefore, to examine the mechanism of these processes both independently and when combined together in reinforced concrete, so that an understanding of the controlling kinetics of the inhibition process can be developed.

The efficiencies of the organic amine based inhibitors were evaluated in a calcium hydroxide solution under an accelerated corroding environment using the linear polarisation resistance technique and corrosion potential measurements. The calcium hydroxide solution not only simulates the environment existing in concrete, but it also provides much simplified conditions than those existing in concrete, especially with respect to inhibitor transport. Based on the findings of these experiments, it was suggested that the mechanism of inhibition of the organic amine-based inhibitors is predominantly through the build up of a protective barrier layer, which hinders both anodic and cathodic reactions, whereas the nitrite-based inorganic inhibitors function by oxidising ferrous to ferric ions at the anodic sites thus preventing the anodic dissolution. An understanding was also gained of the likely factors, such as nature, molecular structure as well as concentration of inhibitors, which affect both the level and the mechanism of inhibition.

However, inhibition at the steel surface is a part of the overall inhibition process. Another equally important issue is the ability of these inhibitors to migrate through the concrete cover. Hence the research program then concentrated on the estimation of diffusion characteristics of these inhibitors. The commonly used diffusion cell technique for monitoring chloride diffusion, was used for monitoring inhibitor diffusion. Fickian diffusion laws for steady state and non steady state conditions were applied for calculating diffusion coefficients and a simplified model for inhibitor diffusion in concrete was developed. According to this model inhibitor transport in

concrete is a time dependent phenomenon having two different characteristics i.e. the behaviour obeying fickian laws and a non fickian diffusion anomaly. The coefficients were also found to vary as a function of permeability/thickness of the concrete cover and the size, polarity and concentration of inhibitor.

The inhibitor systems selected on the basis of good inhibition and diffusion properties from the earlier experiments were investigated further for their performance in reinforced concrete specimens. Inhibitors were either admixed in the fresh concrete while casting the specimens so as to simulate the condition of the rebar in the new structure, or were surface applied after the casting of the specimens to mimic an advanced stage of corrosion activity in a corroding structure. The investigations demonstrated the ability of amine based inhibitors to reduce corrosion by diffusing through concrete and forming a protective film at the steel surface regardless of the method of application /treatment. An inhibition model in reinforced concrete has been proposed, which highlights the fact that, even though corrosion inhibition in concrete is comprised of protection and diffusion processes, it is mainly the diffusion kinetics of inhibitors, that controls the overall inhibition process.

Having examined the performance of inhibitors in concrete, attention was now focussed on investigating the possibility of combining inhibitor application with some other protection method, which can extend their capacity to inhibit or ability to penetrate or both. This was achieved by simultaneous application of a constant protective current and inhibitor to the previously corroded reinforcement. It was contemplated that the amine-based inhibitors are likely to get protonated when mixed with water. Hence when electric field is applied between anode and cathode, it facilitates the movement of such positively charged molecules towards the cathode having a negative charge. This may in turn result in an acceleration of inhibitor transport through concrete and its subsequent adsorption on the metal surface. Two levels of current density, high and low, were applied and the mechanism of protection in both cases was examined. It appeared that the mechanism by which steel was protected in the two cases was completely different. In the case of low current density, steel is protected primarily due to the passive film, which is generated at the high pH conditions. Whereas with the higher current density, the mechanism of protection is by forming an inhibitor reinforced passive film due to the "electrical field assisted" inhibitor ionic transport.

DECLARATION

To the best of my knowledge and belief, this thesis contains no material which has been previously published or written by another person, except where due reference is made in the text. It does not contain any material, which has been accepted for the award of any other degree or diploma at any other university.


Alka Phanasgaonkar

ACKNOWLEDGMENTS

I wish to thank my supervisors Maria Forsyth for her enthusiasm and support throughout the course of this research program, and Prof. Brian Cherry for his guidance, criticism and humour.

The financial support provided by Australian Maritime Engineering Cooperative Research Centre is gratefully acknowledged. Thanks to the Savcor division of Remedial Engineering for their professional support and particularly to Zita Lourenco for her help during the initial stages of this project.

I wish to acknowledge Andrew Peek of Taywood Engineering Ltd., Australia for helping me with estimation of non steady state diffusion coefficients presented in chapter 6 and also for useful discussions.

The help provided by Matthew Jeffrey, Department of Chemical Engineering, Monash University during analysis of cyclic voltammograms presented in chapter 5 is gratefully acknowledged.

Thank you to Lex Edmond for ideas and valuable comments on the thesis and his help in proof reading the thesis.

I would also like to thank Julie Fraser for taking photographs, technical staff of the Materials Engineering Department, Monash University for their cooperation and help at various stages of this project. Also to Pam Hermansen and Leeann Hilborn for photocopying and general administrative help. Thanks to Peter Dunbar and other technical staff of Civil Engineering Department, Monash University, who managed to make concrete making enjoyable.

Lastly and perhaps most importantly a big thank you to Dilip and my parents for their encouragement, support and patience they have shown all these years during my involvement in this project.

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GLOSSARY

Control	A specimen exposed to aggressive chloride ions in the absence of an applied protection
Control _{CP}	"Control" specimen with application of cathodic protection
Control _{EM} /Control _{HCD}	"Control" specimen with application of high current density
CP	Cathodic protection
CPP	Cyclic potentiodynamic polarisation
D _{app}	The apparent diffusion coefficient (for non steady state conditions)
DAREX	Commercial inorganic inhibitor based on calcium nitrite
D _{eff}	The effective diffusion coefficient (for steady state conditions)
DICHAN	Dicyclohexylamine nitrite (C ₆ H ₁₁) ₂ NH.HNO ₂
DMEA	Dimethylethanolamine HOCH ₂ CH ₂ N(CH ₃) ₂
ECE	Electrochemical chloride extraction
E _{corr}	Corrosion potential
FHWA	Federal Highway Administration
i _{corr}	Corrosion current density
i _{inh}	Corrosion current density after addition of inhibitor
IP	Imperfect passivity
ISS	Ion scattering spectroscopy
MCI	Migratory Corrosion Inhibitor
mV _{SCE}	(potential measurement in) millivolts with respect to a saturated calomel electrode
NACE	National Association of Corrosion Engineers
OCP	Open circuit potential
PP	Perfect passivity
ppm	Parts per million
pzc	Potential of zero charge
R _{pcontrol}	Polarisation resistance of a control sample
SCE	Saturated calomel electrode
SHRP	Strategic Highway Research Program
SIMS	Secondary ion mass spectroscopy
SNMS	Secondary neutron mass spectroscopy
VCI	Vapour phase /volatile corrosion inhibitor
w/c ratio	Water/cement ratio

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CHAPTER 1

INTRODUCTION

1.1 - DURABILITY OF REINFORCED CONCRETE STRUCTURES

Reinforced concrete, because of its durability, has been the most widely employed building material for over 50 years. The concrete matrix provides a protective alkaline environment (pH 12.5-13) to the embedded steel and the steel provides ductility to the concrete. The steel is protected from corrosion by a passive oxide layer on its surface, which is sustained by a high alkalinity provided by the concrete matrix. However, a number of reinforced concrete structures have shown an early demise due to destruction of the passivity at the steel/concrete interface. The two principle mechanisms by which passivity is destroyed are carbonation and chloride attack. Carbonation is a process whereby the alkalinity of the cement matrix is reduced because of reaction of carbon dioxide with calcium hydroxide resulting in the loss of its passivating ability and the subsequent inevitable corrosion of the steel rebar. Another major factor causing corrosion of steel reinforcement has been identified as the chloride ion and its role in destroying the passivity of iron. In alkaline fresh concrete, a threshold level of about 7500-8000 ppm of chloride is required to start corrosion, but once the alkalinity is reduced the chloride threshold drops down to a significantly lower value i.e. below 100 ppm.

The corrosion products of steel (iron oxides or hydroxides) occupy a much greater volume than the steel (4-12 times the volume). This increase in the volume exerts significant tensile stresses within the concrete, inducing cracking, accompanied by rust staining and ultimately spalling of the concrete cover. Chloride-induced corrosion is found to be the major cause of premature reinforced concrete deterioration worldwide and it has resulted in a large scale, premature failures of reinforced concrete structures in a fraction of their design life. A number of concrete structures are affected by this problem including those ones particularly exposed to marine environments such as maritime bridges, jetties, wharves or coastal structures. Other structures such as bridge

decks and car parks, which are subjected to the action of deicing salts, are also affected by chloride-induced corrosion. This is particularly relevant in North America and Europe where harsh climatic conditions prevail. It has been estimated that in the USA alone corrosion of bridges and car parks costs around half a billion dollars a year (SCPRC, 1995).

1.2 - SOLUTIONS TO MITIGATE CORROSION

Various methods have been used for protecting and repairing these concrete structures to counteract the corrosive effects of carbonation and chlorides. The commonly used mitigation techniques include conventional patch repair, the use of sealants or coatings, cathodic protection, electromigration removal of chlorides by application of an electric field, or the use of inhibitors. The advantages and disadvantages of these techniques have been discussed by several authors (Page, 1989; Schiessl, 1992). One of the recommended alternatives is incorporation of inhibitors in potentially corrosive environments. A corrosion inhibitor is a substance which, when added in small concentrations to an environment, effectively reduces the corrosion rate of a metal exposed to that environment (Harrop, 1988; Riggs, 1973). These inhibitors form a protective film around the reinforcement bar, which retards significantly both the onset and the rate of corrosion. There have been many classifications of inhibitors proposed in the literature. The two commonly used are, either based on their nature of action (e.g. adsorption/film forming; oxidising/non-oxidising; organic/inorganic) or on the basis of their electrochemical mechanism of action at the steel surface (i.e. whether they affect the anodic process, the cathodic process or both) (Turgoose, 1988). "Anodic inhibitors" are those that result in the formation or maintenance of a passive film on the iron surface and this film essentially reduces the rate of anodic dissolution of the metal. "Cathodic inhibitors" reduce the rate of oxygen reduction by forming a film on the cathodic metal surface, which prevents access of oxygen to the cathodic reaction sites.

1.2.1 - Inhibitors

A considerable amount of research has been carried out with respect to inorganic corrosion inhibitors such as chromates, phosphates, hypophosphates, alkalis and fluorides (Griffin, 1975). However, the main effort has concentrated on the use of

nitrites and benzoates. Corrosion inhibiting concrete admixtures based on calcium nitrite are presently being employed in new concrete structures and have been commercially successful in the U.S.A. and Japan. A major drawback of this corrosion inhibiting admixture is that, being purely anodic in the nature of action, its performance is concentration dependent. This means that the use of insufficient quantities of this inhibitor may accelerate the corrosion rate in unprotected areas. Another limitation is that, this inhibitor being a concrete additive, is more applicable for new installations or in patch repairs of the existing structures. There have also been some concerns about its toxicity level, which has resulted in the limitations for its use in some countries.

Recent studies have shown that 'organic corrosion inhibitors' based on amines or both amines and carboxylate groups can be used as an alternative approach for protecting steel reinforcement (Nmai et al., 1992). These inhibitors are currently marketed as 'migratory corrosion inhibitors' or MCIs (Martin and Miksic, 1989; Rosignoli et al., 1995). The main advantage of these inhibitors is that they can be used either as admixtures (inhibitor is added to the fresh concrete) or in remedial applications. In the latter case the inhibitor is applied to the surface of a corroding structure or admixed with concrete in the patch material and is expected to diffuse through pores in concrete to reach the steel reinforcement. Once it is in contact with the steel surface, it inhibits corrosion reactions.

1.3 - SCOPE OF THIS PROJECT

Although organic inhibitors appear to be a viable option for corrosion mitigation of reinforced concrete structures, questions still remain. Does inhibitor performance meet expectations, how long does the mitigating effect last, and what is the exact mechanism by which these inhibitors are able to protect? From previous reports, the predominant mechanism by which organic inhibitors protect steel involves an adsorption of the inhibitor onto the metal thus providing a barrier to the corroding species (McCafferty, 1978; Nathan, 1973). However, whether the inhibition process involves just the formation of a chemical barrier to diffusion of reactive species or whether there is some further mechanism of operation of these MCIs, whereby the metal reactivity is reduced, is unclear. Furthermore, the kinetics of formation and breakdown of the inhibitor film as well as the reaction mechanism at cathodic and anodic sites on the steel surface are

also not well understood. Besides the mechanism of inhibitor action, the influence of certain factors, such as inhibitor concentration, on the level of protection and the long-term performance are also unknown.

It should be remembered that inhibition mechanism is just a part of inhibitor performance in reinforced concrete. Another issue, which is equally important in the case of MCIs, is their transport mechanism in concrete. The penetration behaviour is particularly relevant in the rehabilitation application of inhibitor systems e.g. as an injection, spraying or application in the gel form in the existing structures, where the ability of these inhibitors to control further corrosion driven deterioration depends upon their rate of migration through concrete.

There remains a considerable debate about the performance of these organic inhibitors in concrete. Hence evaluating the effectiveness of these organic inhibitors, against the established commercial corrosion mitigation techniques, such as cathodic protection or inorganic inhibitor admixtures, has become a matter of increasing importance. Since concrete structures are expected to provide a long service life, it is necessary to verify the inhibitors' true corrosion protection value in terms of both inhibition and diffusion over the planned life of the project. These factors have dictated an urgent need for basic research on evaluating inhibitors and inhibitor application systems under different corroding environments.

1.4 - GOALS OF THIS PROJECT

This research aims to develop an understanding of the mechanism of action of a group of organic inhibitors which are preferentially used in developing migratory corrosion inhibitors (MCIs) for corrosion mitigation of reinforcement in concrete. Corrosion inhibition processes in reinforced concrete, as already discussed, require a balance between the two processes namely the protection afforded by inhibitors at the steel/concrete interface and their transport through the concrete pores. It is difficult to assign the contribution of each of these two processes towards the overall reduction in the corrosion rate. It is also possible that the mobility of inhibitor molecules in concrete is limited; however, corrosion rate reduction can still be achieved because of the ability

of the molecules available at the steel/concrete interface to form a highly protective film at the steel surface.

Thus the specific goals of this study are:

- to evaluate inhibitor efficiencies initially on the basis of their inhibition capacities (independent of their diffusion properties) and to examine inhibition mechanism at the steel/electrolyte interface. Additionally, the effect of various factors such as inhibitor concentration, the molecular structure and the long-term performance on the extent of inhibition needs to be determined.
- to study the transport behaviour of inhibitors in concrete and to investigate the influence of various factors such as permeability and thickness of the concrete cover. Also the effect of size, polarity and concentration of inhibitor molecules on inhibitor diffusion rates needs to be investigated.
- the next goal of this work will be to develop an appropriate model to describe overall inhibitor performance in concrete. While doing this consideration will be given to different corrosion conditions that can be encountered in the service life of the structure.
- thus having understood the performance of inhibitors in concrete, the last logical step will be to find ways of improving inhibitor performance and to determine the factors, which will influence this enhancement.

The scope of this investigation will ultimately be decided after a critical review of the pertinent literature, the results of which are summarised in section 2.8 and chapter 3.

CHAPTER 2

LITERATURE REVIEW

2.1 - INTRODUCTION

The use of corrosion inhibitors to protect against the corrosion of reinforcing bars, prestressing cables and other steel components embedded in concrete structures has been a topic of great interest and ongoing research for the last few years. Application of these inhibitors, both as a preventative measure and as a repair will be most effective when the mechanism of the inhibition process in concrete and the factors affecting this process are well understood. The precise mechanism by which these inhibitors function is a matter of debate and there are also conflicting reports over what are the various factors influencing these mechanisms. Various views have been advanced and some measure of agreement has been obtained, although anomalies and uncertainties still exist.

This project specifically aims to investigate the inhibition mechanism of corrosion inhibitors in concrete as an intermediate goal in seeking the ways of enhancing the inhibitor performance. Accordingly, it is important that an understanding is gained of the likely inhibition mechanism and the factors, which affect this mechanism, so that an appropriate research program can be worked out. This chapter will review the earlier research work carried out on the performance of different inorganic and organic inhibitors for protecting reinforcement in concrete. Since the performance of inhibitors comprises of two individual processes, protection afforded by these inhibitors at the steel surface and their transport through concrete, the research contributions on these two individual aspects have been reviewed separately in sections 2.4 and 2.5. This will be followed by the discussion on the overall performance of inhibitors in reinforced concrete and the factors influencing the performance in section 2.6. Finally section 2.7 will discuss the literature on the enhancement of inhibitor efficiencies by application of electric field.

It must, however, be recognised that the mechanism of inhibition in concrete is best understood in the context of the corrosion process induced by aggressive chloride ions. Hence sections 2.2 and 2.3 that follow set out the fundamentals of passivity and corrosion process in concrete. Section 2.3 concludes by discussing different protection methods to control corrosion. This literature review will provide the basis for the formulation of the research program that follows.

2.2 - NATURE OF CONCRETE

The corrosion of steel in reinforced concrete is considerably different from the corrosion of steel exposed to the atmosphere, since the concrete around the reinforcing steel changes its chemical environment significantly (Bentur et al., 1997). The primary function of the concrete cover with respect to corrosion is two fold - its chemical composition can provide the alkaline passivating environment whereas its physical structure includes important aspects such as total porosity, pore size distribution and the interconnectivity of the coarser pores. The author will therefore review some of the characteristics of concrete especially those relevant to steel corrosion before attempting to discuss corrosion behaviour of steel in concrete in the following section 2.3.

Concrete is a composite material composed of coarse and fine aggregates embedded in a matrix of hardened hydrated Portland cement. The aggregate is more or less chemically inert and impermeable, whereas the hardened Portland cement ("cement paste") is porous and contains chemically active pore solution. The physicochemical characteristics of cement paste such as pore structure and pore solution chemistry are the dominant factors controlling the effectiveness of the concrete cover. The chemical reaction between water and cement (termed as "hydration") takes place slowly as a result of which important properties such as strength and permeability of concrete are developed (Bakkar, 1988). The porosity of the cement paste continues to decrease as a consequence of the "space-filling effect" of this hydration process. The pores present in the hydrated cement paste are considered to be of two types: larger so called "capillary pores" which constitute 0-40% of the paste volume depending upon the water/cement ratio and degree of hydration and gel pores constituting about 28% of the paste volume (Neville, 1982). Capillary pores are subdivided into much finer gel pores, (Powers, 1958). In the low water/cement (w/c) ratio concretes the total porosity is contributed by

the ultra fine gel pores, whereas in the high w/c ratio concretes not only is the total pore volume higher but there is a network of the interconnected coarse capillary pores.

Another important matter with respect to corrosion prevention, as already mentioned, is the pH of the pore solution in the concrete at the steel surface. As the composition of the pore solution is determined by the reaction between cement and water, the chemistry of pore solution is controlled by the composition of cement. In this work concrete made with only Portland cement will be considered. The reaction of Portland cement with water is in fact the reaction of four constituents of the clinker with water. These constituents are (Bakkar, 1988; Neville, 1982): tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$ conventionally termed as C_3S), dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$ termed as C_2S), tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 - \text{C}_3\text{A}$) and tetracalcium alumino-ferrite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 - \text{C}_4\text{AF}$). These minerals react with water giving insoluble precipitates of calcium silicate hydrates (like $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$) and calcium aluminate hydrates (like $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), together called the cement gel (C-S-H). Apart from the cement gel the tricalcium silicate and dicalcium silicate produce sparingly soluble free lime i.e. $\text{Ca}(\text{OH})_2$. During the first hours of the hydration process the pH of the aqueous solution in the pores is believed to originate from the calcium hydroxide and minor quantities of sodium and potassium hydroxide originally present in the cement clinker. At later stages this free lime reacts with sodium and potassium salts giving rise to the formation of very soluble sodium and potassium hydroxides. Hence pH is determined mainly by sodium- and potassium hydroxides present in the solution. The pH values in excess of 13 are reported in Portland cement pastes after a few weeks of curing (Page and Treadaway, 1982). Under such high pH conditions a passive oxide film develops on the steel protecting it from the corrosion.

2.3 - CORROSION BEHAVIOUR OF REINFORCEMENT IN CONCRETE & PROTECTION METHODS TO MITIGATE CORROSION

2.3.1 - Passive State

As seen in the earlier section, due to a highly alkaline environment in concrete ($\text{pH} \cong 13$), reinforcing steel develops an oxide film on the surface, which renders the steel passive to the corrosion process. According to the Pourbaix diagram, i.e. the potential-

pH diagram, for iron in alkaline solutions (Pourbaix, 1966) as shown in Figure 2.1, this passive film is stable over a range of potentials in the absence of aggressive ions. The composition of the passive film is believed to be γ Fe_2O_3 (Pourbaix, 1974a, Pourbaix, 1974b) or in the range of Fe_3O_4 : γ Fe_2O_3 (Sagoe-Crentsil and Glasser, 1990).

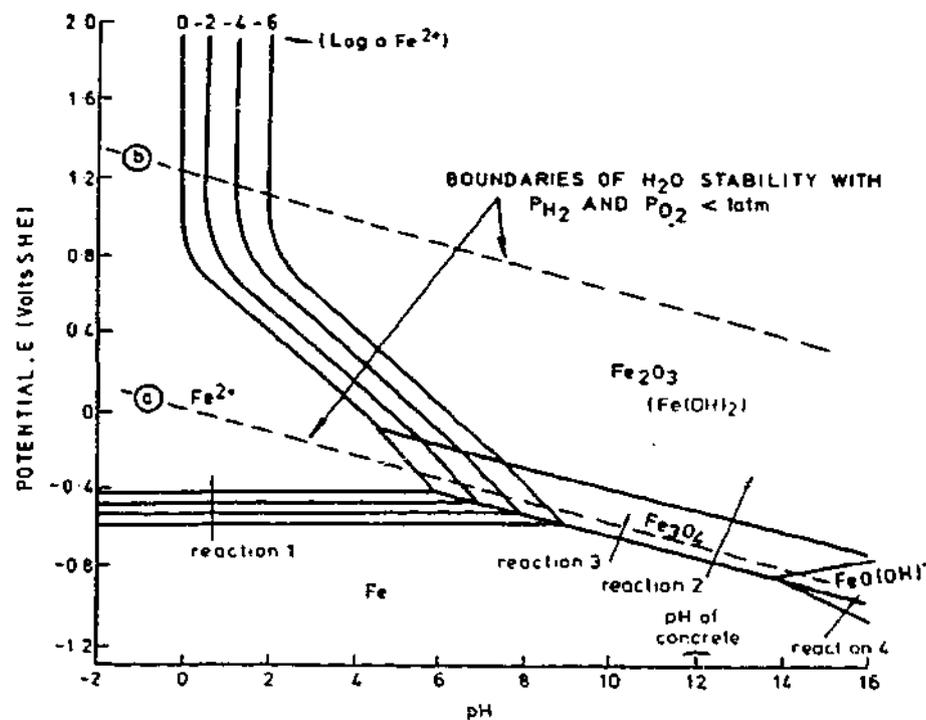


Figure 2.1 - Diagram for Fe-H₂O at 25⁰ C. Theoretical conditions of immunity, corrosion and passivity of iron (Pourbaix, 1966).

2.3.2 - Breakdown of Passivity due to Chloride Attack

The passivity of steel in an alkaline environment may be destroyed by the presence of chloride ions leading to initiation of pitting corrosion. Penetration of chloride to the steel surface is presented in a modified potential/pH Pourbaix diagram (Figure 2.2) (Pourbaix, 1974a). Besides displaying the domains for immunity, corrosion, passivity and pitting, this diagram also exhibits a zone of perfect passivity indicating that corrosion of steel in concrete exposed to a high chloride environment can be prevented by polarising steel to a potential within this zone (Hausman, 1969; Robinson, 1972).

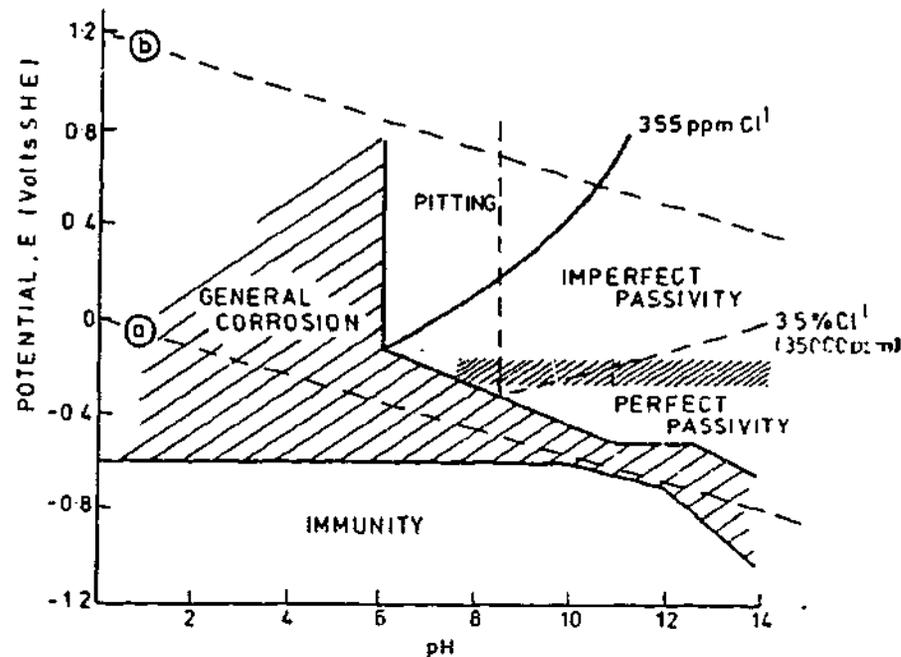


Figure 2.2 - Potential/pH diagram for Fe in chloride solutions. PP, perfect passivity, IP, imperfect passivity and pitting region (Pourbaix, 1974a)

2.3.3 - Mechanism of Corrosion

Corrosion is likely to occur under two specific sets of conditions. These conditions are: (i) decrease in the concrete alkalinity due to reaction with atmospheric CO_2 (carbonation) and (ii) attack of aggressive chloride ions. Since the present work concentrates on the chloride-induced corrosion, the mechanism of depassivation due to chloride ions will be reviewed here.

Sources of chlorides and transport of chlorides through concrete

Chlorides can be introduced in the concrete mixing process either as an admixture component, e.g. calcium chloride as a set accelerator, or in chloride contaminated aggregates or mix water. Additionally chlorides can diffuse into concrete as a result of exposure to sea water, salt laden air, grit or sand sourced from sea bed or deicing salts.

Chloride attack mechanism

It has been found that a minimum concentration of chloride is required to break down the passive oxide layer on the steel surface. In concrete, threshold chloride level may be specified in terms of percentage by weight of the original cement used. Building research establishment guidelines (Anon, 1982) suggest a chloride ion content of less

than 0.2% of the cement used may present a low risk of steel corrosion, whereas 1% may present a high risk. In the case of existing structures critical chloride level is specified in terms of weight of chloride per unit volume of concrete i.e. 0.9- 1.2 kg/m³ (Bentur et al., 1997).

While the reactions at the steel/concrete interface in the presence of chloride have been studied by a number of researchers (Hausman, 1967; Leek and Poole, 1990; Sagoe-Crentsil and Glasser, 1990), the exact mechanism of the breakdown of the protective film at the reinforcing steel is unknown. In Foley's review of the role of chloride ion in iron corrosion, he described the work of earlier investigators and discussed the adsorption and the oxide film theories (Foley, 1970). The adsorption theory proposes that chloride ions are adsorbed preferentially to the oxygen and hydroxyl ions at the adsorption sites on the metal surface. Since the reaction rate of chloride with iron is faster, it forms a soluble complex leading to pitting. The oxide film theory suggests that chloride ions preferentially penetrate the oxide film through the defects and pores within the film, which leads to pitting. Both suggest that localised high concentrations of chloride ions render pitting. Figure 2.3 shows a schematic representation of the typical corrosion process.

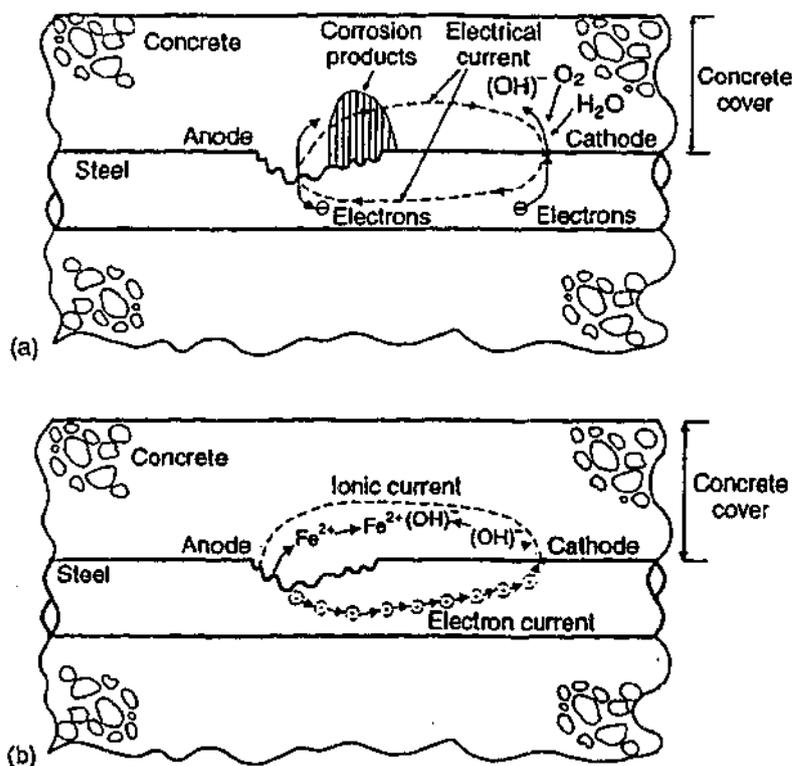


Figure 2.3 - Corrosion processes on the surface of steel (a) Reactions at anodic and cathodic sites and electric current loop (b) Flow of electrical charge in the electric current loop during the corrosion process (Bentur et al., 1997)

2.3.4 - Protection Methods

In the earlier part of this section it was discussed that corrosion of reinforcement in concrete is a result of various electrochemical reactions. From this discussion it follows that stopping or slowing down any one of these reactions should prevent or at least restrict steel from corroding. In fact all the currently available protection methods attempt to limit one or more stages in the corrosion process and can be classified into three different types: i.e.

1. modification of the environment around the reinforcement (concrete modification)
2. isolation of the reinforcement from the corrosive environment by means of a physical or chemical barrier
3. changing the electrochemical nature of the surface, e.g. by imposing impressed current.

Concrete modification

Under normal environmental conditions durability of reinforced concrete structures can be achieved by ensuring good quality of concrete, which includes good consolidation and curing and by maintaining adequate cover and low water/cement ratio or permeability (Slater, 1983). Use of pozzolans, penetrating sealers, silanes, siloxysilanes and other materials to prevent corrosion by reducing permeability to chlorides is common. (Broomfield, 1997a).

Formation of physical or chemical barrier against the attack of aggressive ions

Corrosion protection can also be achieved by physically separating the steel reinforcement from concrete pore water environment (Berkeley and Pathmanaban, 1990). This can be done by application of polymer coating or by a galvanisation process, or by insulating rebar from the corrosive environment using "corrosion inhibitors" which form a chemical barrier at the steel/concrete interface. A corrosion inhibitor is a substance which when added in small concentrations to an environment, effectively reduces the corrosion rate of a metal exposed to that environment (Harrop, 1988; Riggs, 1973). Corrosion inhibitors and their mechanisms of inhibition are discussed in the following section.

Electrochemical prevention methods

Electrochemical methods function by making the whole of the reinforcement metal surface cathodic by applying current from a deliberately introduced external anode source. Based on this arrangement three techniques can be described. The most popular and established technique is cathodic protection (CP). A recent alternative for the treatment of chloride contaminated concrete structures is electrochemical chloride extraction (ECE). In the case of carbonated concrete a similar method of rehabilitation is called realkalisation. The mechanisms of cathodic protection and electrochemical chloride extraction are discussed later in sections 2.7.2 and 2.7.3.

2.4 - CORROSION INHIBITORS AND THEIR INHIBITION MECHANISMS

2.4.1 - The Overview

The definition of corrosion inhibitors at the simplest level has been described in section 2.3.4. However, a more appropriate one in the case of concrete as cited recently by Berke and Hicks (Berke and Hicks, 1997), says, "A corrosion inhibitor for metal in concrete is a chemical substance that reduces the corrosion of the metal without reducing the concentration of the corrosive agents". This is a paraphrase from the ISO definition of a corrosion inhibitor, and is used to distinguish between a corrosion inhibitor and other additions to concrete that improve corrosion resistance by reducing chloride ingress into the concrete. According to DIN 50900, corrosion inhibitors are defined as substances whose presence inhibits corrosion in a medium of attack (aggressive medium) (Tritthart et al., 1999).

2.4.2 - Classification of Inhibitors

Inhibitors have been classified in the literature in several different ways depending upon the type, nature of action or chemical properties. e.g. adsorption or film forming, oxidising or non-oxidising, organic or inorganic, safe or dangerous. Perhaps more useful from a mechanistic view is the inhibitor classification according to their electrochemical nature of action i.e. whether they influence anodic reaction (anodic inhibitors) or cathodic reaction (cathodic inhibitor) or both (mixed inhibitors) (Turgoose, 1988). It should, however, be remembered that classification of a substance

as a particular type of inhibitor should be done with care, as the mechanism of action of inhibitor varies with: (i) the environment to which it is added, (ii) the metal to be protected and/or (iii) the inhibitor chemistry (Harrop, 1988).

McCafferty has classified inhibitors in two main types: adsorption inhibitors and film forming inhibitors (McCafferty, 1978). According to this report, adsorption inhibitors are believed to form a chemisorptive bond with the metal surface so that ongoing electrochemical reactions are impeded e.g. organic inhibitors. The film forming inhibitors can be further subdivided into passivating inhibitors and precipitation inhibitors. Passivating inhibitors are assumed to promote the formation of passive films and can be either oxidising such as chromate (Kubachewski and Brasher, 1959) or non-oxidising such as benzoate, which adsorb onto the oxide covered surface before acting to induce/maintain passivity (Thomas, 1970). With the precipitation inhibitors such as phosphates and silicates, a precipitation reaction between the inhibitor and a corroding metal results in deposition of a barrier film on the surface of the metal (Hackerman and Snively, 1969). Discussion of the mechanism of all types of inhibitors is beyond the scope of the current section. The author will therefore restrict the discussion only to those types of inhibitors, which are truly relevant to the current work. These are inorganic (oxidising type such as nitrites) and organic (adsorption type) corrosion inhibitors.

2.4.3 - Mechanism of Inhibitor Action

Before reviewing the mechanisms of action of inorganic and organic inhibitors, it is important to understand the influence of inhibitors on the cathodic and anodic reactions in an electrochemical corrosion process. This effect can be expressed graphically in the form of an Evans type polarisation diagram based on a mixed potential theory, which is cited frequently in the literature (Harrop, 1988) (Figure 2.4). Figure 2.4 shows a simple corrosion reaction defining corrosion potential, E_{corr} , and corrosion current, i_{corr} , and six basic changes that can result from addition of a corrosion inhibitor (Harrop, 1988). The corrosion current (i_{inh}) has reduced in all cases on inhibitor addition. However, the corrosion potential is shifted anodically (positively) for an anodic inhibitor and cathodically (negatively) for a cathodic inhibitor. In the case where inhibitor affects both the half reactions, the shift in corrosion potential depends upon which one is the dominant effect of the two. The remaining situation is pictured in the figure at the

bottom (right) in the presence of an ohmic resistance. This may result from the presence of a potential drop in solution or in the presence of a highly resistive/poorly conducting inhibitor film (Harrop, 1988).

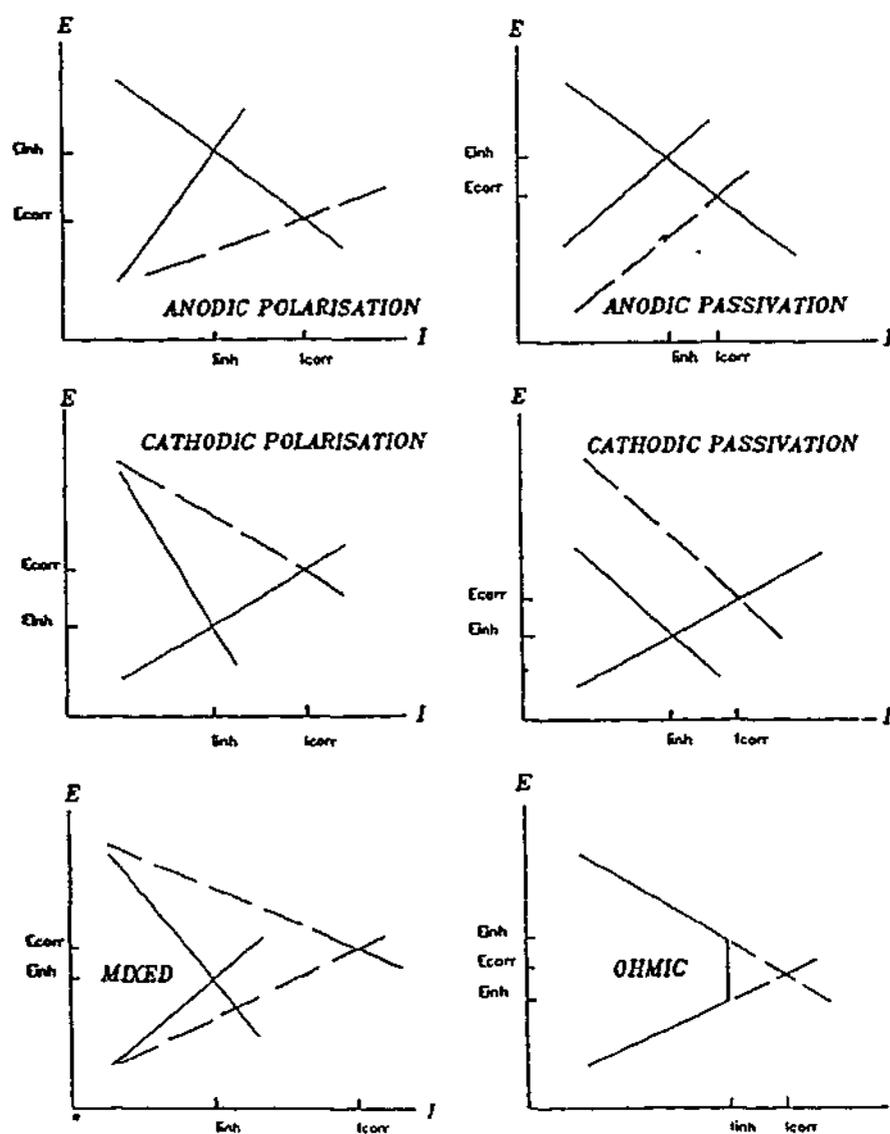


Figure 2.4 - Evans type polarisation diagram describing the mechanism of action of cathodic, anodic and mixed inhibitors (Harrop, 1988)

Inorganic inhibitors

From the range of inorganic inhibitors, the selection has been restricted to only the passivating oxidising inhibitors such as nitrite based inhibitors, e.g. sodium/calcium nitrite. Extensive research has been carried out to investigate the corrosion inhibiting properties and the mechanism of inhibition of sodium nitrite and calcium nitrite (Andrade et al., 1986; Lundquist et al., 1979; Rosenberg and Gaidis, 1979). It is proposed that the mechanism by which this inhibitor inhibits corrosion is associated with the stabilisation of the passivation film on the steel surface by oxidation of ferrous

ions (Fe^{2+}) to ferric ions (Fe^{3+}) to form a more stable ferric oxide as per the following reaction (Lundquist et al., 1979)



The nitrite ion does not react with iron metal (Pyke and Cohen, 1948), ferric ion (Rosenberg et al., 1977) or ferric oxide. Ferrous ions and ferrous hydroxide react with nitrite to form gaseous nitric oxide and precipitate a hydrated ferric oxide (Rosenberg et al., 1977). Kinetically, the oxidation of ferrous ion by the nitrite ion is rapid compared to transport of the ferrous ion away from the corroding area. Thus, the nitrite ion prevents, via oxidation, migration of ferrous ions away from the anodic areas thereby resulting in passivation of the steel reinforcement (Lundquist et al., 1979). However, it has been proposed by a number of researchers (Berke and A. Rosenberg, 1989; El-Jazairi and Berke, 1990), that the performance of the nitrite-based inhibitors is subject to maintaining a minimum concentration with respect to that of chloride at the steel surface. Since these inhibitors function by inhibiting active anodic sites, if not present in sufficient quantities, they can promote localised corrosion. For this reason they are sometimes called “dangerous inhibitors”

Organic inhibitors

The organic corrosion inhibitors in general include different types of amines, organic acid derivatives, fatty amine derivatives, and quaternary ammonium salts (RNH_4^+). The mechanism of action of organic inhibitors has been postulated by many researchers and is believed to involve physical adsorption and/or chemical adsorption of inhibitor onto the metal thus providing a barrier to the corroding species (Incorvia and Contarini, 1989; McCafferty, 1978). It is relevant to discuss both physical and chemical adsorption in turn.

Physical Adsorption: According to Kobayashi (Kobayashi, 1989) when an organic cation or anion is added to the acid, where an iron surface is corroding, electrostatic attraction may cause the cations to be adsorbed on the cathodic sites and the anion on the anodic sites thus establishing a physisorbed surface film through van der waals forces (McCafferty, 1978). This phenomenon is called physical or electrostatic adsorption. Physical adsorption depends upon the surface charge of the corroding metal, which may be estimated from the knowledge of the potential of zero charge (pzc)

and the corrosion potential. For example, tetra-alkyl ammonium cations are known to be an effective inhibitor against iron corrosion in hydrochloric acid (Antropov, 1967; Driver and Meakins, 1977). This is caused by changes in the potential of zero charge of iron because of the adsorption of chloride ion. Since the pzc is made more negative because of the adsorption of chloride ion, this permits the positive ammonium cation to be adsorbed more strongly in hydrochloric acid. This effect was termed as a "cooperative adsorption effect" by McCafferty and was reported for a system containing halide ions and organic inhibitors (Cavallaro et al., 1964; McCafferty, 1978). The effect is shown schematically in Figure 2.5. Besides the above factors, the type of adsorption also depends on the structure of the electrical double layer. During the adsorption process, intrusion of organic molecules into the electrical double layer changes its composition and structure by displacing or rearranging some of the molecules (McCafferty, 1978).

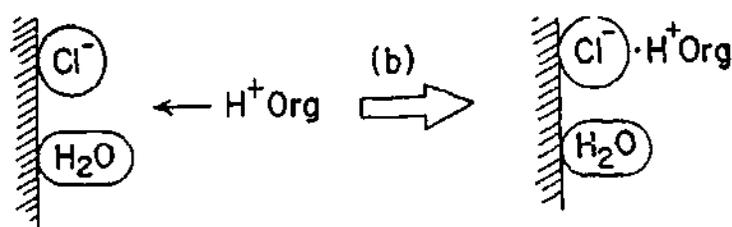


Figure 2.5 - Cooperative adsorption (McCafferty, 1978)

Chemisorption: Another important type of adsorption is chemisorption, which operates by sharing electrons between the inhibitor molecule and the metal surface. The mechanism of chemisorption is proposed by Nathan (Nathan, 1973), which suggests that adsorption of inhibitor onto the metal surface takes place through their polar group or head. The non-polar tail of the inhibitor molecule is oriented in a direction generally perpendicular to the metal surface. It is believed that the hydrocarbon tails mesh with each other to form a tight film which repels aqueous fluids, establishing a barrier to the chemical and electrochemical attack of fluid on the base metal. Extending on Nathan's theory (Thomas, 1976) proposed that once the inhibitor has adsorbed on the metal surface it can then affect the corrosion reactions in a number of ways: by offering a physical barrier to the diffusion of ions or molecules to or from the metal surface; by direct blocking of anodic and/or cathodic reaction sites; interaction with adsorbed corrosion reaction intermediates; by changing the make up of electrical double layer

which develops at the metal/solution interface thus affecting the rate of electrochemical reactions taking place there.

The role of adsorption processes in corrosion inhibition has been investigated in detail by McCafferty (McCafferty, 1978), who proposed that chemisorption usually occurs through donation of electrons from a nitrogen, sulphur or oxygen functional atom to the metal surface. McCafferty proposed the mechanism of action of organic inhibitor in the presence of chloride ions in terms of a "competitive adsorption" situation where organic inhibitor must compete with Cl^- ions for sites on the metal surface. The heat of adsorption of a chloride ion on iron has been calculated to be 45 kcal/mol (McCafferty and Hackerman, 1973), which is close to the energy of metal-amine bond (McCafferty, 1978). The competitive adsorption is shown schematically in Figure 2.6.

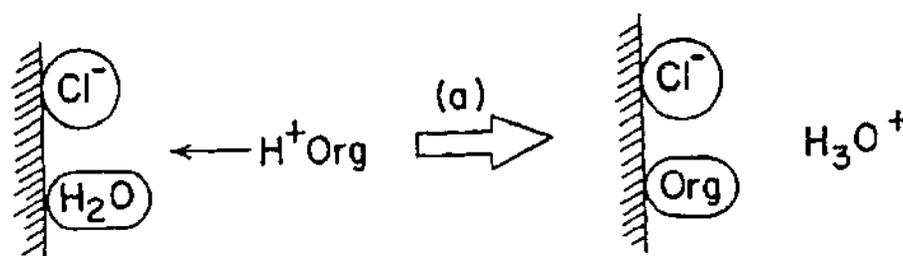


Figure 2.6 - Competitive adsorption (McCafferty, 1978)

McCafferty (McCafferty, 1978) also discussed various factors, which contribute to the effectiveness of the inhibitor. These factors are the size of the organic molecule, aromaticity and/or conjugated bonding, carbon chain length, the type and number of bonding atoms in the molecule and ability of layer to become compact or cross-linked. The substituents in the ring compounds such as electron withdrawing substituents (chloride ions) or electron donating substituents (CH_3 group) further influence the effectiveness of inhibitors.

Incorvia and Contarini (Incorvia and Contarini, 1989) who studied the structure and bonding at the iron/amine interface using X-ray photoelectron spectroscopy (XPS), proposed that amine chemisorption proceeds without the oxidation of the surface iron atoms and without the displacement of either the oxide or hydroxide anions from the passive film. The mechanism appears to be either a nonoxidative, nonsubstitutive expansion of the surface iron atom coordination number, where amine nitrogen is

coordinated to the surface iron (Figure 2.7A), or by hydrogen bonding of the amine to the surface of oxy-hydroxy passive film (Figure 2.7B), or a combination of both. Non-chemisorbed, protonated amine groups may also be present (Figure 2.7C). The existence of both a coordinated and protonated amine group has been documented.

A later mechanism of protection of vapour phase inhibitors (VCIs) based on organic amines, DICHAN (dicyclohexylamine nitrite) (Shell and Company, 1945) and benzotriazole, was also studied by Miksic (Miksic, 1983; Miksic and Tarvin, 1989) using XPS, ISS (Ion Scattering Spectroscopy) and SIMS (Secondary Ion Mass Spectroscopy) and was in accord with the previously quoted work. The observation of the metal in these spectra indicated that the inhibitor layer is extremely thin, less than about 60Å deep.

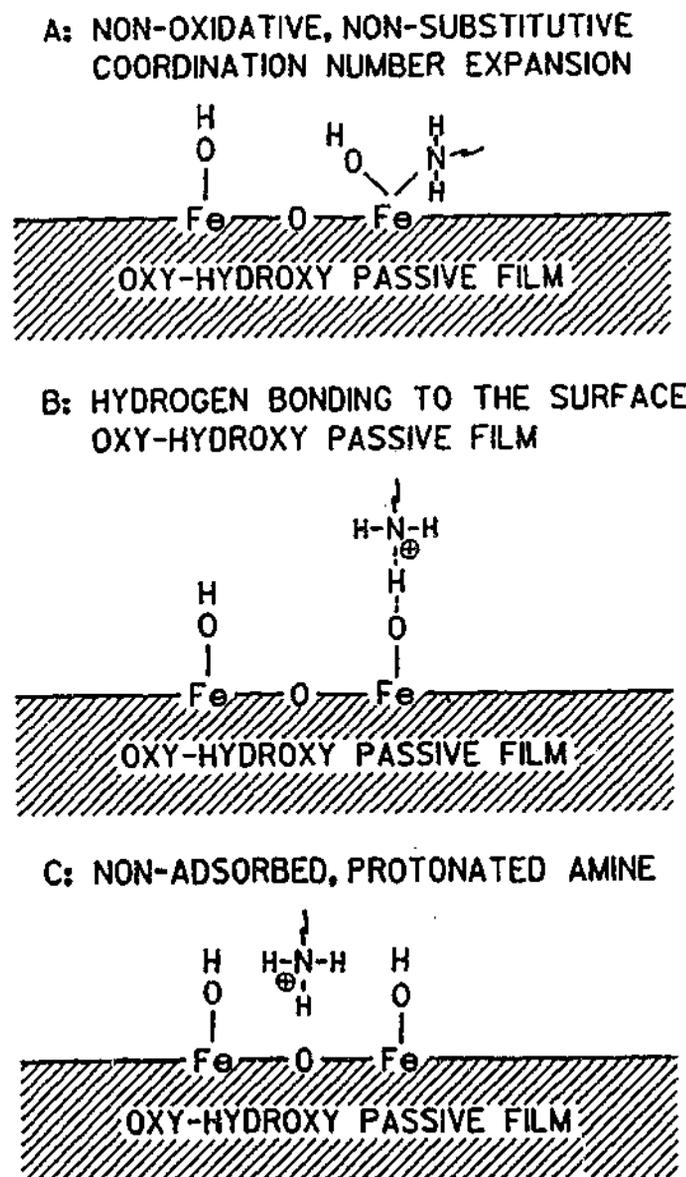


Figure 2.7 - The possible amine adsorption mechanisms (Incorvia and Contarini, 1989)

2.4.4 - Techniques for Measurement of Corrosion Inhibitor Efficiency and Mechanism

From a review of the literature it appears that short-term electrochemical methods (using a solution electrolyte) have been used for screening inhibitors. This is mainly because of the sensitivity of these methods to the changes occurring due to the corrosion/inhibition process, the mechanism of inhibition and the stability of the inhibitor film (Jovancicevic and Hartwick, 1997). Long-term electrochemical measurements performed on the rebar embedded in concrete under realistic application conditions are however, considered the more accurate and reliable means to determine inhibitor performance. The short-term tests are generally carried out by immersing a steel specimen (a coupon) in an appropriate solution (e.g. simulated pore solution with or without addition of chloride or inhibitors) (Yunovich and Thompson, 1998). The simulated pore solutions used are either saturated calcium hydroxide (lime water) (Berke, 1986) or saturated lime water with the addition of sodium- and potassium hydroxide (Alonso and Andrade, 1990; Tullmin et al., 1995). The extent of corrosion/inhibition is estimated by comparing the inhibited specimen with the control sample i.e. without addition of inhibitor using visual examination, weight loss test and electrochemical measurements.

Corrosion/inhibition of reinforcement being an electrochemical process, the measurement of various parameters in such a system either in its undisturbed state or after application of an external signal, enables the identification of corrosion/inhibition and estimation of its rate. The available electrochemical approaches can be classified as, either "perturbation methods" which include linear polarisation resistance, AC impedance (EIS), cyclic potentiodynamic polarisation, cyclic voltammetry, constant concentration potentiostatic (potentiostatic transients) or "passive methods" such as corrosion potential measurement, macrocell current measurement or electrochemical noise measurement (ECN). The techniques relevant to the present work only are discussed in this section.

Corrosion potential measurements

This technique, pioneered by Stratfull and coworkers (Stratfull, 1972) has been widely used and has become the subject of ASTM Test for Half Cell Potentials of Reinforcing Steels in concrete (ASTM C876-91, 1999). It is determined by measuring the voltage

difference between the steel and a reference electrode in contact with the concrete using a high input impedance (>10 mohm) voltmeter. Some difficulties associated with this technique are as follows:

Firstly, the potential gives only an indication of the corrosion activity of the metal (in a qualitative sense), and it is exceedingly difficult to assign a corrosion rate to a given potential. Secondly, it must be remembered that the corrosion potential is a poor indication of absolute corrosion activity. As given in ASTM C876 (ASTM C876-91, 1999), if corrosion potentials fall between -200 and -350 mV_{SCE} the corrosion activity of the reinforcement in that area is uncertain. However, the level of water saturation in concrete affects the potential value to a great extent and hence the data obtained should be interpreted with care. For water saturated concretes, potentials more negative than -350 mV_{SCE} are not necessarily indicative of corrosion, as the wetting of the surface with water causes a drift of the potential (Videm and Myrdal, 1996a). Wetting increases the electrical conductivity in the concrete and causes a shift in the current flow between anodes and cathodes. As pointed out by Bazzoni and Lazzarri (Bazzoni and Lazzarri, 1994), the overall effect is a slight shifting towards more positive potential values in correspondence of anodic sites, vice versa, more negative for cathodic sites. According to some researchers, so-called liquid junction potentials can also introduce significant errors in the measurement of the corrosion potential of steel in concrete (Sagues, 1993; Videm and Myrdal, 1996b). This indicates that the excessively dry concrete might lead to a positive shift in the potential, whereas highly saturated concrete is likely to give a cathodic shift in the potential. Nevertheless a “potential mapping survey” is the increasingly used, on-site, electrochemical technique for detecting corrosion activity of reinforcement.

In the case of a system containing inhibitors, corrosion potential measurements have been used as an indication of the nature of inhibitor action. A positive shift in the corrosion potential on addition of inhibitor indicates anodic characteristics and a fall indicating a cathodic effect (Harrop, 1988). This could be somewhat misleading as a mixed inhibitor can influence both anodic and cathodic reactions. However, the potential can vary only in one direction depending upon whichever of the cathodic or anodic is a dominant reaction.

The linear polarisation resistance technique (LPR)

The most common method used to determine the inhibitive capacity of any given inhibitor, as reported by many researchers in this field (Hackerman et al., 1966; Hausler, 1977), utilizes linear polarisation resistance measurements, based on the method of Stern and Geary (Stern and Geary, 1957). This technique is described in ASTM G59 (ASTM G59-97, 1999). A controlled potential scan is applied to the specimen starting from E_{corr} and extending a few millivolts in the cathodic and anodic direction. The resulting current is plotted versus potential and the slope of the $\Delta E/\Delta I$ plot at E_{corr} is the polarisation resistance R_p . This slope is related to the instantaneous corrosion rate through the Stern-Geary equation

$$i_{\text{corr}} (\mu\text{A} / \text{cm}^2) = \frac{\beta_a \times \beta_c}{2.303(\beta_a + \beta_c)} \times \frac{\Delta I}{\Delta E} \quad \text{Equation 2.2}$$

where β_a and β_c - slopes of the linear portions of anodic and cathodic polarisation curves respectively, on a E vs $\log I$ plot, i_{corr} - corrosion current density, R_p - polarisation resistance (ohm.cm^2). The direct determination of i_{corr} via the Stern-Geary equation (Stern and Geary, 1957) requires the assumption that the corroding system is under activation control and observes Tafel behaviour. According to Gonzalez et al (Gonzalez et al., 1985a, Gonzalez et al., 1985b) in the case of steel embedded in concrete, the corrosion reaction is controlled by diffusion-or the metal is passivated; and a passivated metal is unlikely to obey Tafel kinetics. Other limiting factors defined by Gonzalez and coworkers are high resistivity due to passive film or corrosion product layer and the lack of linearity of the polarization curve in the vicinity of the corrosion potential. According to Videm (Videm and Myrdal, 1996a) perturbations in the working electrode/electrolyte interface during measurement may add to the complexity of the situation. This is mainly due to the formation of anodic films under anodic polarisation and the reduction of film thickness during cathodic polarisation (Videm and Myrdal, 1996a). Another major problem identified by Slater (Slater, 1983) with the use of this technique is the existence of macrocell action, which means that the corroding reinforcing steel is polarised away from its normal free corrosion potential.

Nevertheless, measurement of polarisation resistance is considered to be valuable in making a qualitative comparison of the relative inhibition capacities of different

inhibitors (Hettiarachchi and Gaynor, 1992). From this technique the corrosion current i_{corr} can be related to the polarisation resistance R_p simply by

$$i_{\text{corr}} = (B/R_p) \quad \text{Equation 2.3}$$

where

$$B = \frac{\beta_a \times \beta_c}{2.303(\beta_a + \beta_c)}$$

For steel in aqueous media, β_a and β_c values equal to 120 mV are normally used (Saricimen et al., 1997). However, in the absence of sufficient data on β_a and β_c for steel in concrete, a B value equal to 52 mV for steel in passive condition and a value equal to 26 mV for steel in active condition are normally used (Saricimen et al., 1997; Yunovich and Thompson, 1998). Further if one assumes I_{control} is the blank corrosion rate representing the total number of 'active sites', I_{sample} is the inhibited corrosion rate representing the total number of active sites minus the inhibited sites, % inhibition is calculated as

$$\% \text{ Inhibition} = \frac{I_{\text{control}} - I_{\text{sample}}}{I_{\text{control}}} \times 100$$

since I (corrosion rate) is proportional to i (corrosion current),

$$\% \text{ Inhibition} = \frac{i_{\text{control}} - i_{\text{sample}}}{i_{\text{control}}} \times 100$$

on substituting the value of $i = B/R_p$ in the above equation

$$\% \text{ Inhibition} = \frac{R_{p_{\text{sample}}} - R_{p_{\text{control}}}}{R_{p_{\text{sample}}}} \times 100 \quad \text{Equation 2.4}$$

Even though the LPR technique has been used successfully for the laboratory investigations, its application to the real structures has certain limitations. This is mainly because the electric signal used, which is applied with a counter electrode (CE), spreads and gradually decreases across the structure as far as a critical, unknown distance that varies with each concrete reinforcement condition. This problem has been addressed by confining the current lines from the central electrode (CE) to within a specific area of the working electrode (WE) with the aid of an additional ring-shaped CE known as the "guard ring" concentric to the central CE (Andrade and Alonso, 1996;

Feliu et al., 1990a; Feliu et al., 1990b). In this case the main lines that originate from the central CE are counter-balanced by this guard ring electrode and are confined within a known area of the reinforcements (Videm and Myrdal, 1997).

Measurement of macrocell current

The standard test generally used for predicting the inhibitive properties of admixtures to be used in concrete in the laboratory is described in the ASTM G109 (ASTM 109-99, 1999). The method implies measurement of the spontaneous current flowing between the bar in the chloride-containing environment and the bar in the chloride-free environment. The use of this technique is based on the assumption that the corrosion in the structure could be a result of the “macrocell” current, i.e. the structure may show different regions of corrosion activity of the reinforcing steel with certain regions being more active than the others thus creating widely separated “macrocells”. On comparing the linear polarisation technique with the macrocell technique, it has been observed (Berke et al., 1990) that both the macrocell and the linear polarisation resistance techniques can indicate that corrosion is occurring; however, the linear polarisation technique, (which is based on the assumption of a microcell current) is able to determine localised corrosion in addition to macrocell corrosion effects. It should be noted that, in this work the author determines % inhibition using the linear polarisation resistance technique, but this is accepted to be semiquantitative.

Cyclic voltammetry

In cyclic voltammetry a potential sweep is applied between two set points at a faster scan rate performing multiple cycles. This technique can help in gaining an insight into the mechanism of inhibition at the steel surface, and can also assist in understanding the kinetics of protective film formation and breakdown or the oxidation reduction reactions occurring at the steel surface. The technique has been used by Hinatsu and coworkers (Hinatsu et al., 1988; Hinatsu et al., 1990) for carrying out in situ study of the passivity of steel in alkaline solution and differences in the behaviour caused by addition of chloride and inhibitor such as sodium nitrite.

Cyclic potentiodynamic polarisation technique

Another method, to understand how an inhibitor works, involves the use of cyclic potentiodynamic polarisation technique (CPP). In this method the anodic polarisation scan is reversed at some point to scan back to (or near) the starting potential. Since the

potentials at which the passive film is broken down on the forward scan (pitting potential) and is reformed at some point in the reverse scan (protection potential) are characteristic of a particular metal-environment combination, these plots are often used as a qualitative measurement for detecting pitting/inhibition mechanisms at the steel surface in chloride/inhibitor containing environments. The technique has been used by Berke and Hicks (Berke and Hicks, 1997) and Fear (Fear, 1996) to determine the mechanism of action of inorganic inhibitor calcium nitrite and an organic amine-based inhibitor, "Ferrogard", respectively in chloride containing simulated concrete pore water environments.

Potentiostatic Transients

This potentiostatic technique is a newer electrochemical approach to inhibitor evaluation and has been used recently by Jovancicevic and Hartwick (Jovancicevic and Hartwick, 1997) for mechanism of corrosion inhibitors' action in neutral aqueous solutions. This technique identifies the anodic/cathodic components of corrosion inhibition, and measures the "long-term" anodic/cathodic current stability of an inhibitor/oxide film at constant inhibitor concentrations and constant potentials near the initial open circuit potential.

In all the above techniques the experimental set up and test conditions used are similar to those used in the LPR method. It may be recognised that since the approach used in these techniques results in a qualitative understanding, the techniques cannot be used as stand-alone techniques and should be used in conjunction with other techniques such as LPR.

2.5 - DIFFUSION OF INHIBITORS IN CONCRETE

Modeling diffusion of inhibitor molecules in concrete enables prediction of time dependent inhibitor concentration at the steel surface. Knowledge of inhibitor diffusion rates combined with its capacity to protect can help in calculating the appropriate dosage levels and the frequency of treatment. A glance at the literature suggests that considerable attention has been given to the transport of aggressive species (chloride, oxygen) in concrete; however, little has been published on the mobility of organic molecules and hence inhibitor diffusion is an issue that merits discussion.

2.5.1 - Diffusion of Chloride and Oxygen

Several studies have been published addressing the rate of diffusion of chloride ions through cement and concrete (Colleparidi et al., 1972; Gjorv and Vennesland, 1979; Goto and Roy, 1981; Page et al., 1981), where researchers have mainly concentrated on ionic diffusion as the primary process involved in chloride penetration. Page (Page et al., 1981) has demonstrated that diffusion processes in hardened cement pastes obey the diffusion laws (i.e. Fick's first law of diffusion applied in a steady state condition) and that different cementing materials exhibit different degrees of resistance to chloride ion diffusion. Diffusion coefficients (at 25°C) in this case were found to be in the range of $(2-11) \times 10^{-12} \text{ m}^2/\text{s}$. Colleparidi et al (Colleparidi et al., 1972) modeled penetration of chloride ions into cement pastes and concrete using Fick's second law for non steady state conditions and obtained similar results to those obtained by Page (Page et al., 1981) i.e. $0.25 \times 10^{-12} \text{ m}^2/\text{s}$ for Portland cement paste and $0.17 \times 10^{-12} \text{ m}^2/\text{s}$ for Portland cement concrete.

Later, observations made by Grace (Grace, 1987) who investigated marine structures in the field in addition to laboratory work, indicated that ionic diffusion is not the only important transport process. Chloride ions are borne by seawater which itself penetrates the concrete. A mathematical model has been developed by Grace (Grace, 1991), which incorporates diffusion and the dispersion which occurs on wetting and drying cycles. The studies of various researchers (Colleparidi et al., 1972; Gjorv and Vennesland, 1979; Grace, 1991) have shown that chloride ions undergo physico-chemical interactions with the cement matrix that affect the apparent "diffusion rate. Goto and Roy (Goto and Roy, 1981) studied diffusion of Na^+ and Cl^- ions through the hardened cement paste and found that the effect of water/cement ratio in the range studied on the diffusion coefficients of Na^+ and Cl^- ions was small. This suggested that a strong interaction of these ions with the surface of hydrates occurs during the diffusion process.

A number of researchers (Gjorv et al., 1976; Yu and Page, 1979) have undertaken a study of oxygen diffusion in the water-saturated concrete and cement paste. Gjorv et al estimated diffusion coefficients for oxygen $(2-7 \times 10^{-10} \text{ m}^2/\text{s})$ and found that both quality and thickness of concrete had a very small effect on the flux of oxygen and the rate of oxygen diffusion is lower through mortar than that through concrete. Yu and Page (Yu and Page, 1979) undertook the study of oxygen diffusion in the water-

saturated concrete and cement paste and have found that, in comparison with chloride diffusion, oxygen diffusion is relatively faster.

2.5.2 - Diffusion of Organic and Inorganic inhibitors

The organic inhibitors which are investigated in the literature include commercial MCI series (manufactured by Cortec Corporation, USA) based on alkanolamines and salts of carboxylic acid (Martin and Miksic, 1989), "Ferrogard" series (manufactured by SIKA Chemicals, Switzerland) a blend of an amino-alcohol especially dimethylethanolamine DMEA in a water carrier and an inorganic inhibitor (Wolfseher and Partner, 1997).

Martin and Miksic (Martin and Miksic, 1989) in their patent on "Corrosion Inhibition in Reinforced Concrete" have suggested that organic inhibitors, especially those based on amino-alcohols, have significant partial pressures and hence can exist in both the liquid and the vapour phase. It follows from this that the mechanism of transport of these inhibitors in concrete could be a complex process and may possibly involve different steps that are mutually interdependent.

Bjegovic, and coworkers (Bjegovic et al., 1993) developed a method for monitoring the process of diffusion of migratory corrosion inhibitors (MCI 2000/admixture and MCI 2020/surface applied) using a simple two compartment diffusion cell. Since volatile amine is the active ingredient in these MCIs, the concentration of volatile amine, which diffused through the concrete membrane was monitored using a specific amine sensitive electrode technique. Diffusion coefficients were determined using Fick's first law and were found to be in the range of $0.4 - 4 \times 10^{-12} \text{ m}^2/\text{s}$ for given concrete having water/cement ratio ranging from 0.45 to 0.55. It was shown that the coefficients were in good correlation with gas permeability coefficients for the tested concrete specimens and were also found to be comparable with those for diffusion of chloride ions. Later in 1998 Bjegovic and coworkers (Bjegovic et al., 1998) analysed diffusion of the MCI inhibitors in concrete using Fick's second law for non steady state conditions by taking into account factors of time and distance. Using a specially developed computer program, they also claimed to have predicted a period when the concentration of inhibitors at the reinforcement would reach a protective value. The coefficient values obtained using this method were in the range of $1.2 - 4.2 \times 10^{-12} \text{ m}^2/\text{s}$, which were comparable with those obtained earlier using the first law.

Analysis of diffusion rate of MCI 2000 (admixture type) in concrete was also done using a radioactive isotope tagging technique by Eydelnant et al (Eydelnant et al., 1993), where a radioactive (^3H) MCI was created and was applied directly on the concrete surface. Their findings were consistent with those of Bjegovic and coworkers. When used as an admixture, and overlaid on the existing concrete, 30% of the inhibitor was shown to diffuse into the old concrete over 24 days to a distance of 40 mm.

The investigation of diffusion of corrosion inhibitors "Ferrogard"s was undertaken by Fear and coworkers (Fear, 1996), who showed that when applied on the outer surface, these inhibitors can penetrate through concrete at a rate of between 2.5 to 20 mm per day and to a depth of at least 80 mm in 28 days, depending on the quality of concrete. A reference was also made to the work undertaken by Bentz and Goschnik (Bentz and Goschnik, 1994), who obtained the spatial distribution of corrosion inhibitors in concrete and mortar samples. Mortar and concrete blocks were subjected to different wetting times at a range of relative humidities. The depth of penetration and distribution of the amino-alcohols was determined by breaking open the blocks and taking dust samples for analysis using the Secondary Neutron Mass Spectroscopy (SNMS). The depth profiles thus obtained showed that a concentrated band of "Ferrogard" passed through the cover concrete over a period of days, allowing the distribution of inhibitor to all steel surfaces in its path.

Penetration depth of "Ferrogard" 903 (repair material), after application to the concrete slabs was investigated by Wolfseher and Partner AG (Wolfseher and Partner, 1997) using a photometric estimation of nitrogen content. "Ferrogard" was detected in a concentration $\geq 0.9 \mu\text{g}$ per gram of concrete down to a depth of 50 mm. It was further found that the effect of carbonation level, capillary porosity and water saturation level on the penetration capacity of "Ferrogard", evaluated by analysis of its concentration as a factor of depth, is insignificant. Hence it was concluded that the penetration mechanism of this inhibitor in concrete involves more than one transportation mechanisms such as capillary action and diffusion through the liquid phase and through the gas phase, resulting in much greater penetration depth. Further findings of this investigation were that for a given depth of concrete cover the "Ferrogard" 903 concentration of the specimens with higher porosity (higher water/cement ratio) was higher and that penetration of inhibitor improves slightly if the specimens are dried before its application.

In view of the results discussed so far, the investigation of Tritthart (Tritthart et al., 1999) warrants attention. Tritthart's work focussed on the binding in addition to diffusion of "Ferrogard" 903 inhibitors (reported as FG 903 by Tritthart) in cement paste. These studies have shown that the inorganic component of FG 903 is completely bound by cement and/or precipitates out of the pore solution. The organic active ingredient i.e. the amino-alcohol - contrary to the inorganic component- is not bound at all or very weakly by cement and remains dissolved in the pore solution. Tritthart and coworkers further suggested that penetration of FG 903 into concrete and its redistribution within concrete take place primarily via both capillary action and diffusion into water-filled pores due to the concentration gradient. However, on examining penetration of FG 903 into the cement paste by diffusion, they observed that it happened much more slowly than was anticipated. It must be further pointed out that the laboratory experiments carried out by Goschnik et al had shown that, depending on the concrete density, the amino-alcohol reaches reasonably good penetration speeds of 2-20 mm per day (Goschnik et al., 1998). Tritthart then attributed this quick uptake of the active ingredient of inhibitor mainly to transport via capillary action.

Most of the work reviewed so far is focussed on the transport behaviour of organic inhibitors in concrete except for Tritthart's work, which has commented on the diffusion characteristics of nitrite based inorganic inhibitors as well. Besides Tritthart, Tomosawa et al (Tomosawa et al., 1992) investigated diffusion characteristics of nitrite in concrete in an attempt to develop a non-destructive repair method using a calcium nitrite inhibitor solution for chloride-induced corrosion of reinforcement. This group observed that the corrosion inhibiting effect of surface impregnation of inhibitor method was limited. They assigned this to insufficient nitrite concentration at the rebar, due to low dispersion/migration rate of the nitrite ions in concrete as compared with that of chloride.

Recently, Li and coworkers (Li et al., 1999), while studying the nitrite content in the concrete pore water by an in situ leaching method, observed that the leaching of nitrite from concrete into the cavity water was a slow process. Assuming that the effective volume porosity of concrete was ~10% and all the admixed nitrite had gone into the water-saturated pores, the concentration of nitrite present in the pore solution corresponded to only ~1/10 of the admixed inhibitor. The remaining inhibitor was believed to be retained in the concrete matrix because of the strong binding

characteristics of this inorganic (nitrite) group. It was estimated that ignoring the binding or similar effects, application of a model by Sagues et al (Sagues et al., 1997) to the observed conditions would yield 10^{-12} m²/s as an order-of-magnitude estimate for the apparent nitrite diffusion coefficient.

Elsener et al (Elsener et al., 2000), while investigating diffusion rate of migrating corrosion inhibitor, demonstrated high mobility of the hydroxyalkylamine molecule in porous cement paste. However, it was found that the non volatile component of the inhibitor i.e. the carboxylic acid reacted with the calcium ions present in the concrete pore solution leading to the precipitation of the carboxylate. It was assumed that this further resulted in a pore blocking effect reducing the permeability of the mortar/concrete surface. Thus these results are consistent with those obtained for the nitrite ions.

2.5.3 - Determination of Diffusion Coefficients

It should be recognised that, as compared with the work on determination of chloride diffusion coefficients, only little has been published on the diffusion coefficients of inhibitors in concrete (Bjegovic et al., 1993; Bjegovic et al., 1998). The equations used for the estimation of diffusion coefficients under steady state and non steady state conditions can be derived as follows:

Steady state conditions

For steady state diffusion, the concentration profile of the diffusing species is time-independent, and the rate of mass transfer of diffusing substance per unit area is proportional to the negative of the concentration gradient measured normal to the section according to Fick's first law (Crank, 1975).

$$J = -D \cdot \delta C / \delta X \quad \text{Equation 2.5}$$

Where J is the rate of mass transfer per unit area of section, C is the concentration of the diffusing substance, X is the path length and D is the diffusion coefficient.

It is assumed (Page et al., 1981) that when diffusion becomes established across the thickness of the concrete membrane in a two compartment diffusion cell (Figure 2.8

showing a schematic diffusion cell), there is a linear increase with time in the diffusant concentration C_2 of the solution in the downstream cell (the compartment with zero initial concentration of diffusant); the concentration C_1 in the upstream cell (the compartment containing the diffusant) remaining effectively constant over the period of measurements. The flux (J) in $\text{mol/m}^2/\text{s}$ of inhibitor molecule entering the downstream compartment is given by:

$$J = \frac{VC_2}{At} = D_{\text{eff}} \frac{C_1 - C_2}{l}$$

where D_{eff} is the effective diffusivity of inhibitor through the membrane in m^2/s (assumed to be independent of concentration), V is the volume of solution in the downstream cell in m^3 , A is the cross-sectional area in m^2 , l is the thickness of the disc in m and C_1 and C_2 , the solution concentrations in the two compartments. Hence, for $t > t_0$ and $C_1 \gg C_2$, the expression for the concentration of the diffused substance after time t is

$$C_2 = D_{\text{eff}} C_1 \frac{(t - t_0)A}{Vl} \quad \text{Equation 2.6}$$

Thus D_{eff} may be calculated from the slope of the line of plot of C_2 vs t . In the steady state condition, diffusion of ions is considered to be driven by a constant concentration difference, ΔC . It should be noted that this situation might be expected at longer times when an effective concentration gradient $\Delta C/C$ has been established.

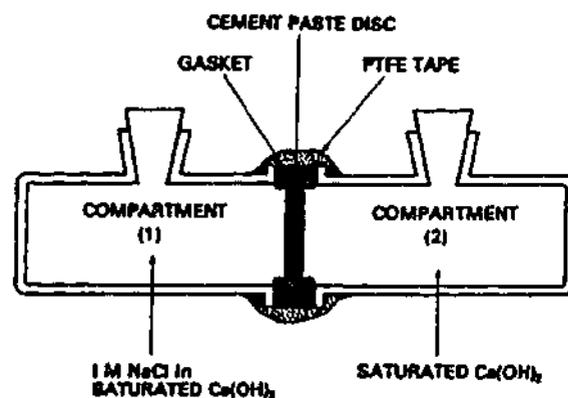


Figure 2.8 - Schematic diagram of a diffusion cell (Page et al., 1981)

Non steady state conditions

When the diffusion flux and the concentration gradient at some particular point in a solid vary with time, this is defined as a non steady state condition and is expressed in terms of a partial differential equation (Crank et al., 1981)

$$\frac{DC}{dt} = -D_{app} \frac{d^2C}{dx^2} \quad \text{Equation 2.7}$$

where C is concentration, t is time, D_{app} is the apparent diffusion coefficient and x is the distance. The solution most frequently applied for computing the diffusivity is the error function solution based on the following:

Boundary Condition: $C(0,t) = C_0$

Initial condition: $C(x,0) = 0$

Based on these initial and boundary conditions, the solution to Equation 2.7 is as follows:

$$\frac{C(x,t)}{C_0} = \text{erfc} \frac{x}{2\sqrt{Dt}} \quad \text{Equation 2.8}$$

Where erfc is the error function complement, equal to the (1- the error function). An iterative approach is then employed to determine the value of D, which best fits the experimental data (MacDonald and Northwood, 1996). This solution has received widespread application and appears to have been the primary solution employed in the literature. In concrete structures, non steady state diffusion would be expected initially, although one must be aware of the capillary action effects in the case of dry or partially dry concrete.

2.6 - EVALUATION OF PERFORMANCE OF INHIBITORS IN CHLORIDE CONTAMINATED CONCRETE

2.6.1 - The Overview

Several types of chemical admixtures have been tested both in laboratory and in the field (Berke et al., 1988), but there is not yet a general consensus on the accelerated experimentation to be carried out to determine their effectiveness. The standard test method for determining the effects of chemical admixtures on the corrosion of embedded steel reinforcement in concrete exposed to chloride environments is described in ASTM G109 (ASTM109-99, 1999), but some researchers believe that the specimens described in the specification are very small and it is very hard to imagine that they can produce the real conditions in which the steel reinforcement usually finds

itself. Larger dimension specimens better simulate a real structure, and can be used to evaluate the inhibitor effectiveness in concrete, but the time needed to get meaningful results may be long. Hence, in this section the findings of various researchers on the performance evaluation of inorganic (nitrite based) versus organic (amine based) corrosion inhibitors in chloride contaminated reinforced concrete are compared and the factors influencing their performance are discussed.

2.6.2 - Inorganic Inhibitors

The use of inhibitors in concrete has been reviewed extensively by Griffin (Griffin, 1975), Craig and Wood (Craig and Wood, 1970), Treadaway and Russel (Treadaway and Russell, 1968). These pre-1980 studies looked at various inhibitors with the main focus on the inorganic compounds such as sodium nitrite, potassium chromate and stannous chloride. Corrosion testing carried out by these researchers showed that only sodium nitrite inhibited in the presence of chloride. Treadaway (Treadaway, 1966) and Treadaway and Russel (Treadaway and Russell, 1968) reported a decrease in the compressive strength of concrete when sodium nitrite and sodium benzoate were added to concrete. Hence there was a need for a corrosion inhibitor, which could protect reinforcement from corrosion and would not be detrimental to concrete properties.

The use of calcium nitrite admixtures to protect steel in concrete had already been reported by Rosenberg et al in 1977 (Rosenberg et al., 1977). Following the nitrite approach, Gaidis and coworkers (Lundquist et al., 1979; Rosenberg and Gaidis, 1979) and Berke et al (Berke, 1991; Berke et al., 1988) have published several papers on the use of calcium nitrite as an inhibitor in reinforced concrete. Unlike sodium nitrite, calcium nitrite is non-detrimental to the concrete properties. Rosenberg et al (Rosenberg et al., 1977) found that this inhibitor meets ASTM 494 specifications as a set accelerator for concrete. Rosenberg and Gaidis (Rosenberg and Gaidis, 1979), while investigating the mechanism of nitrite inhibition in chloride contaminated alkaline environment, observed that calcium nitrite effectively inhibits corrosion in the presence of chloride by oxidising ferrous ions to ferric, thus forming an insoluble ferric oxide film and blocking passage of ferrous ions from the metal into electrolyte.

The first large-scale results reported by a government agency Federal Highway Administration (FHWA) were released in 1983. Even though the FHWA used

water/cement ratio greater than 0.5 and added chlorides to the mix water, it was concluded that calcium nitrite can provide more than an order of magnitude reduction in the corrosion rate (Virmani et al., 1983).

Berke et al (Berke et al., 1993) while examining corrosion of steel in cracked concrete, observed that calcium nitrite additions to concrete significantly improved corrosion resistance of embedded steel when cracks were present. Collins et al (Collins et al., 1993) while evaluating different inhibitors in an accelerated test program observed that calcium nitrite was most effective when applied as a ponding solution in the case of the partially exposed rebar and when placed in backfilled mortar after removal of chloride-contaminated concrete. The term ponding generally refers to (inhibitor) solution contained in a dike attached to the top surface of a concrete specimen.

Thus the investigations of many researchers appear to be consistent and confirm that nitrite can inhibit corrosion of reinforcement in concrete in the presence of chloride ions. Regarding the concentration of nitrite required to inhibit corrosion in the presence of chloride, it was Virmani and coworkers (Virmani et al., 1983) who examined calcium nitrite admixture and epoxy-coated reinforcing bars as corrosion protection systems in time-to-corrosion study of reinforcing steel slabs under the Federal Highway Administration Research Program (FHWA). They observed that the higher the dosage of nitrite the higher the chloride ion threshold for corrosion and the longer the time-to-corrosion. As the Cl^-/NO_2^- ratio increases, the ability of nitrite ions to protect the film decreases and subsequently corrosion damage increases. Later it was found that these findings were in accord with those of the Strategic Highway Research Program, SHRP-S-666 (Al-Quadi et al., 1993), which proposed that calcium nitrite is effective in reducing corrosion current densities only when it is applied at a 0.1M concentration. The concentration dependency of calcium nitrite was observed by other researchers as well, however, the critical Cl^-/NO_2^- ratio at which corrosion occurs was somewhat disputed and ranged from 0.92 to 1.6 (Berke and Rosenberg, 1989; Nmai, 1995). Berke and coworkers (Berke and Rosenberg, 1989; El-Jazairi and Berke, 1990), while examining the effect of inhibitor concentration on the level of inhibition, recommended the Cl^-/NO_2^- ratio be less than 2 in the case of calcium nitrite, for any meaningful inhibition to occur.

Application methods

Various application methods have been proposed by researchers for the nitrite based inorganic inhibitors. These inhibitors are generally added to the concrete mix as chemical admixtures during the batching process, usually in small concentrations (Yunovich and Thompson, 1998). Another method described in the SHARP-S-666 (Al-Quadi et al., 1993) applicable for the existing structure involved removing the free water out of concrete by heating the grooved deck surface and then impregnating the concrete with calcium nitrite solution. The grooves are filled with 15% calcium nitrite solution for 24h, the excess solution is removed from the grooves and the grooves are filled with a calcium nitrite rich, latex-modified grout.

Recently, Tomosawa et al (Tomosawa et al., 1992) have suggested a repair method where a nitrite corrosion inhibitor (calcium nitrite) can be injected at a low pressure into concrete in which cracks are beginning to occur, due to corrosion-induced deterioration of the rebar. The corrosion mitigation is achieved because of the inhibitor seepage through the minute cracks occurring on the surface of the concrete.

Limitations

As pointed out by Nmai et al (Nmai et al., 1992) calcium nitrite inhibitor has limitations. Its main limitation being that it is purely an anodic inhibitor, and so, if not present in sufficient quantities, it can promote localised corrosion, being unable to inhibit active anodic sites. Also, it is primarily an admixture type inhibitor, which is to be mixed with concrete at the time of commissioning, hence it is more appropriate in the case of new structures. Being toxic and environmentally unacceptable there are some limitations imposed on its use in some countries such as Switzerland and Germany. This necessitated the development of new, more effective, and/or more environmentally compliant corrosion inhibitors for corrosion in reinforced concrete.

2.6.3 - Organic Inhibitors

Besides MCI series and "Ferrogard" series inhibitors, which were described in the diffusion section 2.5.2, there are other combinations, which include a proprietary oxygenated hydrocarbon Alox 901. This is produced by partial oxidation of an aliphatic hydrocarbon, which is believed to form a protective film by conversion to a metallic soap (Al-Quadi et al., 1993). In addition to these, a wide range of chemicals reported in

the literature have been studied mostly in laboratory trials, and these have been compiled by Yunovich and Thompson (Yunovich and Thompson, 1998).

Nmai et al (Nmai et al., 1992) carried out comparative studies of both organic corrosion inhibitors and calcium nitrite on a precracked beam under accelerated corroding environment. They found that the quantity of organic inhibitor required to facilitate inhibition is lower than that required in the case of inorganic inhibitors (Nmai et al., 1992). The results showed that calcium nitrite treated concrete specimen (20 litres/m³ admixture) showed signs of corrosion after approximately 30 days whereas organic corrosion inhibitor admixture - OCIA (5 litres/m³ admixture) treated concrete specimen showed no signs of corrosion even after 180 days.

In 1993 a Strategic Highway Research Program (SHRP-S-666) (Al-Quadi et al., 1993) identified a number of corrosion inhibitors, surface applied and concrete admixtures (Alox 901 and MCI series) as promising for rehabilitation of reinforced concrete structures subjected to chloride-induced corrosion. A model for service life prediction was developed, which proposed that drying of concrete a day prior to inhibitor ponding will increase the service life by at least 50%. This investigation also concluded that removing chloride-contaminated concrete above the reinforcing steel and replacing it with fresh concrete was an effective method, which facilitated the application of corrosion inhibitors.

Investigation of effectiveness of similar MCI inhibitors was also undertaken by Rosignoli et al (Rosignoli et al., 1995). in the cracked-beam test specimens. They observed that both MCI 2000 (an admixture type inhibitor) and MCI 2020 (a surface applied inhibitor) delayed the onset of corrosion.

Collins et al (Collins et al., 1993), based on the post-treatment electrochemical (corrosion current) measurements, found that the two organic inhibitors i.e. a surface injected blend of surfactants and amine salts in a water carrier, which is designed to migrate through concrete, and another admixture type alkanolamine inhibitor, yield highly effective short term and long term results. Also a combination of admixture and surface applied inhibitors proved to be a highly effective treatment during the initial period.

A number of research groups have undertaken investigation of “Ferrogard” inhibitors under different conditions and using different monitoring techniques. For instance, Cigna et al (Cigna et al., 1998) evaluated effectiveness of an admixture based amino-alcohol (“Ferrogard” 901) in 250 x 100 x 150 mm concrete specimens using an innovative technique for a forced acceleration of chloride ingress. The results demonstrated that in the presence of this inhibitor a very good passivation was obtained even in the presence of considerable amount of chlorides. Further the minimum time-to-corrosion initiation for the concrete slabs containing the corrosion inhibitor, estimated using chloride diffusion coefficients, was estimated to be much higher than that for the similar concrete mix without inhibitor.

The application and long-term behaviour of the product “Ferrogard” 901 (concrete additive) or 903 (repair material) was evaluated by Wolfseher and Partner, AG (Wolfseher and Partner, 1997). It was concluded that “Ferrogard” 903 provides protection to steel reinforcement by forming a thin film i.e. about 10 nm at both anodic and cathodic sites. Further, the leaching studies demonstrated that the protective film already adhering to the steel is extremely resistant to weathering (leaching). Findings of Fear and coworkers (Fear, 1996) on the “Ferrogard” inhibitors concurred with the above observations. Their studies have shown “Ferrogard” inhibitor to be effective in cases where concentrations of chloride ions are up to 2.0% by weight of cement at the depth of the reinforcement, which accounts for the vast majority of repairable structures.

However, in contrast to the above, the observations of Sprinkel and coworkers (Sprinkel et al., 1996), who evaluated the long-term performance of corrosion inhibiting admixtures (calcium nitrite and “Ferrogard” 901) and surface applied inhibitor (“Ferrogard” 903), were found to be somewhat controversial. They observed that measurements made on the structures and slabs that were patched and overlaid with concrete containing inhibitors after approximately one year of exposure showed no significant difference between the slabs repaired with and without corrosion inhibitor admixtures and topical treatments (Sprinkel and Ozyildirim, 1998).

Recently, Elsener and coworkers (Elsener et al., 1999), while investigating the efficiency of a migrating corrosion inhibitor, based on ~95% of the volatile hydroxyalkylamine (mainly dimethylethanolamine) and nonvolatile carbonic acid (mainly benzoic acid) in saturated calcium hydroxide solution and in mortar, found that

the results were contradictory to all previously quoted work. According to these workers, high concentrations (~10%) of inhibitor were required to inhibit pitting corrosion initiation in solution containing 1M/L sodium chloride (NaCl). At lower concentrations, it was observed that even though the corrosion rate was lowered by the presence of the inhibitor, there was an initiation of pitting corrosion. Another important observation was that inhibiting properties were lost by evaporation of the volatile constituent of the inhibitor or by the precipitation of the nonvolatile fraction of the inhibitor in the presence of calcium ions. Contrary to the experiments in solution, in the case of mortar it was demonstrated that addition of inhibitor blend to mortar yielded a retardation of the corrosion initiation in the case of chloride induced corrosion, but no significant reduction in corrosion rate. It was further found that the estimation of the long-term effect on corrosion initiation on real structures was difficult, since the inhibitor was found to evaporate from the mortar, resulting in a loss of inhibition.

Later the same group of researchers found a high mobility of one of the components (hydroxyalkylamine) of this inhibitor through mortar (Elsener et al., 2000). The discrepancy between the observed high diffusion rate and the lack of corrosion mitigation was rationalised by the fact that the diffusion measurements were based on the monitoring of the concentration of volatile hydroxyalkylamine, which did not have significant inhibiting properties. Migration of the non-volatile component (carboxylic acid) was assumed to have a low diffusion rate and was, further, found to react with calcium ions in concrete pore water solution precipitating calcium carboxylate resulting in blocking the concrete pores.

It is clear therefore that much controversy exists in the field of organic inhibitor application to reinforced concrete structures. Yet these inhibitors are being marketed and used in various forms worldwide.

2.7 - THE SYNERGY BETWEEN INHIBITORS AND ELECTRIC FIELD

2.7.1 - The Overview

With somewhat conflicting reports from research groups regarding the limited performance of inhibitors in concrete, it is relevant to look for a possibility of

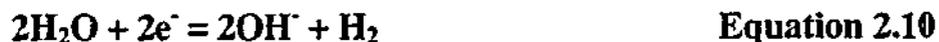
enhancement of inhibitor performance. One possible way of doing this is by combining inhibitors with some other protection method, which can extend either their protection capacity and/or their mobility in concrete. One of the methods, examined by researchers, to enhance the protective effect of inhibitor, is the application of an electric field. The application of cathodic protection (CP) to a metal already having a protective coatings such as organic coating, has been reported in the literature for the case of under water concrete structures (Kuznetsov, 1996). However, although the effect of simultaneous application of electric field and inhibitors in aqueous solution has been explored in the last few years, its actual application to reinforcement embedded in concrete has not received much attention. This section outlines the importance of simultaneous application of inhibitors and electric field in concrete and discusses the work of various researchers in this area.

2.7.2 - Application of Inhibitors and Cathodic Protection

Before considering a simultaneous action of the two protection methods, cathodic protection and inhibitors, it is important to understand the mechanism of each of these protection methods separately. Mechanism of action of organic corrosion inhibitors has been discussed extensively in section 2.4.3. Hence the mechanism of cathodic protection and different criteria used to examine the efficiency of the CP system are discussed in this section.

The mechanism of cathodic polarisation - theoretical considerations

Cathodic protection in general consists of lowering the electrode potential of a metal to a value where the corrosion rate is adequately low (Jones, 1971; Pourbaix, 1995). This can be thermodynamically achieved by placing the potential of the metal to be protected in a state of immunity or passivity (Jones, 1971; Pourbaix, 1995) depending on the environment. When the metal is undergoing pitting corrosion, as is likely to be the case in chloride contaminated concrete, the metal can be adequately protected by lowering the electrode potential into the passive range of the potential-pH-Cl diagram (Figure 2.2). The passive range seems to be dependent on the conditions existing at the metal/concrete interface such as the pH and chloride ion concentration. One of the effects of the application of cathodic polarisation is to generate more alkalinity at the acidic sites. This alkalinity may be generated by reduction of oxygen (depending on the availability) or water according to the following equation (Thompson and Barlo, 1989).



Both these reactions produce hydroxyl ions and tend to increase the pH. Evidence of increase in the pH with the cathodic polarisation has been encountered by researchers (Thompson and Barlo, 1989). Another likely effect of cathodic polarisation is the transport of negatively charged chloride ions away from the steel concrete interface and therefore it is expected that the chloride ion activity would decrease with cathodic polarisation.

The next step after outlining the mechanism of CP is how to estimate whether the corrosion rate has been reduced to an appropriate level. Several criteria such as the absolute potential criterion, the 100 mV potential decay, the potential shift and the E vs log I curve have been adopted in practice, which to a greater or lesser degree correlate with the reduction of the corrosion rate to an acceptable level (Berkeley and Pathmanaban, 1990; Chess, 1998). Each of these criteria is discussed below.

The absolute potential criterion: This criterion is based on the thermodynamics of the behaviour of steel in concrete. It gives the minimum negative value of electrode potential necessary to move the steel into a "immune" region in the potential-pH diagram (Chess, 1998). A recent variation of the absolute potential measurements is to measure the "instant-off" potential between the cathodic protection anode and the cathodically protected steel.

Determination of the "Instantaneous Off" Potential: When the polarised potential is measured during the passage of current the value measured may include an ohmic potential drop and the measured value may be different from the true polarised potential. The current interruption technique can be used to remove the ohmic component of the polarised potential and the true polarised potential is determined as the potential measured immediately after current interruption i.e. "the instantaneous off potential". According to Schwenk (Schwenk, 1963) the ohmic component of the polarisation may disappear in about 10^{-8} second, hence the first reading taken after the current was switched off, at 0.1 second, would according to Schwenk be IR drop free.

The 100 mV potential shift/decay criterion: This criterion is based on the assumption that protection of the steel is afforded provided that the steel is polarised at least 100 mV into the negative direction at anodic locations (NACE, 1990). This criterion is applied in practice by adjusting the current in the system over time to provide a difference (decay) in potential of 100 mV from the time immediately after switching off of the current (the instant-off value or the true polarised potential) and the potential measured after a set period of time from when the current has been switched off. The depolarisation time has been proposed to be between 4 and 24 hours.

Simultaneous application of inhibitors and cathodic polarisation

There are different mechanisms by which a synergy can be obtained in a combined protection. More than forty years ago Rosenfel'd (Rosenfel'd, 1953) discovered a marked increase in the protective action of certain corrosion inhibitors e.g. chromates, zinc and calcium salts, in soft water when cathodic polarisation from sacrificial anodes was applied to the steel. The mechanism proposed by Rosenfel'd is that cathodic polarisation of steel causes alkalisation of the near-electrode layer and favours the deposition of sparingly soluble calcium and zinc compounds on the surface thus reducing the activity of the steel surface.

Another proposed mechanism of a combined protection is a change of metal surface charge caused by cathodic polarisation resulting in increase in the adsorption of cations of the inhibitor. This is pronounced especially in the case of acid solution in the case of cation active inhibitors. Antropov explained the combined protection in terms of ϕ -potential scale concept (Antropov, 1963). According to this concept, the adsorbability of the species on "clean" metal at a given potential of metal (E) will depend primarily on its value in relation to the potential of zero charge of the metal ($E_{q=0}$): In this case

$$\phi = E - (E_{q=0}) \qquad \text{Equation 2.11}$$

If the ϕ value becomes negative as a result of the metal's cathodic polarisation, an adsorption of cation active inhibitor increases under the action of electrostatic forces. Cations of quaternary ammonium salts are adsorbed from acid solutions mainly by this mechanism and can be used conjointly with cathodic polarisation.

Thus considering the above two mechanisms Kuznetsov (Kuznetsov, 1996) classified all cases of combined protection of metals by cathodic polarisation and inhibitors into two types. One of them can be by improvement of inhibitor adsorbability (at negative potentials) on application of cathodic polarisation as explained by Antropov, which is more applicable in acid solutions. The second one involves not only adsorption of inhibitor but also the formation of the cathodic deposit, which results in the formation of a more protective film. According to Kuznetsov and coworkers (Agalarova et al., 1988; Kuznetsov and Rosenfel'd, 1980) the inhibitor can be involved directly in the composition of the film, changing its structure and improving its protective action. This modification of cathodic deposit by inhibitors is capable of providing a strong post treatment effect. They proposed this mechanism for combined protection of steel in seawater. Agalarova and coworkers (Agalarova et al., 1988) have shown that the combined protection with zinc phosphonates or their formulations provides a significant post treatment effect which is retained both during "the switching off" of cathodic polarisation and also when the inhibited sea water is replaced by clean seawater. It was observed that the film began to lose its protective properties only after 26 days. Another important observation from this investigation is that the post treatment effect is enhanced with an increase in the duration of formation of the protective film.

It is interesting to note that sodium nitrite and its formulations exhibit a degradation of protection under conditions of cathodic polarisation of metal to be protected (Kuznetsov, 1996). Certain carboxylates and phosphonates are promising corrosion inhibitors for the combined protection of various metals even in fresh water.

2.7.3 - Electromigration of Inhibitors under the Influence of High Current Density

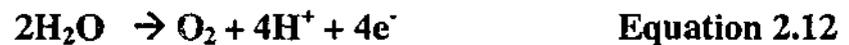
It is evident that most of the work discussed above has been done in the aqueous solution. Use of a similar protection technique has also been reported in the case of reinforced concrete. However, the current density used in this case is much higher i.e. almost 1000 times that required for the cathodic protection. The method used in this case is similar to the one used in the case of electrochemical chloride extraction (ECE).

Electrochemical chloride extraction (ECE)

This technique was first investigated in concrete in the seventies (Lankard, 1978; Morrison et al., 1976). More recent laboratory tests (Bennett et al, 1993b) and field

investigations (Bennett et al, 1993a; Broomfield, 1997b; Clemena and Jackson, 1996) have shown that ECE can be effectively used in the treatment of chloride contaminated concretes. ECE is achieved by inducing an electrical field between the embedded steel reinforcement and an external anode (Elsener et al., 1993). This is accomplished in a manner similar to cathodic protection with the exceptions of the higher currents utilised. A direct current is applied between the reinforcement (cathode) and an external anode in electrolytic contact with the concrete. CP is a permanent installation with design currents below 10mA/m^2 , electrochemical chloride removal is only temporary using currents up to 1A/m^2 . As in the case of CP, the electrochemical reaction at the cathode (the rebars) produces hydroxyl ions leading to an increase of the pH near the rebar (Equation 2.9). This facilitates passivation of the steel. Equation 2.10 is possible at very high current densities, and produces hydrogen.

At the anode the possible oxidation reactions are either chlorine evolution or water decomposition



These reactions lead to an acidification of the electrolyte around the anode. The DC current flowing from the rebars to the external anode facilitates the movement of negative ions (OH^- and Cl^-) from the reinforcement to the external anode, and that of positive ions (Na^+ , K^+ , and Ca^{2+}) towards the reinforcement. Since the anode is external to the concrete, the chloride ions will leave the concrete and concentrate around anode. Thus the chloride content of the concrete is reduced, particularly on and around negatively charged reinforcing steel/cathode.

Electrical injection/ electromigration of corrosion inhibitors

On the lines of ECE, a feasibility study was undertaken by Asaro et al (Asaro et al., 1990) on the injection of synergistic corrosion inhibitors for protection of concrete bridge components for the Strategic Highway Research Program (SHRP) under contract SHRP 87-C-102C. These inhibitors included quaternary ammonium and phosphonium corrosion inhibitors with the chloride, nitrite and molybdate anions. The process of injection required approximately 1000 times higher current densities than those used for

cathodic protection. The major findings of the investigations were that effective inhibitor injection occurred at an electrical field of 5-10V/cm at a current density of 0.46 to 1.24 mA/cm² within a period of 10-15 days, which provided 78-85% corrosion protection to the rebars in the chloride contaminated concrete specimens. Doubling the current density provided a significant increase in the inhibitor injection as determined by measuring polarisation resistance. After switching off the current the system was monitored for 3-4 weeks during which it was observed that the rebar potential continued to shift in the positive direction indicating that chloride remigration, if it does occur, is not effective in increasing the rebar corrosion rate. Since the corrosion monitoring in the above investigation was done only for 3-4 weeks, the long-term (>12 months) effectiveness of the treatment especially against chloride remigration could not be commented upon. In this work, corrosion inhibitor efficiency (IE) was defined as

$$IE = \frac{R_p^1 - R_p^0}{R_p^1} \times 100 \quad \text{Equation 2.15}$$

Where R_p^1 and R_p^0 were the polarisation resistances with and without inhibitor, respectively assuming B in equation to be a constant.

Another interesting finding of these studies was that quaternary phosphonium inhibitors provided superior corrosion inhibition than their quaternary ammonium counterparts especially under high pH conditions (pH ~ 10.5). Hence it was concluded that in alkaline environments (such as that existing in concrete) corrosion inhibitors based on quaternary phosphonium salts perform better than those based on the corresponding ammonium salts.

2.8 - SUMMARY

Section 2.2 discussed the chemical environment around the reinforcement especially with respect to corrosion/inhibition process. The importance of the physico-chemical functions of the concrete cover such as the pH around the reinforcement and permeability of concrete were discussed. These issues were particularly relevant to the inhibition process, as the passive environment around reinforcement influences the

kinetics of inhibition process at the steel surface whereas permeability of concrete controls the transport properties of inhibitor molecules.

Section 2.3 discussed the electrochemical environment prevailing at the steel surface under passive conditions and the changes occurring during the breakdown of passivity due to aggressive chloride ions. Understanding the mechanism of corrosion is important as it can help in understanding the process of inhibition and can also assist in designing an appropriate protection system. The latter part of this section described selected protection systems.

Mechanisms of inhibition in the case of organic and inorganic inhibitors are discussed in section 2.4. Nitrite-based inorganic inhibitor are assumed to function by interfacial reaction of repassivation of the oxide film whereas organic amine based inhibitors are shown to protect steel by chemisorption (through nitrogen bonding) and/or physisorption of amine molecules. However, some researchers have also proposed amine chemisorption to proceed by hydrogen bonding of the amine to the surface of oxy-hydroxy passive film. The existence of both a coordinated and non chemisorbed protonated amine groups has been documented. These mechanisms of bonding not only play a major role in deciding the barrier/protective properties of the film, but they also influence significantly the persistency of the film or the long-term efficiency of the inhibitor. Finally this section highlights various electrochemical techniques such as potential measurement, LPR and the other polarisation techniques and their usefulness, in the evaluation of inhibitor efficiency and the mechanism of protection.

The work reviewed in section 2.5 underlines the fact that amino-alcohol based organic inhibitors have significant partial pressure and hence can exist in both the liquid and the vapour phase. It follows from this that the mechanism of transport of these inhibitors in concrete is likely to be a complex process and may possibly involve different steps that are mutually interdependent. It is further pointed out that the penetration mechanism of inhibitors in concrete involves more than one transportation mechanisms such as capillary action and diffusion through the water-filled pores and through the gas phase, resulting in much greater penetration depth. Most of the investigations covered in this part of the review have studied penetration of these inhibitors in concrete by establishing and estimating the concentration profiles of these inhibitors in concrete. Only one group of researchers has estimated inhibitor diffusion coefficients using

Fickian laws. Further, it may be emphasised that most of the monitoring of the diffusion process has been done over a short period of time i.e. for a few days. Hence long term behaviour of inhibitor transport in concrete is not known. For example, whether the diffusion process follows steady state or non steady state kinetics or there is any possibility of interaction between inhibitor and the cement constituents at longer times, resulting in an anomalous behaviour, is unknown. Contrary to the organic amines, the inorganic component e.g. nitrites have been reported to exhibit insignificant diffusion rates in concrete and are also shown to be retained in the concrete matrix because of its strong binding characteristics.

The studies described in section 2.6.2 indicated the ability of nitrite to inhibit corrosion in the presence of aggressive chloride ions when used as a concrete additive. However, its performance is found to be concentration dependent and has been expressed in terms of a threshold Cl^-/NO_2^- ratio. The findings of various researchers on the performance of organic inhibitors summarised in section 2.6.3 seem to be somewhat controversial. A number of investigations have concluded that organic inhibitors offer excellent protection when surface applied, as they can diffuse through concrete and can form a highly protective barrier film. However, poor performance of these inhibitors has also been reported by some researchers. It has been observed that measurements made on the structures and slabs treated with inhibitors after approximately one year of exposure showed no significant difference from those without corrosion inhibitors. A group of researchers has observed the loss of inhibiting properties due to evaporation of the volatile constituent of the inhibitor or by the precipitation of the nonvolatile fraction of the inhibitor in the presence of calcium ions in saturated calcium hydroxide solution or mortar.

From section 2.7 it can be concluded that combining inhibitors with electric field can extend their protective effect and/or their mobility in concrete. Previous researchers have suggested that the synergy can be obtained either by reducing the activity of the steel surface through the deposition of sparingly soluble salts on the surface because of alkalisation of the near-electrode layer or due to increased adsorbability of inhibitor on the metal surface facilitated by a change of metal surface charge. It should be pointed out that all the reported experiments were carried out in solution, hence it will be interesting to investigate the effect on the results if the solution medium is changed to

concrete, as the concrete medium is completely different from a solution medium especially in relation to transport properties of inhibitor species.

Increase in the level of protection under the influence of high current density has also been reported in section 2.7.3. This has been assumed to be due to electromigration of inhibitors. However, it is possible that electrochemical removal of chloride has also contributed towards the increased inhibition effect. The influence of changing some of the parameters has been discussed. For instance, doubling the current density appears to have provided an approximate 3-4 times increase in the inhibitor injection rate. A question that needs to be answered is, what will be the effect of increasing the application time of current density on inhibitor injection? Further, in the investigations previously reported the monitoring has been done only for 3-4 weeks, hence the long-term (>12 months) effectiveness of the treatment especially against chloride remigration could not be commented upon and warrants further attention.

CHAPTER 3

RESEARCH PROGRAM

3.1 - INTRODUCTION

An extensive review of the literature in the preceding chapter has demonstrated that various approaches have been used to examine the effectiveness of corrosion inhibitors and the mechanism of the inhibition process in reinforced concrete. These investigations were either focussed on the accelerated laboratory tests or the long-term testing in concrete specimens in the laboratory and/or in the field. Although the past studies, carried out by different groups of researchers, have generated a greater interest in this area, these studies concentrated mainly on individual aspects of the inhibition process in concrete. These studies primarily used different inhibitor systems and employed different experimental methods and monitoring techniques for evaluation of inhibitor efficiencies. Indeed, there appeared to be a lack of a comprehensive approach, which could evaluate the concept of inhibition in concrete starting from understanding the fundamental mechanism of each individual process to a combination of processes occurring at the reinforcement in concrete. Besides, these investigations appeared to have monitored inhibition as well as diffusion processes in concrete for a short period only. The long term kinetics of these processes such as the persistency of inhibitor film formed at the rebar surface, steady state/non steady state conditions of inhibitor transport, or the possibility of inhibitor/concrete interaction and its subsequent effect on the pore structure or permeability of concrete still remain unexplored.

This thesis presents a consolidated approach, using a set of organic amine-based inhibitor systems to develop an understanding of various mechanisms, namely protection by inhibitor molecules at the steel surface, their transportation through concrete pores, the interdependence of these processes in concrete, and finally the dominant mechanism controlling the overall inhibition in concrete. The study also investigates the influence of a number of key factors on these mechanisms. Further, the methodologies and monitoring techniques used for different tests will be maintained

throughout the tenure of this work to allow a meaningful comparison of the results. The final objective of this thesis is to explore ways of enhancing the inhibition process. A comprehensive research program is developed, involving a set of experiments ranging from relatively short term accelerated laboratory methods in a simulated environment to long term exposure investigations in concrete.

3.2 - THE PROPOSED PROGRAM

The program outlined below consists of four parts: i) to examine the efficiency and the protection mechanism of various inhibitor systems at the steel surface, and to determine the factors which can influence their efficiency ii) to assess the transportation behaviour of inhibitor molecules in concrete and the effect of various parameters on their rate of transport iii) to evaluate the effectiveness of inhibitor systems in actual concrete specimens and investigate the effect of different methods of application iv) and finally to investigate the methods of improving inhibitor performance by combining inhibitors with other protection methods.

The inhibitors selected in this work can be classified into four different types – amine based organic inhibitors, preferentially used in developing migratory corrosion inhibitors; the nitrite based inorganic inhibitors having inhibition mechanism similar to that of a commercially available nitrite based admixture; an organic-inorganic inhibitor which may combine the effects of both organic amines and an inorganic oxidising anion; and finally a commercially used organic inhibitor blend comprising of an alkanolamine and a carboxylic acid (MCI).

It can be recalled that in section 2.4.3 it was discussed that various factors such as size and aliphatic/aromatic nature of organic molecules, and the substituents in the ring compounds influence the effectiveness of inhibitors. Hence under the category of organic inhibitors, both systems containing aromatic rings and the aliphatic compounds will be investigated.

3.2.1 - Evaluation of the Efficiency and the Protection Mechanism of Inhibitors at the Steel Surface

As discussed in section 2.4.3 the predominant mechanism by which organic inhibitors protect steel involves an adsorption of inhibitor onto the metal thus providing a barrier to the corroding species (McCafferty, 1978; Nathan, 1973). Although many postulations have been made regarding the mechanism of action of inhibitors, the exact mechanism by which these inhibitors are able to protect steel embedded in concrete and the parameters governing their action are still topics of debate. Besides the mechanism of film formation, the ability of this film to resist the attack of corroding species over longer duration and the reaction mechanism at the anodic and cathodic sites are also not clearly understood. In view of this, investigations will be carried out in a saturated calcium hydroxide solution under accelerated conditions to evaluate inhibitor efficiency and the protection mechanism using the linear polarisation resistance technique and corrosion potential measurements and the results are described in chapter 4. The level of protection obtained due to addition of inhibitor will be at least semi quantitatively determined by comparing the polarisation resistance/corrosion potential of an inhibited sample with that of a control sample without inhibitor. A calcium hydroxide solution is preferred to actual concrete mainly because a solution medium allows the determination of the effectiveness of inhibitor system purely on the basis of its ability to form a protective film whereas in the case of concrete the inhibition process is the net result of the combined abilities of inhibitor molecules to penetrate through concrete and protect at the steel/concrete interface. Besides this, calcium hydroxide solution approximates the chemical conditions in concrete pore water and it also provides, to a certain extent, a degree of reproducibility compared to concrete.

It may be stated that even though the polarisation resistance (R_p) and corrosion potential shifts measured under the above conditions can estimate the reduction in the corrosion rate and suggest the mechanism of action of inhibitors, they do not indicate whether corrosion inhibition is obtained due to the prevention of the anodic dissolution reaction or by inhibiting the oxygen reduction reaction. Hence further experimentation using the additional polarisation techniques including cyclic voltammetry and potentiostatic transients are also considered here and the results are discussed in chapter 5. Cyclic voltammetry is also assumed to help understand the kinetics of electrochemical oxidation and reduction reactions at the steel surface and the

differences in the behaviour caused by addition of chloride and inhibitor at the steel solution interface. "Long-term" stability of the film under potentiostatic condition will be determined using potentiostatic transients.

In sections 2.4.3 and 2.6.2 it was discussed that the performance of anodic inhibitors such as nitrite-based inhibitors is concentration dependent (Berke and Rosenberg, 1989; El-Jazairi and Berke, 1990). If a threshold ratio of an aggressive ion to anodic inhibitor is not maintained, the ability of nitrite ions to inhibit decreases resulting in an accelerated corrosion rate. In view of these observations, the effect of changing inhibitor concentration on the level of inhibition will also be investigated. Further, the long-term protection capacity of the various inhibitors and application systems will also be estimated, as this is thought to be a crucial factor in determining the long-term suitability of a particular inhibitor system. Indeed this would further help in recommending the frequency of inhibitor treatment for a chosen system.

While planning these experiments consideration will be given to different phases that can be encountered in the service life of a structure. This will be achieved by examining the effect of inhibitor addition to an already passivated steel (as would be found in the new structure) or a precorroded steel (simulating the state of reinforcement in an existing corroding structure).

3.2.2 - Examination of Transport Characteristics of Organic Corrosion Inhibitors in Concrete

The effectiveness of these migratory corrosion inhibitors to protect steel depends upon their ability to migrate through the concrete cover to maintain an adequate concentration in the vicinity of steel/concrete interface. It is this property which makes them appropriate for rehabilitation application in the case of an existing structure, since when they are surface applied, they can access corroding steel by penetrating through concrete. Section 2.5.1 has summarised literature available on diffusion of chloride, where researchers have concentrated on determination of chloride diffusion coefficients using Fickian laws. However, in comparison with chloride, little has been published on diffusion coefficients of organic inhibitors, and most of the published results have been obtained by monitoring diffusion for a short period of time as against the requirement of long term monitoring to simulate real life conditions. Hence the aim of this part of the

research program is to study penetration behaviour of selected inhibitor systems through concrete and to examine the short term/long-term kinetics associated with it and this will be described in chapter 6. The commonly used technique for monitoring diffusion of chloride through concrete will be used for monitoring inhibitor diffusion as well. This technique consists of a two-compartment diffusion cell (Figure 2.8) separated by a concrete membrane where the concentration of inhibitor diffused through concrete membrane is determined using a specific amine sensitive electrode. Diffusion coefficients will be calculated using Fick's laws for steady state and non steady state conditions where possible. The influence of various parameters such as concrete permeability, concrete cover depth, the molecular size and the concentration of inhibitor on the diffusion coefficients will be assessed.

3.2.3 - Performance of Inhibitors in Reinforced Concrete

Evaluation of the effectiveness of various inhibitors obtained in the earlier part of this program using a saturated calcium hydroxide solution cannot be extrapolated directly to reinforced concrete. The literature review has unequivocally emphasised the need to conduct additional laboratory experiments on the reinforced concrete specimens as the concrete specimens can simulate field conditions better than the simulated pore water solutions. It may be recognised that the factors such as transportation rates of inhibitor through concrete pores, possibility of interaction between inhibitor and concrete ingredients and complex diffusion mechanisms including ionic diffusion, capillary action etc. may make the determination of inhibitor efficiency in concrete complicated.

Hence the inhibitor effectiveness in concrete will be examined in chapter 7 by preparing reinforced concrete specimens in the laboratory and monitoring the rebar activity over extended periods. Chloride will be admixed at the time of casting of these specimens in order to provide accelerated corroding conditions to the embedded rebar. The inhibitor systems screened on the basis of good inhibition and diffusion properties in the earlier part of the work (using calcium hydroxide solutions) will be either admixed in the fresh concrete while casting the specimens and/or will be surface applied after the casting of the specimens. The prior addition of inhibitor in the fresh concrete may simulate the condition of the rebar as would be found in the new structure, whereas surface application of inhibitor to an actively corroding specimen is assumed to mimic remedial treatment in the case of an advanced stage of corrosion activity of the rebar. The level

of protection obtained due to addition of inhibitor will be determined by comparing an inhibited sample with a control sample using the linear polarisation resistance technique and corrosion potential measurements. The dominant issues, controlling the overall kinetics of the corrosion inhibition process in concrete, will be determined by monitoring both short term and long term results. These results will be compared/correlated with those obtained earlier in inhibition experiments in the calcium hydroxide solution and the diffusion experiments.

3.2.4 - Combining Inhibitors with Electric Field

Having examined the performance of inhibitors in reinforced concrete, the next step is to look for a possibility of combining inhibitor application with some other protection method, which can extend their capacity to inhibit, or ability to penetrate, or both. The review of literature in section 2.7 has suggested different ways of obtaining synergy in a combined protection, the most recommended one being by application of an electric field along with inhibitor application. It seems from the literature that increase in the protective action of inhibitors by application of cathodic polarisation to the steel immersed in aqueous solutions has been used for some time. It may be recalled here that cathodic protection is increasingly used as a rehabilitation method for protecting reinforcement in concrete. Hence the objective of the final stage of the research program is to investigate the simultaneous action of a constant protective current and a surface application of inhibitor to the corroding reinforcement in chloride contaminated concrete. This will be achieved by applying a small magnitude current (approximately 10-20 mA/m²) between titanium mesh serving as an external anode (which will be laid on a sponge soaked in the inhibitor solution at the surface of the concrete specimen) and an embedded rebar. It is contemplated that the amine-based inhibitors are likely to become protonated when mixed with water. Hence when an electric field is applied between anode and cathode, it is postulated that this facilitates the movement of such positively charged ions towards the cathode. Indeed, in a high pH environment such as that existing in concrete, it is unclear whether charged inhibitor ions or neutral inhibitor molecules predominate. This may in turn result in an acceleration of inhibitor transport through concrete and its subsequent adsorbability on the metal surface. The corrosion behaviour of the concrete specimens subjected to the combined treatment of inhibitor and cathodic protection will be monitored over an extended period using the linear polarisation resistance technique and corrosion potential measurements. Additionally,

in the case where cathodic protection will be applied, depolarisation tests will be carried out at the end of each cathodic polarisation cycle in order to examine the effectiveness of cathodic protection.

Another method by which synergy could be obtained is by increasing the magnitude of the applied current to approximately 7400 mA/m^2 . In this case a similar set up as used in the earlier case will be employed; however, the period of application of electrical field will be much shorter i.e. about two weeks. The system will be allowed to depolarise for a longer time and will be monitored using the linear polarisation resistance technique and corrosion potential measurements. This method is similar to the one used in electrochemical chloride extraction (ECE) and as noted in section 2.7.3, the application of the same method has been documented for the injection (accelerated transport) of synergistic corrosion inhibitors in the Strategic Highway Research Program. The results obtained on the simultaneous application of inhibitors and both low and high current density will be compared with those observed using only a single protection method such as inhibitor or electric field. The results will be presented and discussed in chapter 8. This will help in understanding the mechanism of the enhancement of the protective effect on combining the two methods.

The remainder of this thesis consists of five chapters, each of which will present the appropriate experimental procedures, results and discussion. The final chapter will summarise the conclusions and future work suggestions.

This work may lead to a better understanding of the mechanism of protection offered by inhibitor molecules at the steel surface, diffusion of these molecules in concrete and the key factors, that affect these processes.

CHAPTER 4

EVALUATION OF INHIBITOR EFFICIENCY AND MECHANISM IN A SATURATED CALCIUM HYDROXIDE SOLUTION

4.1 - INTRODUCTION

Various inorganic and organic based inhibitors, developed for the abatement of rebar corrosion in reinforced concrete structures, have been described in chapter 2. The role of nitrite-based anodic inhibitors as concrete admixtures and their possible mechanism of action to repair the passive film, ruptured by the attack of the chloride (Rosenberg and Gaidis, 1979), has also been discussed. In contrast to the inorganic anodic inhibitors, organic amine based "migratory corrosion inhibitors" MCIs, seem to be more versatile in that they can be used as a rehabilitation measure in existing structures, as well as admixtures in concrete patch repair or in a new structure. They have the claimed advantage that when applied at the surface of the concrete, these inhibitors can diffuse through the concrete matrix towards the steel reinforcement and protect the steel from further corrosion (Bjegovic et al., 1993; Nmai et al., 1992). Although attempts have been made to postulate their mechanism of action, the exact mechanism by which these MCI's are able to protect the steel and the parameters governing their action are not clearly understood. For example, whether the inhibitor provides a chemical barrier to diffusion of oxygen, chloride and other reactive species, or whether there is some other mechanism by which these MCI's operate needs to be investigated. Furthermore, the ability of this film to resist the attack of the corroding species for longer duration, and the possibility of the reaction of the inhibitor with chlorides is uncertain.

Hence, evaluating the performance of these organic inhibitors against the established inorganic nitrite-based admixtures is important. In this chapter an initial screening of a number of potential organic amine inhibitors and commercial inhibitors has been carried out. A select number of these inhibitors are then used for further investigation in terms of the level of protection they offer, time dependency of this protection, and finally

attempts are made to postulate the mechanism of inhibition at the steel/solution interface. Three amine-based inhibitor systems selected for further assessment, based on the initial screening results in this chapter. These are, a simple organic amine, dimethylethanolamine (termed as DMEA); a quaternary amine nitrite, dicyclohexylamine nitrite (labelled as DICHAN), which may combine the effects of both organic amines and an inorganic oxidising anion; and a commercial organic amine-based migratory inhibitor MCI. The performance of these amine-based systems is compared with the action of an inorganic oxidising inhibitor, sodium nitrite. In particular, the influence of these inhibitors on a prepassivated steel surface, representing the state of the steel in a newly built structure, and a corroding steel surface as would be found in the case of an existing deteriorating structure, is investigated. The effect of change in concentration of inhibitors on the inhibition capacity is also investigated. In the case of inorganic nitrite-based inhibitors attempts are made to correlate inhibition capacity to the ratio of chloride:nitrite. The inhibitive capacity of any given inhibitor is estimated in this work using the linear polarisation resistance technique and corrosion potential measurements.

4.2 - EXPERIMENTAL PROCEDURE

4.2.1 - Materials (Preparation of Sample and Solutions)

All the experiments described in this chapter for evaluating the inhibitor efficiencies were carried out using saturated calcium hydroxide solution. The rate of diffusion of reactants such as chloride, oxygen and inhibitors is not limiting in the calcium hydroxide solution as is the case of steel corrosion in the concrete specimen. Hence a rapid determination of the extent of corrosion/inhibition and its mechanism at the steel concrete interface under an accelerated environment is made possible. Further, in the solution experiments the effectiveness of inhibitor systems can be determined purely on the basis of their inhibition capacities without taking significantly into considerations their diffusion characteristics. Besides these factors, the solution medium being a homogeneous medium as compared with solid concrete, makes the environment in contact with the steel more predictable.

It should be recognised that the pH of saturated calcium hydroxide solution is 12.5 (Hausman, 1967) whereas that for actual concrete pore water has been reported to be approximately 13.5 (Gouda, 1970). A solution containing small amounts of calcium hydroxide in 0.1M KOH may simulate concrete environment better than plain saturated calcium hydroxide solution (Hinatsu et al., 1988). Nevertheless for the purpose of simplicity and to avoid influence of additional chemical species on the reaction kinetics, a single component solution of calcium hydroxide has been used as an electrolyte in the present work in order to carry out a comparative evaluation of different inhibitor systems.

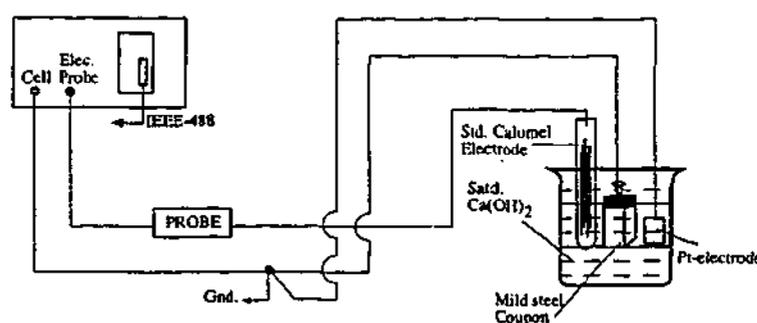


Figure 4.1 – Schematic diagram of a three electrode cell

A standard three-electrode cell design was used. Figure 4.1 shows a schematic diagram of the test cell. The mild steel coupon having dimensions 40x18x4 mm was used as a working electrode and 1000 mm² platinum mesh was used as the auxiliary electrode. Each specimen was drilled, tapped and suspended using a wire lead for the electrical contact. Prior to each experiment, the coupon surface was wet abraded with 400 and 1200 grit silicon carbide papers, washed, rinsed with acetone and dried in a stream of warm air. Experiments were carried out in a test solution of 500 mL of saturated calcium hydroxide. Sodium chloride 2 wt% (chloride 1.2%) was used as a corrosion initiator. A general study on a range of inhibitors was undertaken initially in order to select a few representative inhibitors for further investigations. Calcium hydroxide, sodium chloride, and a range of individual amines such as dicyclohexylamine nitrite (termed as DICHAN), dimethylethanolamine (DMEA), monoethanolamine, triethanolamine, cyclohexylamine, and dicyclohexylamine, used in the initial screening experiments, were of analytical grade and were supplied by Aldrich chemicals. The MCIs- commercial 1, 2 and 3 inhibitors were supplied by Cortec Corporation, USA. The inhibitors selected for further investigations were DICHAN, DMEA, and MCI commercial 1 (hereafter termed as MCI). A purely nitrite based inhibitor sodium nitrite

(supplied by Aldrich chemicals) was also selected for comparing the mechanism of action of organic amines versus inorganic nitrites at the steel surface. The concentration selected for the commercial MCI was 1 wt%, whereas that for the other inhibitors was 0.05M (equivalent to 0.4-1.0 wt % depending upon the molecular weight of each compound). DICHAN 0.05M (1.14 wt%), DMEA 0.05M (0.45 wt%) and sodium nitrite 0.05M (0.35 wt%). This range for the individual amines was chosen assuming that the commercial inhibitor contains about 50 % (or more) active ingredient. The mild steel coupons were immersed in a saturated calcium hydroxide solution with or without chloride or inhibitor, exposed to the atmosphere and left unstirred. All experiments were performed under quiescent conditions.

4.2.2 - Setup and Procedure

It was observed that pH of all the solutions, i.e. calcium hydroxide solution with and without addition of chloride and inhibitor, decreased as a function of time (over a test period of 214hours/~9 days) on exposure to the atmosphere, probably due to the carbonation of $\text{Ca}(\text{OH})_2$. However, since the linear polarisation resistance and corrosion potential measurements for all test systems were carried out under identical conditions they are assumed to be influenced to a similar extent by the carbonation factor in all cases.

Six different experiments were carried out simulating possible exposure conditions experienced by rebar embedded in concrete in real life.

1. Saturated calcium hydroxide solution (passive state): Coupons were immersed in a saturated calcium hydroxide solution without the addition of salt or inhibitor. This experiment provided a simple model of a mild steel rebar embedded in concrete in the absence of the corrosion initiator or inhibitor and also demonstrated the formation (and stability) of the passive film under these conditions.
2. Control sample: The experiments were performed as in experiment 1, but with the addition of 2 wt % sodium chloride to the saturated calcium hydroxide solution. This experiment was designed to simulate the actively corroding rebar in concrete under accelerated corrosion conditions, thus providing a "control" sample ($R_{p\text{control}}$).
3. "Prepassivated" condition: In this case the samples were in a prepassivated condition, where inhibitor was added to the saturated calcium hydroxide solution 2

- hours prior to the addition of chloride in order to allow inhibitor to form a film on the steel surface. Measurements were taken after the addition of sodium chloride.
4. "Corroding" condition: Steel coupons were subjected to a corrosive salt environment before adding inhibitor, representing a "pre-corroded situation". Electro-chemical measurements in these experiments were taken after the addition of inhibitor to the chloride containing saturated calcium hydroxide solution.
 5. Effect of removal of the aggressive species: DICHAH was used under "corroding" test conditions (as in experiment 4) to assess the persistency of inhibitor film at the steel/solution interface after removal of the corroding chloride species. In this case, on reaching the highest polarisation resistance after addition of inhibitor to the corroding environment, the coupon was removed from its original calcium hydroxide bath containing chloride and inhibitor and immersed into another test cell containing 2 wt % solution of sodium acetate (a non aggressive electrolyte) and the trend in the polarisation resistance was followed as a function of time.
 6. Effect of variation in concentration: Additional experiments were carried out using 0.01 and 0.1 M concentrations of nitrite based inhibitors sodium nitrite and DICHAH under prepassivated condition to assess the effect of change in inhibitor concentration on the protection level.

Linear polarisation resistance measurements and corrosion potential measurements were carried out at short time intervals initially in order to monitor any changes in the corrosion rate due to the addition of inhibitor or sodium chloride to the calcium hydroxide solution. Subsequent measurements were made every 24 hours for a period of 214 hours (~9 days). The resistance to corrosion attack due to the presence of inhibiting film on the steel was examined by comparing the scans under "prepassivated" and "corroding" conditions with those obtained in a freely corroding system (control sample) and a passivated system in a saturated calcium hydroxide solution.

4.2.3 - Monitoring Corrosion Behaviour of Steel Using the Linear Polarisation Resistance Technique and Corrosion Potential Measurements

The linear polarisation resistance technique (LPR)

The most common method used to determine the inhibitive capacity of any given inhibitor, as reported by researchers in this field (Hausler, 1977) utilizes linear polarisation resistance (LPR) measurements. The principles of the linear polarisation

resistance method, the theoretical basis for its measurement and its limitations have been discussed in section 2.4.4. In spite of its limitations, measurement of polarisation resistance has been shown to be a valuable technique in making qualitative comparison of the relative inhibition capacities of different inhibitors (Hettiarachchi and Gaynor, 1992). In the present work, the corrosion inhibition was measured via measurement of R_p (Hettiarachchi and Gaynor, 1992) and the percentage inhibition (corrosion inhibitor efficiency) was calculated as per Equation 2.4.

The LPR measurements were carried out using a computer controlled PAR 173 potentiostat using Softcorr Model 332 software and the procedure followed was as per ASTM G59 (ASTM G59-97, 1999). The potential was scanned from -30 mV to +30 mV, relative to the corrosion potential (E_{corr}) of the specimen at a rate of 10 mV/min (0.1667 mV/s) and the resulting current was monitored as a function of time. The change in potential ΔE was plotted against the current density, "i". The slope of the ΔE vs i plot at E_{corr} is the polarisation resistance R_p (assuming the linearity of the plot for values of ΔE between -15 mV to +15 mV relative to the E_{corr}).

Corrosion Potential Measurements

The open circuit potentials (OCP)/corrosion potentials (E_{corr}) of the passivated, control and inhibited steel coupons were measured against a saturated calomel electrode (SCE) using a digital PAN 2710 multimeter having high input impedance ($10^{10} \Omega$). The shifts in the potentials on the addition of chloride and inhibitors were monitored in order to examine the probability of corrosion or inhibition. The nature of the shifts in the measured potential values, was also used to postulate the dominant mechanism of action of different inhibitor systems.

4.3 – EVALUATION OF THE PERFORMANCE OF INHIBITORS IN TERMS OF THE LEVEL OF PROTECTION AND CORROSION POTENTIALS

4.3.1 - Passivation of Steel in Concrete under Ideal Conditions

Following exposure of the steel coupon to a saturated calcium hydroxide solution, (experiment 1) the open circuit potential moved from -310 mV_{SCE} to -115 mV_{SCE}. This

is indicative of a low probability of corrosion, due to the formation of a stable passive oxide film on the surface of the specimen in this highly alkaline environment (Pourbaix, 1966). Under the particular conditions that is mild steel at high pH, an oxide film of thickness probably between 1.7 and 5.0 nm (17-50 Å) (Cohen, 1976; Gilroy and Mayne, 1965; Jurek and Szklarska-Smialowska, 1976; Mayne and Page, 1972; Reinoehl and Beck, 1969) develops on the steel surface which hinders corrosion. The initial rapid increase of the potential (105 mV in 30 minutes) is consistent with the idea that the initial oxide formation, ie when the oxide thickness attains a few atomic layers, is the most important stage of the process (West, 1980). Further thickening of the oxide layer occurs over several days. At longer times, it is likely that equilibrium is reached between oxide formation and dissolution resulting in a stable potential ($\cong -115 \text{ mV}_{\text{SCE}}$).

4.3.2 - Actively Corroding Steel in A Calcium Hydroxide Solution under Accelerated Corroding Conditions

On immersing a clean steel specimen into a saturated calcium hydroxide solution containing 2 wt % sodium chloride (experiment 2), small rust spots developed within 20-25 minutes. This was accompanied by a rapid drop in the corrosion potential, E_{corr} , from $-390 \text{ mV}_{\text{SCE}}$ to $-585 \text{ mV}_{\text{SCE}}$ over a period of 9 days. The polarisation resistance also dropped gradually from 0.57 to 0.16 kohms indicating an increase in corrosion activity, consistent with the visual observations. The decrease in R_p and E_{corr} are consistent with an increase in the relative size of the anodic sites and is indicative of the breakdown of the passive oxide film due to the presence of chloride ions, Iron dissolution follows. As might be expected, the equilibrium potential attained is in the imperfect passive region of the potential/pH diagram. The R_p value measured for this control sample ($R_{p\text{control}}$) was used in determining inhibition capacities in the following experiments.

4.3.3 - Effect of Inhibitors on Corrosion Behaviour of Steel under Alkaline Conditions in the Presence of Chloride ("Prepassivated Situation")

When steel coupons were immersed in a saturated calcium hydroxide solution containing inhibitor (experiment 3), a positive shift of 100 to 150 mV in the open circuit potentials was observed suggesting passivation of the steel. From these potential measurements alone it is not clear whether the passivation of steel surface is due to

ferric oxide formation (as observed in experiment 1) or due to the formation of an inhibitor film. However, R_p and hence % inhibition values obtained for different inhibitors, immediately after addition of chloride, suggest that the inhibitor film formation is likely and the nature of the inhibitor determines the effectiveness of the barrier film. Table 4.1 shows representative R_p values, % inhibition and E_{corr} for DMEA and control sample under the "prepassivated" condition.

Period (h)	Control		DMEA		
	R_p kohms	E_{corr} mV _{SCE}	R_p kohms	E_{corr} mV _{SCE}	Inhibn %
0.01	0.571	-388	3.960	-247	86
0.08	0.496	-396	2.090	-284	76
0.17	0.356	-420	0.960	-394	63
0.25	0.268	-433	0.730	-421	63
0.33	0.264	-450	0.677	-418	61
0.42	0.266	-452	0.620	-425	57
0.50	0.254	-462	0.560	-436	55
0.58	0.249	-466	0.550	-440	55
0.67	0.242	-471	0.534	-445	55
0.75	0.253	-470	0.503	-453	50
0.83	0.249	-470	0.503	-456	50
0.92	0.253	-471	0.504	-458	50
1	0.246	-471	0.502	-459	51
1.17	0.261	-474	0.503	-464	48
1.33	0.246	-477	0.520	-464	53
1.50	0.240	-480	0.527	-464	54
1.67	0.246	-480	0.530	-465	54
1.83	0.248	-482	0.512	-467	52
2.00	0.250	-481	0.514	-469	51
2.33	0.234	-480	0.493	-472	53
2.67	0.236	-482	0.517	-475	54
3	0.239	-484	0.517	-475	54
3.5	0.236	-490	0.509	-477	54
4	0.239	-487	0.525	-477	55
5	0.256	-471	0.462	-485	45
6	0.245	-481	0.420	-491	42
7	0.219	-489	0.414	-488	47
8	0.223	-485	0.407	-491	45
22	0.235	-512	0.404	-507	42
26	0.235	-522	0.414	-507	43
30	0.248	-534	0.412	-507	40
46	0.250	-548	0.456	-525	45
54	0.253	-565	0.494	-531	49
70	0.241	-556	0.540	-519	55
94	0.236	-560	0.488	-519	52
118	0.221	-550	0.592	-522	63
142	0.217	-554	0.433	-517	50
166	0.217	-547	0.374	-519	42
190	0.161	-572	0.221	-554	27
214	0.160	-586	0.178	-532	10

Table 4.1 - Representative data (R_p values, % inhibition and corrosion potentials as a function of time) for DMEA (prepassivated condition) and control sample.

A complete summary of % inhibition and corrosion potentials for various inhibitors evaluated during the preliminary study under prepassivated condition appears in Table 4.2.

Inhibitor	Immediate Level (<0.1 h)		End Level (214 h)	
	Inhibn.	Ecorr	Inhibn.	Ecorr
	%	mV _{SCE}	%	mV _{SCE}
MCI Commercial 1	>90	-230	5	-490
MCI Commercial 2	99	-115	85	-505
MCI Commercial 3	90	-220	5	-480
Monoethanolamine	>90	-240	25	-500
Triethanolamine	80	-240	0	-530
Dimethylethanolamine	85	-250	10	-530
Cyclohexylamine	>90	-235	20	-545
Dicyclohexylamine	99	-135	35	-505
Dicyclohexylamine Nitrite	98	-175	80	-470

Table 4.2 - Comparative data on % inhibition and corrosion potentials - prepassivated condition

Clearly almost all the inhibitors appeared promising at the initial level with efficiencies in the range of 80-99%. However on closely monitoring their long-term behaviour, it was observed that only some inhibitors could perform well in relation to time in an alkaline chloride environment. Hence, only a few representative amine-based inhibitors were selected for further studies. These inhibitors were MCI commercial 2, dicyclohexylamine and dicyclohexylamine nitrite (DICHAN). Additionally,

dimethylethanolamine (DMEA), even though it displayed a moderate performance in the aggressive chloride containing environment, was also included in this group of amine-based inhibitors, as this inhibitor is an aliphatic alkanolamine and represents a different class of compounds from the above cyclic amine based compounds. On analysing commercial MCIs using gas chromatography/mass spectroscopy technique, the following components were found: 1,2 ethanediamine n-ethyl, benzoic acid ammonium salt, 2-propenamide, n-2-(dimethylamino)ethyl, 1,2-benzene dicarboxylic acid bis (2-ethylhexyl) ester, cyclohexylamine, octadecanoic acid, 2-methylpropyl ester.

Since DICHAN and dicyclohexylamine contained the same amine component i.e. dicyclohexylamine group, only DICHAN out of the two inhibitors was selected for further investigations. Further, the selection of this mixed inhibitor was made because of the possibility of combining the effects of both organic amine (dicyclohexylamine) and an inorganic oxidising anion (NO_2^-). Also at this stage a decision was made to include a purely anodic inhibitor, sodium nitrite, in these investigations in order to compare and contrast the mechanism of action of an inorganic oxidising anion (NO_2^-) with that of organic cationic amine molecules. It was presumed here that the nature of protection provided by sodium nitrite would be similar to that offered by a commercial admixture calcium nitrite.

Figure 4.2 presents the % inhibition values for DICHAN, DMEA, MCI and sodium nitrite under the "prepassivated situation", using the average of anodic and cathodic slopes over a period of 214 hours. From these plots it appears that the inhibition behaviour is clearly dependent on the nature of the inhibitor. Figure 4.3 shows corrosion potentials vs SCE for the above inhibitors. On comparing the results for different inhibitors it was observed that DICHAN maintained a high level of inhibition for several days in comparison with the other inhibitors. The initial high level of inhibition (98%) decreased to approximately 80% towards the end of the test period of 214h. As seen in Figure 4.3, the corrosion potentials increased slightly from -175 to -163 mV_{SCE} (1 hour), dropped to -240 mV_{SCE} after 8 hours and then gradually decreased to -470 mV_{SCE} . The slight increase in the potential in the beginning may suggest anodic inhibition. The high level of inhibition observed in the case of this inhibitor is believed to be due to an additional protection offered by the nitrite component at the anodic sites.

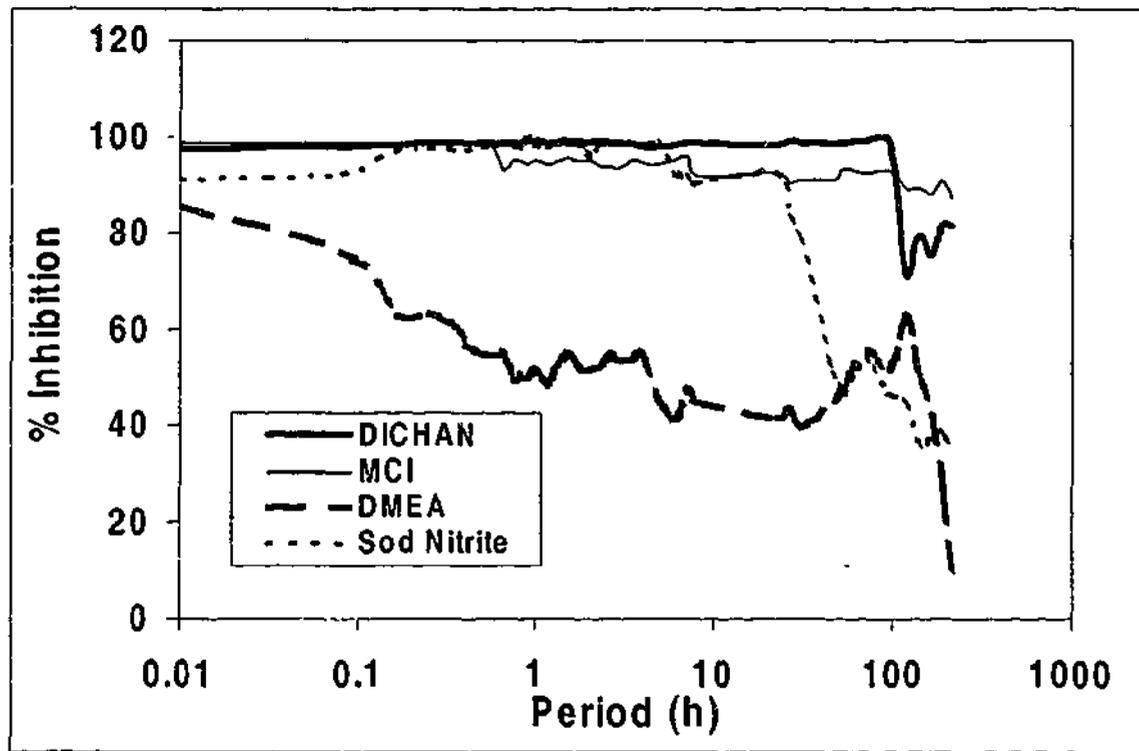


Figure 4.2 – Comparative study of % inhibition for different inhibitors under "prepassivated" condition

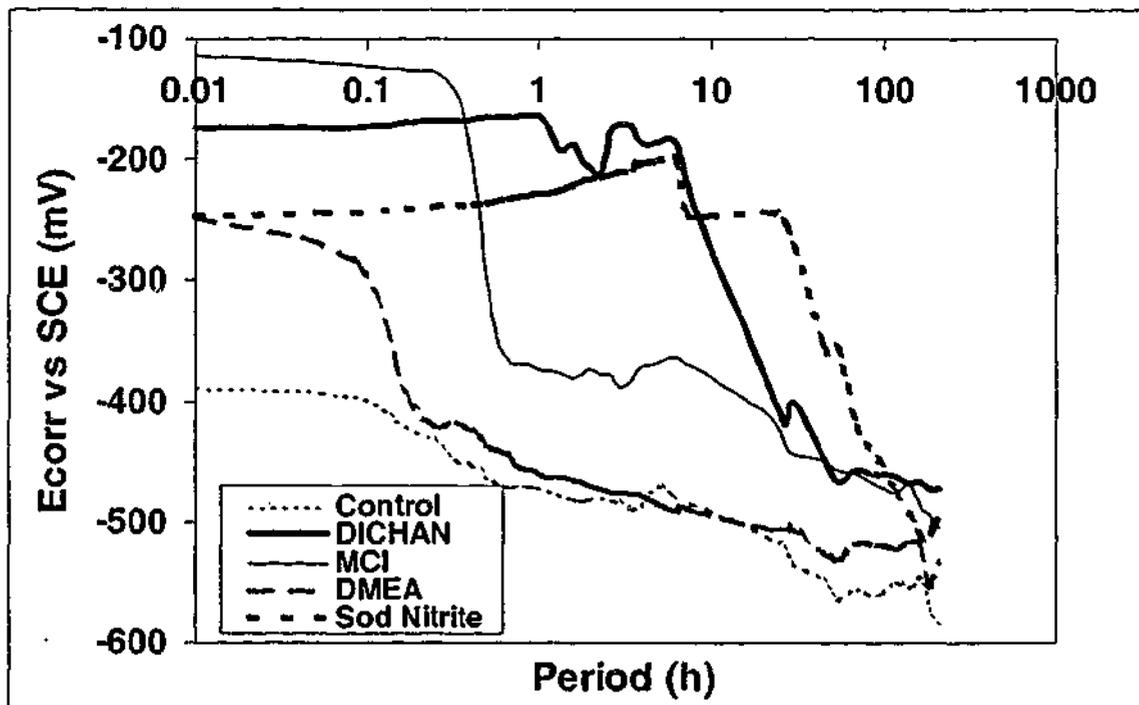


Figure 4.3 – Comparative study of E_{corr} for different inhibitors under "prepassivated" condition

The trends in inhibition and E_{corr} (Figures 4.2 and 4.3), exhibited by the commercial inhibitor MCI were similar to those displayed by DICHAN. In this case the high

inhibition level of 99% was maintained for a long period and gradually decreased to about 90% towards the end of the test period i.e. 214h. This suggests that MCI forms a highly protective barrier film which retains its resistance to the ingress of corroding species for an extended period. The corrosion potential in this case decreased from -115 mV_{SCE} to -505 mV_{SCE} (Figure 4.3). This may be due to an increase in the corrosion activity or the dominant cathodic nature of inhibition process (section 2.4.3). However, the high level of inhibition maintained throughout the test period for MCI in Figure 4.2 for the corresponding decrease observed in the potential in Figure 4.3 supports the possibility of cathodic inhibition.

Dimethylethanolamine (DMEA), although demonstrating a high initial level of inhibition (85 %) (Figure 4.2), became less effective within 30 hours, decreasing to approximately 10 % inhibition after 214 hours. The corrosion potential (Figure 4.3) showed a gradual decrease from -245 mV_{SCE} to -530 mV_{SCE} towards the end of the measurement period. A negative shift in the potential coupled with appearance of tiny rust spots at the bottom of the coupon, and the decreasing trend in % inhibition observed towards the end of the test period, suggest local breakdown of the passive film and accompanying increase in the anodic area.

The nitrite based inorganic inhibitor sodium nitrite demonstrated a high level of inhibition (98 %) in the beginning, as was observed in the case of the amine-based inhibitors. However, the level decreased to 90% after 6 hours and exhibited a sudden drop to 50 % after 46h. The % inhibition exhibited by this anodic inhibitor towards the end of the exposure period was 35 %. Corrosion potential in this case moved in a positive direction from -246 mV_{SCE} to -200 mV_{SCE} in 6 confirming an anodic inhibition mechanism. However, after this point the increasing trend in the potential reversed and the potential then exhibited a continuous decrease to finally reach a highly cathodic value of -500 mV_{SCE} at the end of the measurement period, suggesting breakdown of the protective oxide film and active corrosion due to chloride attack.

4.3.4 - Effect of Adding Inhibitor to the Chloride Contaminated Alkaline Environment Containing Corroding Steel ("Corroding Situation")

Figure 4.4 presents the % inhibition results for the experiments where inhibitor was added to the system after the steel coupon was already corroding due to chloride attack.

A comparison of the time dependence of E_{corr} is demonstrated in Figure 4.5 and may help in understanding the mode of action of inhibitors. In both the figures an initial part of the graph i.e. the part between 0.01 to 0.25 hours indicates the initial conditioning period when steel was exposed to a corroding environment without addition of inhibitor. Rust spots were seen to develop within the conditioning period accompanied by a negative shift in the corrosion potential to $-400 \text{ mV}_{\text{SCE}}$ and a decrease in R_p . The slow fall in the R_p and E_{corr} values initially in all the cases is indicative of the breakdown of the oxide film and the onset of corrosion. The point shown by the arrow on the graph indicates the time when inhibitor was added to this corroding system. Addition of inhibitor to the corroding system at this stage resulted in a dramatic reversal of the corrosion trend with individual inhibitors exhibiting varying degrees of inhibition levels. Table 4.3 presents % inhibition and corrosion potentials at various stages e.g. immediately on addition of inhibitor to the corroding system, on achieving the highest inhibition level and at the end of the monitoring period in the case of DICHAN, DMEA, MCI and sodium nitrite inhibitors. It was observed that, with the exception of commercial MCI, all the inhibitors showed a declining inhibition capacity with the passage of time.

It is apparent from Figures 4.4 and 4.5 that the system subjected to DMEA treatment showed moderate and time dependent remedial inhibition properties. On addition of this inhibitor to the chloride containing solution, inhibition based on the $R_{p\text{control}}$ value (experiment 2) increased from zero level to a maximum 40 % within one hour, and then started to decrease towards the end of the test period to give polarisation resistance measurements equivalent to that of the control sample. Contrary to the trend observed in % inhibition, the corrosion potential exhibited a gradual decrease from $-425 \text{ mV}_{\text{SCE}}$ to $-515 \text{ mV}_{\text{SCE}}$ (as seen in Figure 4.5). The initial fall in potential from $-425 \text{ mV}_{\text{SCE}}$ to $-445 \text{ mV}_{\text{SCE}}$ for one hour as the inhibitor efficiency increased is consistent with a predominantly cathodic inhibition process, whereas a further decrease to $-515 \text{ mV}_{\text{SCE}}$ after one hour could be considered to be due to the onset of active corrosion. A possible explanation of the decrease with time of inhibition by DMEA is that the inhibitor is adsorbed at the bare metal sites, produced by the action of chloride ions on the passive film. The inhibitor molecules compete with the chloride ions resulting in lowering of the overall corrosion rate. However, the moderate level of inhibition and the waning effect with time suggest that the film formed by this inhibitor is not very protective. It is likely that the inhibitor film is porous and partially permeable to the aggressive ions.

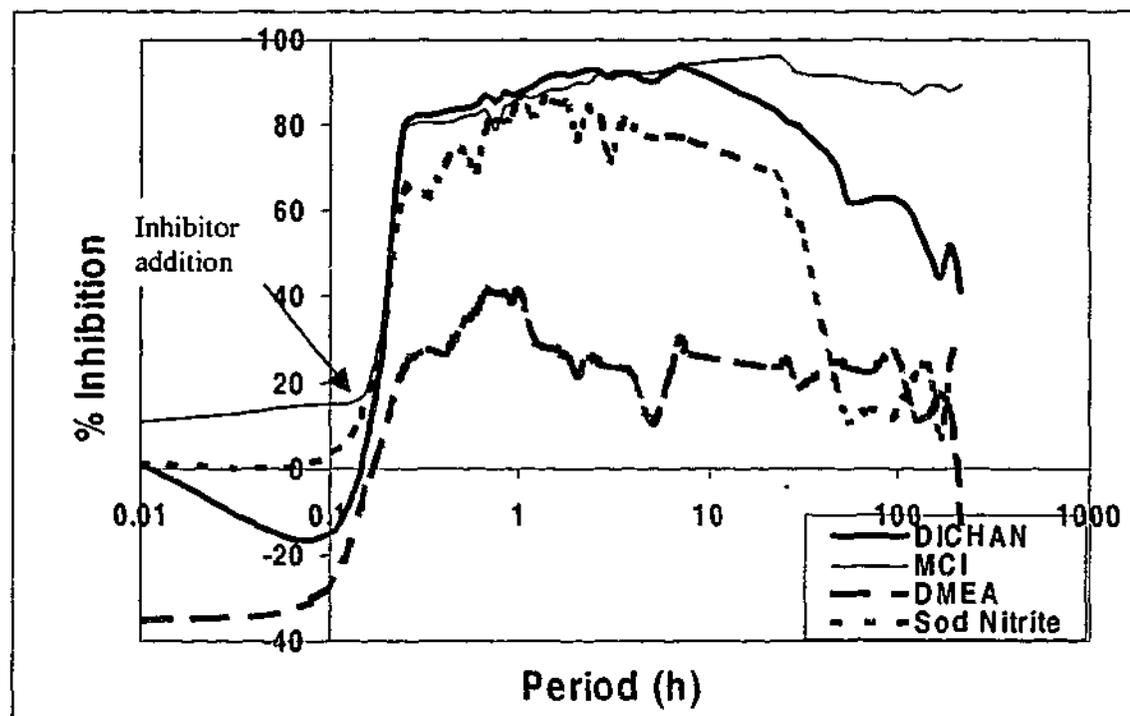


Figure 4.4 – Comparative study of % inhibition for different inhibitors under "corroding" condition

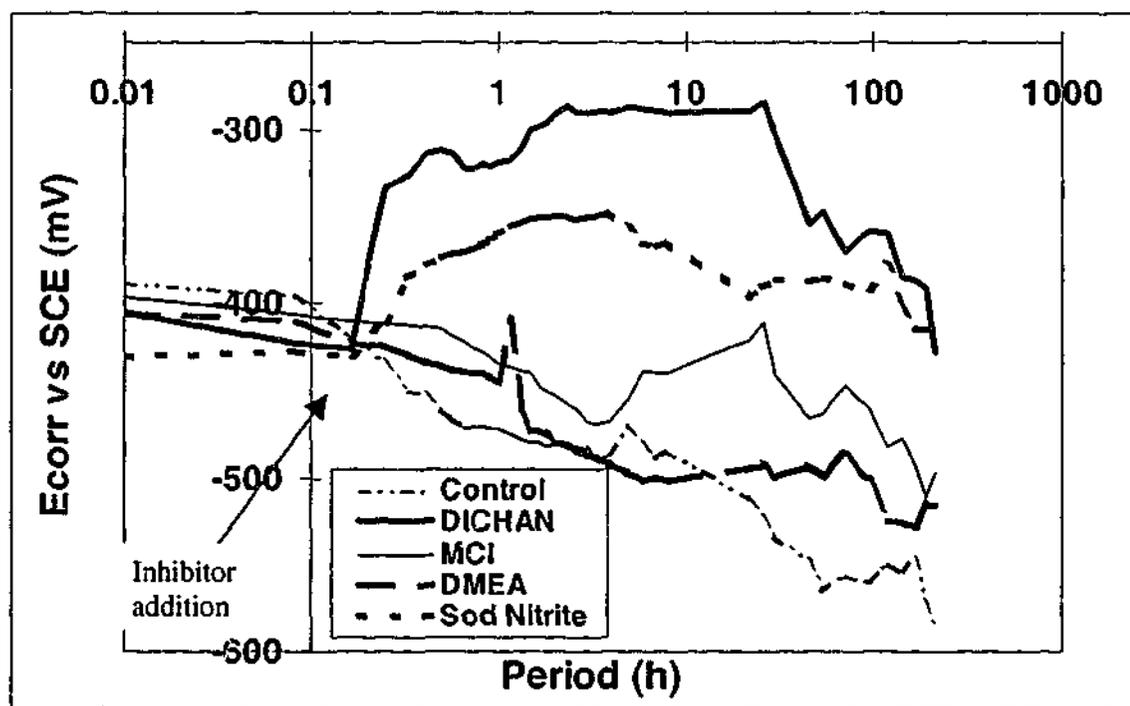


Figure 4.5 – Comparative study of E_{corr} for different inhibitors under "corroding" condition

Inhibitor	Initial Level (Immediately on addition of inhibitor - <0.01 h)		Highest Level			End Level (214 h)	
	Inhibn %	Ecorr mV _{SCE}	Inhibn %	Ecorr mV _{SCE}	Time h	Inhibn %	Ecorr mV _{SCE}
MCI	80	-410	95	-410	26	90	-495
DICHAN	80	-335	95	-290	7	40	-430
DMEA	25	-425	40	-445	1	0	-515
Sodium Nitrite	65	-385	85	-360	1	20	-415

Table 4.3 - Comparative data on % inhibition and corrosion potentials at different stages- "corroding condition"

Hence with the passage of time it ceases to provide a resistive path to chloride ions. This results in the increase in the anodic area on the surface of the steel coupon and a decrease in inhibition. The "delicate" nature of the DMEA film could be attributed to the relatively small straight chain aliphatic constitution of inhibitor molecule. The issue of partial anodic characteristics of this predominantly cathodic inhibitor is studied in chapter 5 using cyclic voltammetry.

A mild steel coupon immersed in chloride containing alkaline environment exhibited excellent remedial properties on addition of DICHAN to the solution as is evident from Figure 4.4. After addition of the inhibitor, the inhibition increased immediately from the control level to 80% and further increased gradually to 95% within 7h. After this the increasing trend reversed and the inhibition started to decrease gradually reaching 40

% at 214 hours. The corrosion potential, E_{corr} , showed an abrupt increase in value from $-425 \text{ mV}_{\text{SCE}}$ to $-335 \text{ mV}_{\text{SCE}}$ immediately on the addition of inhibitor to the corroding system. The trend continued further and peaked at a level of $-290 \text{ mV}_{\text{SCE}}$ around 2h. The potential was maintained around the same value up to 26 hours before dropping to a final level of $-430 \text{ mV}_{\text{SCE}}$ at 214 hours (Figure 4.5). As discussed earlier, when the system is freely corroding in absence of an inhibitor, the chloride ions induce chemical disturbances in the oxide film layer of the underlying metal, and the metal starts dissolving at the points where the oxide film is broken. This results in the potential decreasing to a value below $-400 \text{ mV}_{\text{SCE}}$. When DICHA is added to the corroding system, the nitrite ions may assist in repairing the ruptured oxide film and prevent further corrosion by inducing repassivation. This explains the increase in E_{corr} from $-425 \text{ mV}_{\text{SCE}}$ to $-335 \text{ mV}_{\text{SCE}}$. Thus the dominant mechanism, at least initially, is anodic control due to the NO_2^- reaction. The decrease in both E_{corr} and inhibition at longer time suggests the onset of corrosion process due to attack of chloride ions on the passivating film.

A marked rise in the % inhibition from an accelerated corrosion level to 65% (Figure 4.4) was observed on addition of sodium nitrite to the corroding coupon immersed in a chloride contaminated alkaline environment. The inhibition continued to increase further and peaked at 85% within one hour, fluctuated between 80-85% up to 4 hours and gradually decreased to 55% by 30 hours of exposure time. After this period however, inhibition showed an abrupt fall to 20%. A distinct rise in the corrosion potential from $-430 \text{ mV}_{\text{SCE}}$ to $-360 \text{ mV}_{\text{SCE}}$ was observed in one hour for the corresponding increase in the inhibitor action suggesting the building up of the passive film at the anodic sites. The potential was sustained between $-350 \text{ mV}_{\text{SCE}}$ to $-360 \text{ mV}_{\text{SCE}}$ until 4 hours and then dropped to $-415 \text{ mV}_{\text{SCE}}$ towards the end as the available nitrite is used up.

The steel exposed to commercial MCI inhibitor exhibited similar trends in the percentage inhibition, however the overall level of protection was slightly higher than that observed for DICHA. On addition of inhibitor the protection level increased abruptly to 80% within a few minutes, the increase continued to peak at 95% around 26h, dropping subsequently to 90% at the end of the test period. Thus the inhibition level displayed at the end of the test period in the case of MCI, was much higher than that exhibited by DICHA suggesting a more persistent film formed by MCI on the

steel surface at the remaining portion of the passive oxide film (cathodic sites) as well as in anodic areas of the steel coupon where the passive oxide film is already breached. E_{corr} values in this case showed a gradual decrease from $-410 \text{ mV}_{\text{SCE}}$ to $-495 \text{ mV}_{\text{SCE}}$ (Figure 4.5), in contrast with those demonstrated in the case of steel exposed to DICHAN. Again this may be accounted for by increased corrosion activity or the dominant cathodic nature of the inhibition process. However, a significant increase in the inhibition level in the corresponding part of inhibition - time plot confirms that MCI acts primarily as a cathodic inhibitor (Table 4.3). Thus the overall level of protection offered by MCI was indeed much higher as compared with all the other inhibitors.

4.3.5 - The Inhibition Mechanism and the Effect of Individual Inhibitor Characteristics on this Mechanism:

From the above results it is clear that the inhibitor behaviour is dependent on the chemical makeup of the each inhibitor species. Corrosion inhibitors are known to interact strongly with the metal surface even when it is covered by an oxide layer (McCafferty, 1978). The performance of individual amines has been ascribed to the type and strength of the bond they form with Fe or Fe-O at the steel surface, and the compactness or permeability of the barrier layer formed due to interlocking of their hydrocarbon tails. The bond strength in the case of amine inhibitors is likely to depend upon the ease with which the nucleophilic nitrogen is able to donate its free electron pair. This bonding (adsorption) process may occur on both cathodic and anodic electrochemical sites as is evident from the movement of the cathodic and anodic slopes in case of the LPR measurements at different time intervals. The hydrophobic functionality, exhibited by the non-polar hydrocarbon tail of the inhibitor molecule oriented in the direction of the surrounding electrolyte, shields the metal surface from the aqueous corrosion media (see Figure 4.6). A secondary effect may be the physical sorption of inhibitor molecules from the surrounding fluid (by the barrier film) due to Van der Waals' forces. This may increase the thickness and effectiveness of the hydrophobic barrier (Nathan, 1973). This mechanism suggests that the size and shape of the inhibitor molecule have influence over thickness and density of the inhibitor film. However this barrier is not completely impermeable to chloride attack. The nature of the inhibitor and its ability to form an impenetrable barrier will then effect the extent of inhibition.

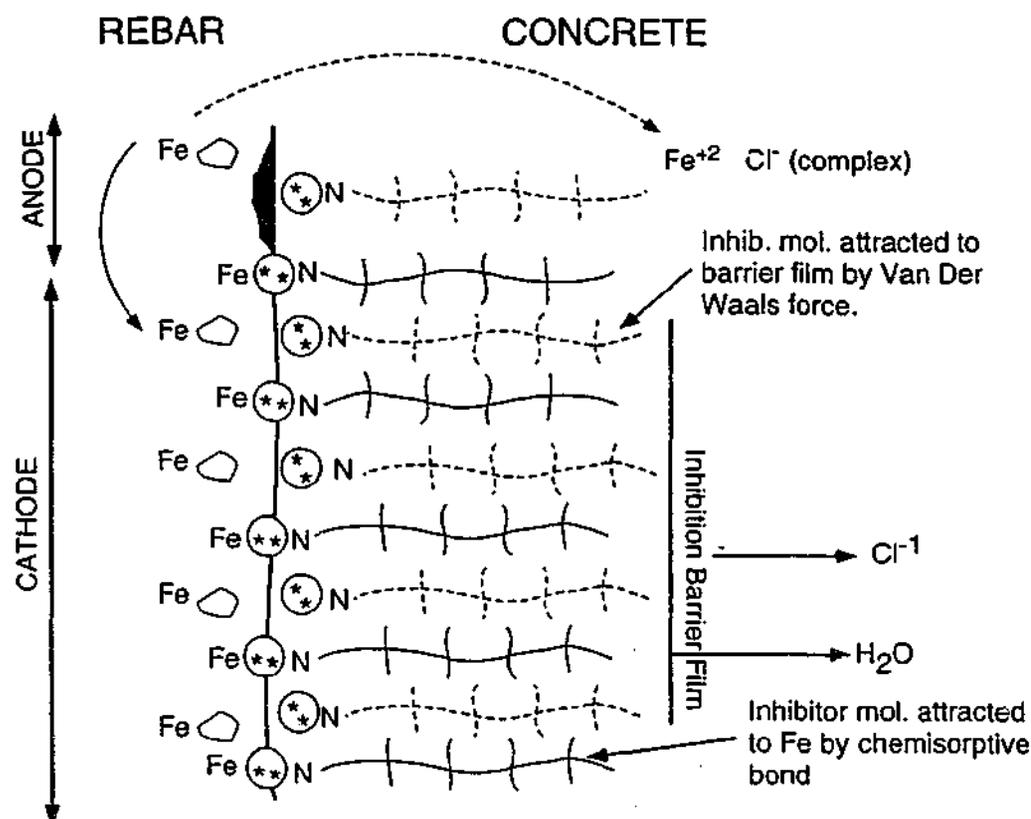
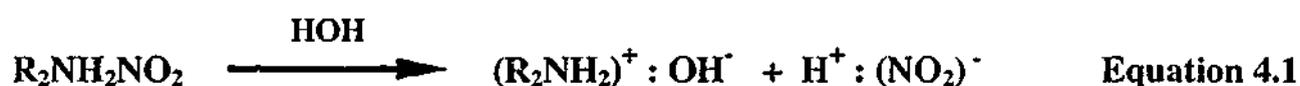


Figure 4.6- Schematic diagram of inhibition mechanism of organic amine-based inhibitors

Also it is observed that amongst the amine-based inhibitors, MCI and DICHAN form a protective film on the steel surface and maintain it for a longer duration, whereas the film formed in the case of DMEA is less resistive and is susceptible to chloride attack. It should be pointed out that the amine-based active ingredient in DICHAN is a dicyclohexylamine group (the other being a nitrite NO_2^- ion), whereas that in DMEA is an aliphatic (alkanol) amine. This suggests that the substituents in the alkanolamines and the cyclic amines may be able to modify the effectiveness of the amine to different degrees while forming a barrier film. Attempts are made here to elucidate the effect of the molecular properties of inhibitor, i.e. presence of aliphatic chain or the aromatic ring, type of amine group present in the molecule on the inhibitive action. As with all nucleophiles, the ability of the adsorption reaction to proceed depends not only upon the electron density at the nucleophilic centre, but also upon the stereochemistry surrounding it (McCafferty, 1978). In a closed ring structure there is a strain in the ring due to the crowding of electrons within the ring. This in turn has an inductive effect on an electron donating centre such as nitrogen in the amine group attached to the ring, thereby making this nitrogen a better electron donor. This may translate into an

increase in the strength of the chemisorptive bond with Fe at the steel surface, and possibly the level of inhibition, as was observed in the case of DICHAN.

Before discussing the high level of inhibition maintained by DICHAN it is important to mention that DICHAN is a quaternary amine compound. It is sparingly soluble in water forming a solution of pH 7, whereas its dissolution in saturated calcium hydroxide is much slower forming oily globules, which dissolve slowly to give a uniform milky solution. DICHAN is likely to ionise in aqueous solution and undergo substantial hydrolysis, the extent of which is almost independent of concentration (Miksic, 1983). The net result of these reactions may be given as follows:



The anion $(\text{NO}_2)^-$ adsorbs strongly on the steel surface with subsequent adsorption of quaternary inhibitor cation $(\text{R}_2\text{NH}_2)^+$ (Hettiarachchi and Gaynor, 1992). The high level of inhibition observed in this case may be due to the cooperative adsorption of the protonated inhibitor $(\text{R}_2\text{NH}_2)^+$, which may be electrostatically attracted to the chloride covered sites in addition to negatively charged oxy-hydroxy sites on the steel surface through the protonated hydrogen. Evidence for this type of adsorption has been reported under acidic conditions (Hackerman et al., 1966; McCafferty, 1978), where it has been postulated that the combination effect of a halide anion and organic cation inhibitor is many fold greater than that of the inhibitor alone (section 2.4.3/Figure 2.5). This synergy in inhibitor efficiency is attributed in part to the stabilisation of adsorbed anion layer by organic cations. Thus the cooperative adsorption mechanism effectively blocks the opening in the inhibitor/oxide film made by the chloride ions, thereby resulting in a greater inhibition capacity as compared to other non protonated organic amines. It may, however, be mentioned that in the high pH environment such as that existing in the saturated calcium hydroxide solution in the above experiments, it is unclear whether $(\text{C}_6\text{H}_5)_2\text{NH}_2^+$ or $(\text{C}_6\text{H}_5)_2\text{NH}$ molecules predominate considering a possibility of some interaction between the protonated inhibitor molecules and OH^- ions in the solution. Additionally the nitrite anion from this inhibitor itself is an anodic inhibitor, and can react to assist in the repair of the oxide film by oxidising ferrous to ferric ions at anodic sites (Equation 4.2) (Rosenberg and Gaidis, 1979). This is evidenced from the increase in the E_{corr} values on addition of inhibitor to the corroding steel.



In the case of MCI a rationalisation of the high inhibition behaviour may not be possible in the absence of the accurate knowledge of its components. MCI is assumed to contain an alkanolamine (section 2.5.2) (Martin and Miksic, 1989). It may be proposed that the nitrogen of the amine group in this case probably forms of a more efficient chemisorptive bond against the attack of aggressive chloride ions. Additionally carboxylic acid present in MCI (as suggested by gas chromatography/mass spectroscopy analysis) may adsorb on the oxide covered surface thus reinforcing the passive film (McCafferty, 1978)

4.3.6 - Waning of Inhibition with Time

All the above experiments (under both a "prepassivated" and "corroding" situation) have demonstrated that, with the exception of the commercial MCI, all the inhibitors showed a declining efficiency with time. Of the others, only DICHAN showed appreciable inhibition capacity after 100 hours. The steady loss in the corrosion mitigation capacity of the inhibitors, observed at longer times in these experiments, is thought to be a crucial factor in determining the long-term suitability of a particular inhibitor system.

It is postulated that inhibition stems from the active competition between aggressive Cl^- ion attack on the protective film and the restoration of this film by fresh inhibitor molecules from the surrounding environment. Anodic inhibitors are assumed to repair the oxide film or adsorb on the bare metal surface exposed by defects in the passive film whilst cathodic inhibitors adsorb on to the passive film thus hindering the cathodic reaction. On this basis the long term trend observed for different inhibition systems, including the steadily decreasing inhibition in most cases, can be modeled as follows: Like all adsorbed species, the chemisorbed amine molecules have a characteristic residence time at the metal surface. This residence time depends on the balance between the strength of the bond between the nitrogen and the iron ions at the steel surface and the solvating effect of the surrounding electrolyte. In a non-aggressive situation, these effects balance and a high level of inhibition is observed. However, in the presence of chloride ions, the site vacated by the inhibitor molecule is equally open for the adsorption of a fresh inhibitor molecule or a chloride ion. The heat of adsorption

of the chloride ions on iron has been calculated to be 45 kcal/mole (McCafferty and Hackerman, 1973), which is close to the energy of the metal-amine bond (McCafferty, 1978). Hence, it is possible that chloride adsorption at vacated sites occurs in competition with inhibitor adsorption and leads to a depolarisation of the anodic reaction and an increase in the rate of corrosion. The competitive adsorption process has been discussed in section 2.4.3. The exact role played by the inhibitor barrier film formed by the secondary adsorption of the inhibitor molecules over primarily chemisorbed inhibitor molecules may also have a controlling effect under this delicately balanced situation.

4.3.7 - Effect of Removal of Aggressive Species (Chloride Ions) From the Corroding Environment

In order to validate the above model of declining inhibition with time as a consequence of chloride attack, a further experiment (number 5) was carried out by removing coupons which had reached maximum protection during a "corroding condition" experiment (experiment 4), and placing them into a chloride free environment with and without added inhibitor. As a result of this change of environment, the inhibition level was maintained at >90% compared to control throughout the test period. This is consistent with the postulation that in the absence of the corroding ions, the inhibitor film remains intact. The corrosion potentials exhibited a slow but steady increase to a value of -95 mV_{SCE}. Figure 4.7 shows the effect of chloride removal on the level of inhibition.

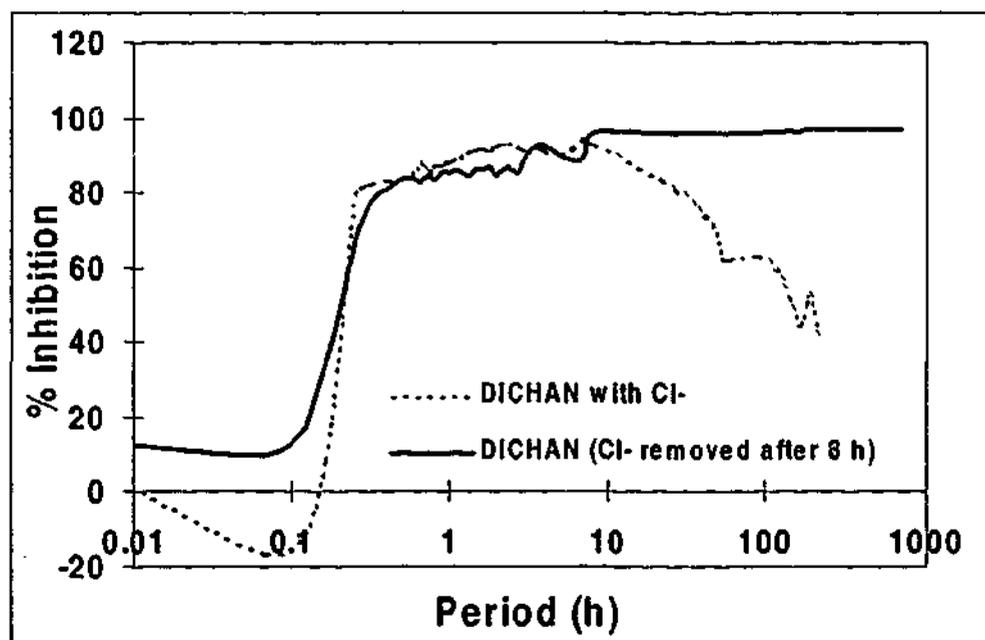


Figure 4.7 - The effect of removal of chloride on inhibition level in the case of DICHAN

4.3.8 - Effect of Change in Inhibitor Concentration on the Level of Inhibition

It is clear from the above discussions that there is a competition between the aggressive Cl^- attack on the protective inhibitor film and the restoration of this film by fresh inhibitor molecules from the surrounding environment. It was thought that the surface concentration of the reactants is most likely the underlying factor determining the kinetics of the corrosion or inhibition reactions in the presence of chloride and inhibitor. A detailed investigation of this factor will assist in determining the precise dosage levels and the frequency of inhibitor treatment and its relationship to the concentration of corroding/inhibiting species in any given environment. Hence the effect of inhibitor concentration on the inhibition level was investigated by carrying out additional experiments (number 6) using different concentrations of nitrite-based inhibitors sodium nitrite and DICHAN under the "prepassivated" condition. Figure 4.8 compares plots of inhibition levels with time for varying concentrations of sodium nitrite and DICHAN.

It is clear from the figure that, for both the inhibitors, an increase in the concentration resulted in a corresponding increase in the level of inhibition. The negative inhibition observed after 94 hours in the case of low concentration (0.01M) of sodium nitrite (chloride:nitrite ratio 26.4) is characteristic of an anodic inhibitor and suggests acceleration of the corrosion process due to depletion of nitrite ions. Table 4.4 summarises percentage inhibition values at the end of the test period (214 hours) *vis-a-vis* chloride:nitrite ratios for all the concentrations of sodium nitrite and DICHAN. It is apparent from the table that on increasing the sodium nitrite concentration level to 0.1M (chloride:nitrite ratio 2.6), the inhibition levels improved to those exhibited by DICHAN. In the case of DICHAN similar behaviour was obtained; however, 36% inhibition was obtained even at the lowest concentration (0.01M), which confirmed that the negative effect due to the depletion of the nitrite ions is compensated by the additional protection offered by the amine component. The concentration dependent action exhibited by purely anodic sodium nitrite is in accordance with Berke and Rosenberg (Berke and Rosenberg, 1989), who have recommended a ratio of chloride to nitrite to be less than 2 in the case of calcium nitrite, for any meaningful inhibition to be obtained.

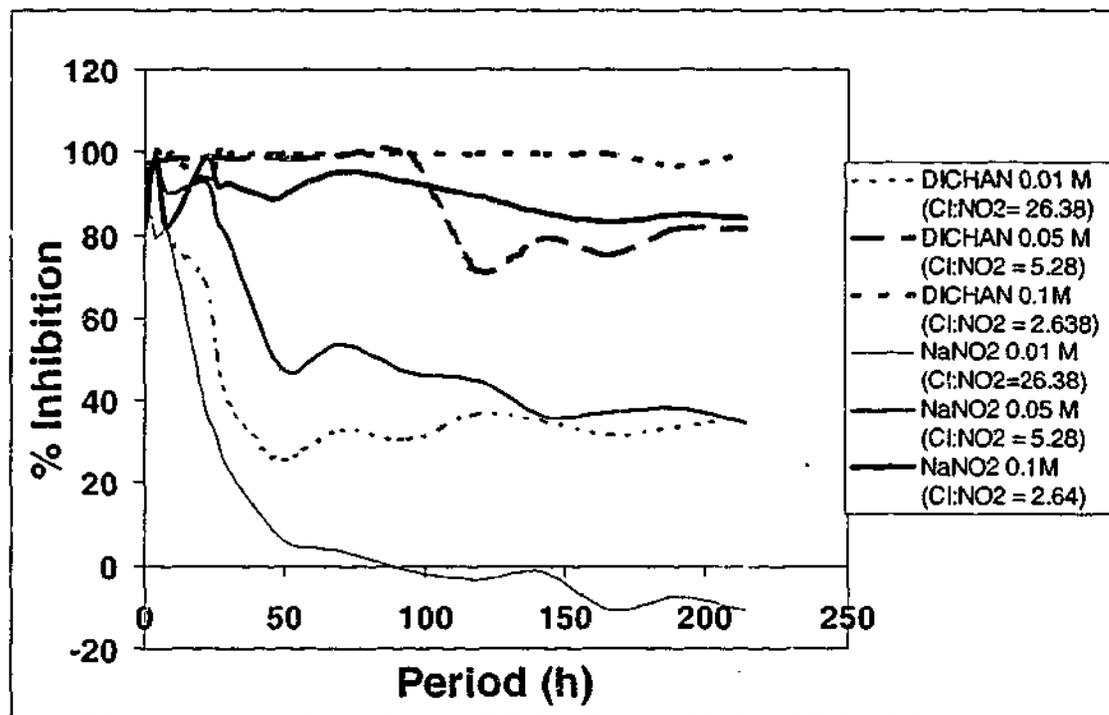


Figure 4.8 - Comparison of % inhibition at different concentrations of DICHAN and sodium nitrite

Chloride:Nitrite Ratio M conc	% Inhibition Sodium Nitrite	% Inhibition DICHAN
26.4 (0.01)	-11*	36
5.3 (0.05)	35	82
2.6 (0.1)	84	~100**
1.3 (0.2)	93	-

* - $R_{p\text{sample}} < R_{p\text{control}}$ resulting in negative inhibition

** - $R_{p\text{sample}} \gg R_{p\text{control}}$ ($R_{p\text{sample}} - R_{p\text{control}} \cong R_{p\text{sample}}$)

Table 4.4 - Comparison of inhibition *vis-a-vis* chloride:nitrite ratios at the end (214h) for different concentrations of sodium nitrite and DICHAN

4.4 – CONCLUSIONS

The results discussed in this chapter indicate that the absolute inhibition capacity as well as the time over which the inhibitor is active, depends on the nature of the inhibitor. The initial positive shift in the open circuit potential, where corrosion inhibition is observed, together with the marked effect on both cathodic and anodic values of R_p , suggest that the mechanism of inhibition is predominantly through the build up of a protective barrier layer which provides a resistive path to either ions or electrons thereby hindering both anodic and cathodic reactions. Organic aromatic amine based inhibitors, DICLAN and commercial MCI, offer excellent inhibition for longer times in contrast to aliphatic alkanolamine DMEA and the inorganic anodic inhibitor sodium nitrite. A very high efficiency observed for the extended periods in the case of a quaternary amine inhibitor DICLAN is attributed to the synergistic effect of the mechanism of barrier film formation by organic amines and interfacial chemical reactions by inorganic component. A positive shift in the corrosion potential in the case of nitrite-based inhibitors is consistent with a greater effect on the anodic reaction, most likely as a result of the NO_2^- ion which itself can act as an anodic inhibitor. A continuous decrease in the corrosion potential of the coupons exposed to the commercial MCI and DMEA suggest that they are primarily acting as cathodic inhibitors; however, the barrier film formed by DMEA molecules is found to be less protective as compared with that formed by MCI.

At longer times, all inhibitors show a decreased inhibition capacity in the presence of chloride ions. There appears to be a competition between aggressive chloride ion attack on the protective film, formed by chemisorption of the inhibitor and restoration of this film by fresh inhibitor molecules. The kinetics of corrosion or inhibition reaction are therefore likely to be dependent on the relative concentrations of chloride and inhibitor species at the steel solution interface, as well as the resistivity of the barrier film and the relative strength of interaction between inhibitor molecules and the iron or iron oxide surface. It is also shown that the effectiveness of these inhibitors is dependent on the surface state of the steel (whether passivated or corroding) at the time of inhibitor addition. Also, the results of removal of the aggressive ions from the solution containing a steel coupon have indicated that care should be taken to reduce the chloride levels in the vicinity of the steel, in order to achieve long term protection due to the unhindered inhibitor film formation process.

In the case of nitrite containing inhibitors it is important to maintain the chloride to nitrite ratio below the threshold level. Hence it is evident that inhibitors such as DICHA having mixed i.e. organic/inorganic characteristics, may be more appropriate for offering long-term protection than purely nitrite based inorganic inhibitors. Since the chloride:nitrite ratio is not a limiting factor in the case of these inhibitors, they do not prove dangerous even after being depleted to low levels.

Thus this investigation, under simplified and controlled conditions, has not only provided a sound basis for interpretation of a more complex situation prevailing in the case of steel/solid concrete interface, but it has also contributed towards the effective planning of the next stage i.e. reinforced concrete experiments. The inhibition models developed here are validated in Chapters 7 and 8 where inhibitors are admixed or surface applied to the chloride contaminated concrete specimens under natural and accelerated diffusion conditions.

CHAPTER 5

A STUDY OF MECHANISM OF INHIBITION IN A SATURATED CALCIUM HYDROXIDE SOLUTION

5.1 - INTRODUCTION

Chapter 4 investigated the potential use of various migratory corrosion inhibitors for corrosion mitigation of steel reinforcement in both new as well as existing corroding structures. The effectiveness of organic and inorganic inhibitor systems was evaluated in terms of level of protection they offer and time dependency of the protection. The author also attempted to develop an understanding of the mechanism of their action at the steel surface using the linear polarisation resistance (LPR) technique and corrosion potential measurements. From these studies it was postulated that the mechanism by which these inhibitors protect steel involves a combination of organic barrier film formation and a protective oxide coating. In the present chapter, an attempt is made to develop a further understanding of the process of formation and breakdown of the protective film on the steel surface and the reaction mechanism at the anodic and cathodic sites. This is achieved by monitoring the electrochemical behaviour of steel immersed in the alkaline environment containing chloride ions and inhibitors using complementary polarisation techniques.

The electrochemical response of the steel surface in the presence of inhibitors is complex and difficult to evaluate, as it covers a wide spectrum of current-potential responses, from predominantly cathodic to primarily anodic depending upon the nature of inhibitor. In addition, the long-term behaviour of different inhibitors appears to vary significantly depending upon the anodic, cathodic or mixed characteristics making their mechanistic evaluation even more difficult. Hence a comprehensive approach involving two different polarisation techniques including cyclic voltammetry and potentiostatic transient methods are used here.

In the initial part of this work a mixed inhibitor system dicyclohexylamine nitrite (DICHAN) has been selected, and inhibitor effectiveness and the dominant inhibition mechanism are investigated as a function of different parameters. These include the state of the steel at the time of inhibitor addition, time dependency of inhibition and concentration of inhibitor at the steel surface. The next aim of this work is to compare the inhibition mechanism of DICHAN with those of the other inhibitor systems such as predominantly cathodic inhibitors dimethylethanolamine (DMEA) and commercial MCI and a purely anodic inhibitor sodium nitrite under a particular set of conditions determined from the initial experiments.

Cyclic voltammetry is used with a view to obtaining valuable information on the kinetics of passive film formation/breakdown in addition to assisting in evaluation of the reaction mechanism at the cathodic and anodic sites. Hinatsu and coworkers (Hinatsu et al., 1988; Hinatsu et al., 1990) have shown that this technique, with the use of a multiple cycling process, can yield a reproducible behaviour between different electrodes. It can be used for the in situ study of the passivity of steel in contaminated alkaline solutions.

It may be noted that the inhibitor systems, being investigated, are the same as those examined in chapter 4. The classification of inhibitors as cathodic, anodic or mixed was primarily based upon their effect on the corrosion potential of the metal; a rise in the potential after the addition of inhibitor indicating an anodic effect and a fall showing a cathodic effect. However, the positive or negative shift in the potential does not necessarily indicate that the inhibitor is purely anodic or cathodic in nature. It is possible that the inhibitor reduces the corrosion rate by influencing both cathodic and anodic reactions; however, the potential can vary only in one direction depending upon whichever of the cathodic or anodic reactions is a dominant reaction. Indeed, if the inhibitor has an equal effect on both anodic and cathodic reactions, the potential may not change at all. The polarisation resistance R_p , obtained using the linear polarisation resistance technique, cannot readily define the extent of suppression of the individual anodic or cathodic reactions. Hence in order to gain a further insight into the actual inhibition process, the cyclic voltammetry technique was used. Potentiostatic transients were also obtained in order to assess the persistency of the passive film. In this technique the growth of oxide/inhibitor film on the steel surface was controlled at a

constant potential and the anodic/cathodic current stability was monitored as a function of time.

5.2 - EXPERIMENTAL

5.2.1 - Experimental Set Up and Procedure

The materials (steel coupons as well as solutions) and the experimental (three-electrode) set up/conditions were as per those maintained in sections 4.2.1 and 4.2.2; however, the inhibitor concentrations used were higher i.e. the concentration of individual amine inhibitors in the solutions were 0.1M and that of commercial MCI was 2 wt %. In the case of DMEA an additional concentration of 0.5M was used in the cyclic voltammetry studies, as the inhibition level obtained at 0.1M concentration was poor. These higher concentrations were mainly used to enhance the inhibition effect so that it could be more readily investigated.

The first four experiments were carried out as per those described in section 4.2.2 i.e. saturated calcium hydroxide solution (passive state - experiment 1), control sample (experiment 2), "prepassivated" condition (experiment 3) and "corroding" condition (experiment 4). The only difference is that the experiments in chapter 4 were monitored for a period of 214 hours with the initial measurements taken at comparatively short time intervals, whereas in the current work polarisation scans were taken 22 hours after immersion of steel in saturated calcium hydroxide solution with or without addition of chloride in "the control sample" or "the passive state" experiments respectively. The polarisation scans in the case of a "prepassivated" condition and "corroding" condition were taken 22 hours after the addition of sodium chloride and inhibitor respectively. This time period was chosen in order to highlight the differences in the longer-term behaviour of various inhibitors.

Effect of concentration on inhibition (experiment 5)

Additional cyclic voltammetry experiments using 0.01M and 0.1M concentrations of DICHAN were carried out under prepassivated conditions to investigate the effect of the concentration variation on the inhibition level.

Long term effectiveness of DICHAN (experiment 6)

Additional cyclic voltammograms for DICHAN under both "prepassivated" and "corroding" condition were taken after 214 hours (~9 days) in order to examine the long-term effect of inhibitor addition on the corrosion behaviour of the steel coupon. These results are compared with those obtained at 22h.

5.2.2 - Monitoring Corrosion Behaviour of Steel Using Cyclic Voltammetry and Potentiostatic Transients

Cyclic voltammetry and potentiostatic transient experiments were performed using a Solartron 1280 b potentiostat and the data was plotted and analysed using Corrware and Corrview software. The mild steel coupon was used as a working electrode and 1000 mm² platinum mesh was used as the auxiliary electrode. All the potentials were measured and reported with respect to a saturated calomel electrode (SCE).

Cyclic voltammetry technique

The cyclic voltammetry experiments were carried out in the case of all the four inhibitor systems i.e. DICHAN, DMEA, MCI and sodium nitrite. Scanning started at -1500 mV_{SCE} and moved in the positive direction up to +500 mV_{SCE}. The scan was reversed at +500 mV_{SCE}, before the onset of oxygen evolution. The anodic polarisation in this case was limited to +500 mV_{SCE} to avoid contamination of the solution by voluminous rust formed because of heavy corrosion beyond this potential. Current was recorded for potentials between -1500 mV_{SCE} and +500 mV_{SCE} and plotted on a linear scale as a function of potential. A linear potential ramp rate of 50 mV/s was used. Repeated cycling (50 cycles) was performed on each sample. Every 10th cycle was recorded and the 50th cycle was presented for comparison purposes.

Potentiostatic transients

Based upon the information obtained from the cyclic voltammograms, two oxidation potentials were chosen in the regions of interest in order to study the transient behaviour of the system. The steel coupons were polarised from the open circuit potential to a particular potential and the current-time curves were recorded by holding the potential constant in each case. In the case of DICHAN the potentials selected were, -380 mV_{SCE} (passive region) and +200 mV_{SCE} (pitting/corroding region). These values were

selected in order to compare the stability of inhibitor film in the active and passive regions. In the case of the other inhibitor systems i.e. DMEA, MCI and sodium nitrite the reaction mechanism at the cathodic and anodic sites was evaluated by comparing the transients in two different regions i.e. cathodic at $-1100 \text{ mV}_{\text{SCE}}$ and anodic at $-380 \text{ mV}_{\text{SCE}}$.

5.3 – INVESTIGATION OF INHIBITION MECHANISMS OF DIFFERENT INHIBITOR SYSTEMS

5.3 1- A Mixed Inhibitor: Dicyclohexylamine Nitrite (DICHAN)

Cyclic voltammetry

Cyclic voltammograms of passivated, corroding and inhibited systems are used to compare and evaluate the dominant inhibition mechanism in the case of different inhibitor systems. Figure 5.1 shows a cyclic voltammogram of the steel/calcium hydroxide solution interface (experiment 1) scanned in the potential range between the hydrogen and oxygen evolution reactions. The open circuit potential of the system (OCP) and the passive current density in the region of interest are indicated in Table 5.1. In this case the steel was exposed to the calcium hydroxide solution for 22h. The open circuit potential of this system was found to be $-300 \text{ mV}_{\text{SCE}}$.

A more detailed investigation of the voltammogram in Figure 5.1 clearly indicates a number of oxidation and conjugate reduction peaks in the forward and reverse sweeps respectively, which are attributable to various stages of Fe oxidation and reduction processes as previously reported in the presence of excess hydroxyl ions (Andersson and Ojefors, 1976; Shrebler-Guzman et al., 1979; Hinatsu et al., 1988; Hinatsu et al., 1990; MacDonald and Owen, 1973). This is in contrast to the behaviour observed in the case of chloride contaminated system. A typical cyclic polarisation curve taken 22 hours after chloride addition (experiment 2 - control sample) is also shown in Figure 5.1. The disappearance of both anodic and cathodic peaks, and the absence of a passive region, indicates a passivity-breakdown. The voltammogram in the case of "control" appears extremely distorted with very large current flowing throughout, especially in the "passive" region, anodic to the oxidation peaks, indicating that significant corrosion has occurred due to chloride addition, as expected.

Specimen	Potentials (mV _{SCE})		Passive Current Density (A/cm ²)
	OCP	E _B	
Ca(OH) ₂	-300		-1.7×10^{-4}
Control	-505	.*	.*
DICHAN _{prepassivated}	-365	100	$(8.0 - 8.5) \times 10^{-4}$
DICHAN _{corroding}	-400	0	-20.5×10^{-4}

* - Cyclic voltammogram of control appears distorted with very high currents in the passive region

Table 5.1 – Open circuit potentials (OCP), breakdown potentials (E_B) and passive current densities for cyclic voltammograms of passive state, control sample and in the presence of DICHAN under prepassivated and corroding condition (after 22h)

Figure 5.2 shows comparative voltammograms for the inhibited solution (experiments 3 and 4), along with those for the control sample. Table 5.1 presents open circuit potentials and the current densities for the respective systems. It is clear that DICHAN inhibits the corrosion of steel. In the case of the scan for the "prepassivated" condition (experiment 3) a poorly defined anodic current peak in the passive region around -950 mV_{SCE} and a well-defined peak at -560 mV_{SCE} are observed. It is believed that the passivation is a result of formation of a more protective oxide film due to the oxidation of iron (II) to iron (III) (Latimer, 1952). Similar oxidation peaks have also been observed by the author in the cyclic voltammogram of sodium nitrite (Figure 5.6), and will be discussed later in this chapter.

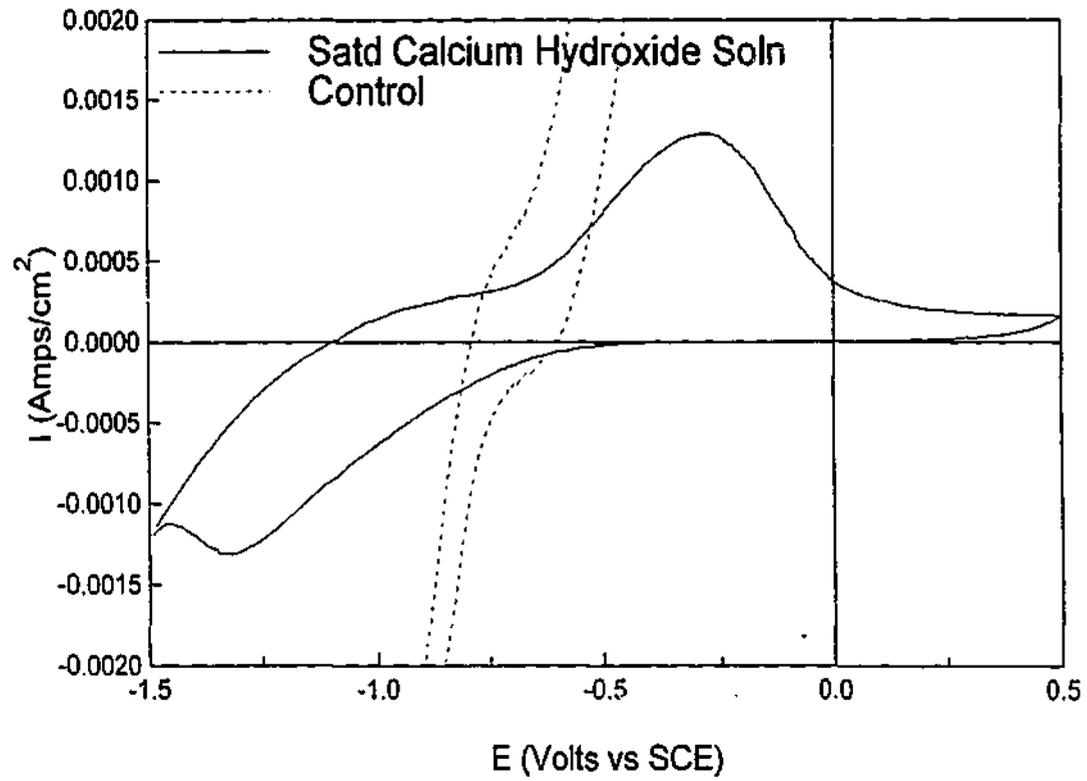


Figure 5.1 – Cyclic voltammogram of mild steel in saturated calcium hydroxide solution (passive state) and after addition of chloride (control sample) after 22h

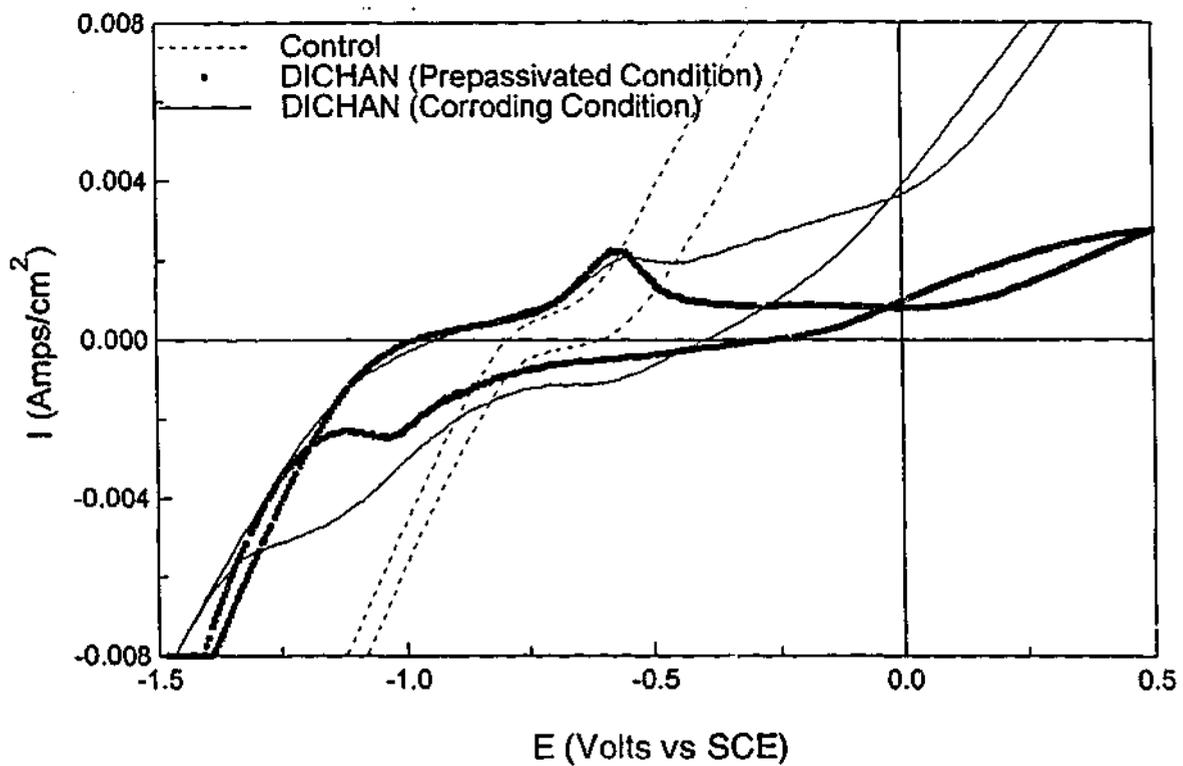


Figure 5.2 – Cyclic voltammograms for control sample and in the presence of DICHAN under prepassivated and corroding conditions (after 22h)

At potentials more positive than the second anodic peak, the passive current densities (Table 5.1) are relatively stable over a range of potentials ($-400 \text{ mV}_{\text{SCE}}$ to $-100 \text{ mV}_{\text{SCE}}$) indicating the presence of a protective film on the metal. The passive oxide film formed here is a poor ionic/electronic conductor and functions as a barrier against the diffusion of metal ions, chloride ions, and the corresponding electron transfer reactions. It is also possible that in addition to the oxide film formed in the presence of the nitrite ions, the amine part of the inhibitor is adsorbed on the metal surface forming a barrier film, thereby causing a further lowering of the passive current densities. In the reverse sweep, a broad cathodic peak around $-1050 \text{ mV}_{\text{SCE}}$ is observed indicating reduction of the oxides formed in the forward sweep. Although, the passive current densities observed in the inhibited system are higher than those observed in saturated calcium hydroxide, they are significantly lower than the current densities observed in the anodic region of the freely corroding system (control sample). These observations may suggest that inhibitor molecules, even though they are in competition with the chloride ions, can still maintain a protective film on the metal surface.

It is further observed that, in the case of the inhibited sample, with the successive polarisation cycles, the passive current densities increase substantially (Figure 5.3). For example i_p for the tenth cycle is $\sim 5 \times 10^{-4} \text{ Amps/cm}^2$ whilst that for the 50th cycle is greater than $20 \times 10^{-4} \text{ Amps/cm}^2$. At the same time, the oxidation peak is becoming more smeared with increasing cycles. This trend suggests increasing susceptibility of the oxide film to chloride attack because of depletion of the nitrite ions at the steel/solution interface. This supports the earlier postulation in section 4.3.8 regarding the stability of the oxide film being dependent upon the relative concentrations of the chloride and the nitrite ions (chloride:nitrite ratio).

It can be seen in Figures 5.2 and 5.3 that, anodic to the passive range, around $100 \text{ mV}_{\text{SCE}}$, there is a sudden increase in the anodic current indicating a breakdown of the inhibitor film and nucleation of pits. However, the reverse sweep after the crossover with the anodic sweep at $-35 \text{ mV}_{\text{SCE}}$ appears to show a partial restoration of the passive region indicating repassivation of the established pits. In the reverse sweep, a broad peak is observed around $-1050 \text{ mV}_{\text{SCE}}$ indicating the reduction of the iron oxides formed in the forward sweep. It is worth noting that the anodic charge passed is higher than the cathodic charge (as evidenced by the unequal anodic and cathodic areas). Such

a result is consistent with the iron oxides not being completely reduced to iron metal during the potential cycling process.

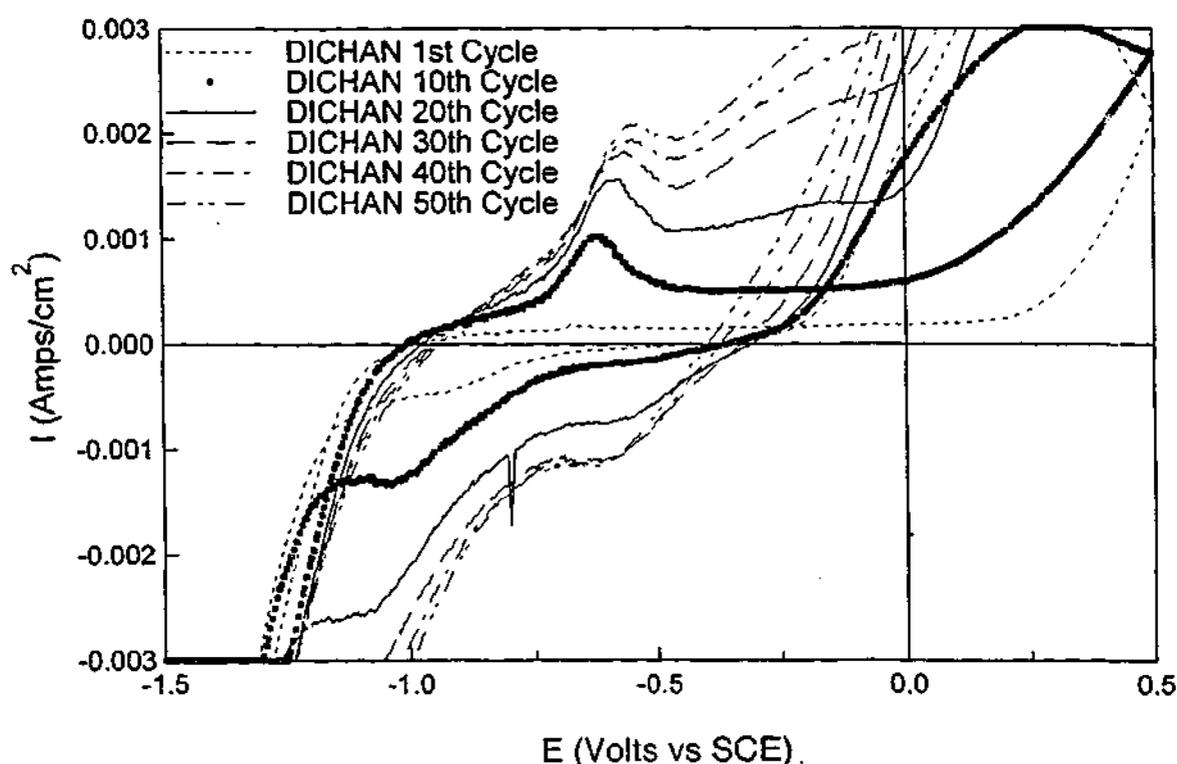


Figure 5.3 – The effect of multiple cycling on cyclic voltammograms of steel immersed in a saturated calcium hydroxide solution containing chloride and DICHAN

Figure 5.2 also presents the cyclic voltammogram for the "corroding" situation, which was taken 22 hours after the addition of inhibitor. The voltammogram shows oxidation peaks in the anodic region, corresponding reduction peaks and a passive region, suggesting formation of a protective iron (III) oxide film as was observed in the case of a prepassivated condition. The passive current density is considerably lower than that observed for the control sample. These features suggest that even in the pre-corroding case the addition of DICHAN can suppress the corrosion reaction. However, on comparing this voltammogram with that obtained in the prepassivated conditions, it was observed that the passive current density in the corroding case is higher than that in the prepassivated situation (see Figure 5.2 and Table 5.1). This suggests the presence of a less resistant inhibitor film in the pre-corroded sample. Further, the oxidation peak at $-550 \text{ mV}_{\text{SCE}}$ is not as well defined as that seen in the prepassivated situation. One possible explanation for this is that when DICHAN is added to the corroding system, some pitting corrosion has already initiated. The film covering these pits is likely to be more porous and less protective than the rest of the film, resulting in a higher passive

current density. Thus the presence of chloride ions before the addition of inhibitor reduces the efficiency of the inhibitor.

Concentration variation studies: Further experiments were carried out to investigate the influence of inhibitor concentration (or the relative concentrations of chloride to nitrite ions) on the shape of voltammograms under prepassivated condition (experiment 5). Three different concentrations of DICHA_N, 0.01M (Cl:NO₂⁻ = 26.4), 0.05M (Cl:NO₂⁻ = 5.3) and 0.1M (Cl:NO₂⁻ = 2.6) were used. The respective cyclic voltammograms are presented in Figure 5.4.

The voltammogram in the case of 0.01M DICHA_N resembles that of a control sample and shows disappearance of the oxidation/reduction peaks and passive region and displays high current densities as compared with those for 0.05M and 0.1M DICHA_N. This indicates active corrosion due to chloride attack. It appears that at 0.01M, the amount of inhibitor (NO₂⁻ ions) is insufficient to provide a protective film and hence the inhibition level obtained at this concentration is insignificant. This is consistent with the observations in chapter 4, where low inhibition (~35%) was obtained at 0.01M concentration of DICHA_N. With an increase in the concentration (decrease in the Cl:NO₂ ratio), there is a corresponding decrease in the current densities and sharpening of the oxidation reduction peaks suggesting onset of passivity. The cyclic voltammogram for steel immersed in the solution having 0.1M concentration of DICHA_N appears to be well defined with sharp oxidation-reduction peaks, and exhibits the lowest passive current density. It is also observed that the open circuit potentials (OCP) of the inhibited system shifts anodically with an increase in the inhibitor concentration (Table 5.2). This suggests that inhibitor efficiency increases with an increase in the concentration. This is consistent with the observations of Berke et al (Berke and Rosenberg, 1989) in the case of calcium nitrite, which show that the ratio of chloride to nitrite is important in defining a minimum effective inhibitor concentration required to obtain meaningful protection. Further, an increase in the inhibitor concentration leads to a corresponding increase in the level of inhibition, and significant inhibition is obtained only when chloride to nitrite ratio is less than 2. The above observations are also consistent with our earlier LPR results discussed in section 4.3.8.

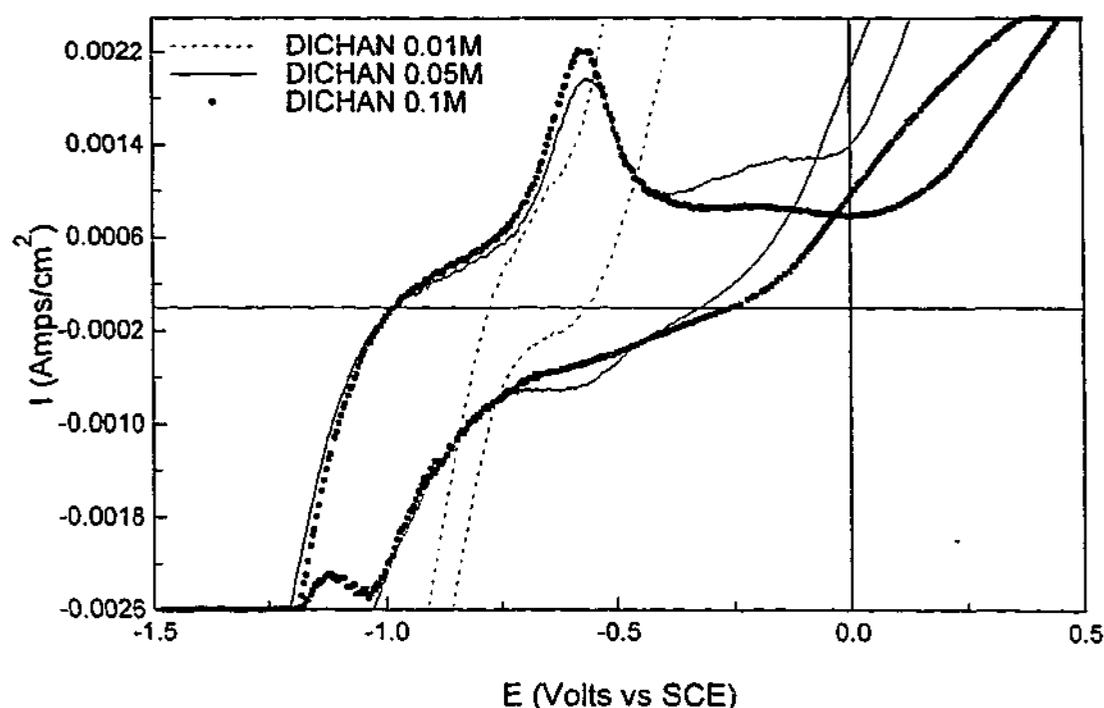


Figure 5.4 – Effect of concentration variation of DICHAN on cyclic voltammograms of steel under prepassivated condition (after 22h)

	Concentrations		
	0.01M	0.05M	0.1M
Cl:NO ₂ Ratio	26.4	5.3	2.6
OCP	-445	-400	-365

Table 5.2 – Open circuit potentials (mV_{SCE}) of steel exposed to different concentrations of DICHAN under prepassivated condition (after 22h)

Long term effectiveness: Experiments with inhibitor addition under both prepassivated and corroding condition (at 0.1M concentration) were continued for up to 214 hours (~9 days) to study the long-term efficiency of inhibitor (experiment 6). Figure 5.5 shows cyclic voltammograms at 22 and 214 hours for the prepassivated and corroding conditions. It can be seen that after 214h, both the curves are shifted to higher current densities and the oxidation current peaks have diminished indicating a decrease in the inhibitor efficiency. There is also a negative shift in the open circuit potentials on increasing the period from 22 hours to 214 hours (prepassivated sample: from -365

mV_{SCE} to -405 mV_{SCE} and corroded specimen: from -400 mV_{SCE} to -510 mV_{SCE}). This suggests the breakdown of the passive film and active corrosion due to increase in the anodic area with time. It may be recalled here that waning of inhibitor efficiency with time was observed in the long-term monitoring of the solution experiments using the LPR technique in sections 4.3.3, 4.3.4 and 4.3.6.

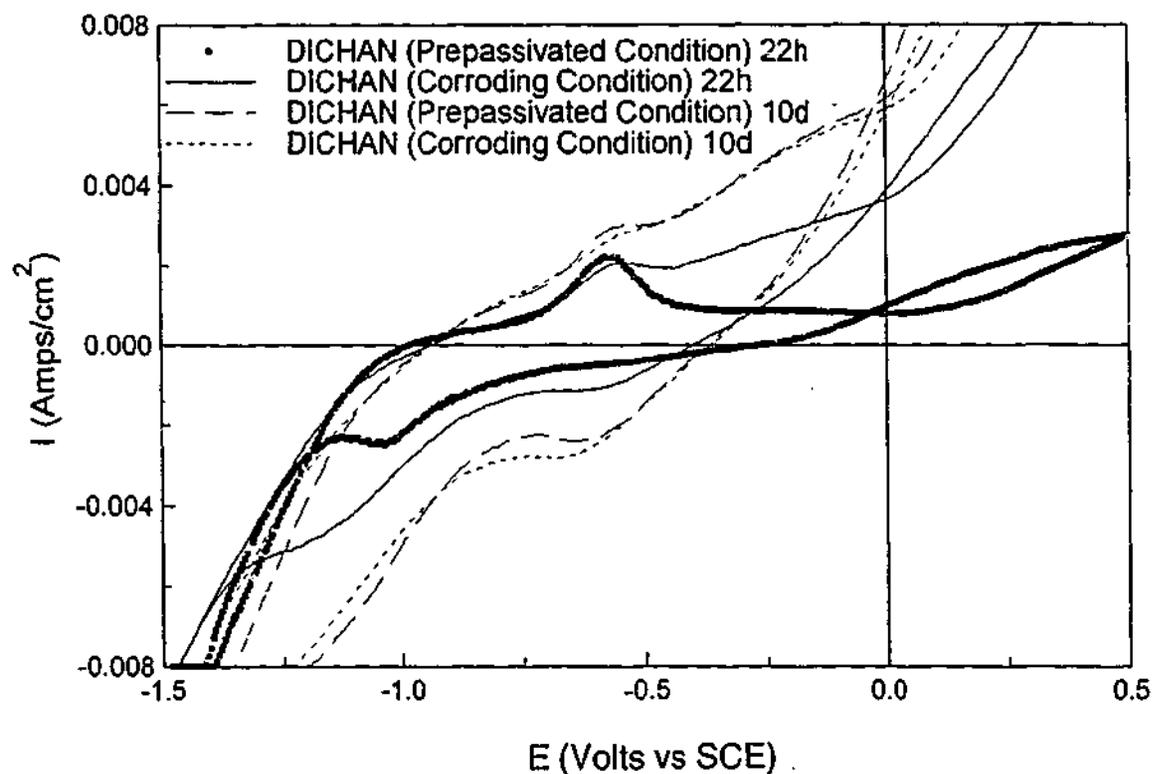


Figure 5.5 – Persistency of the DICHAH (0.1M concentration) film under prepassivated and corroding conditions (after 22 h and 10 days)

Potentiostatic transients

Based on the information obtained from the cyclic voltammograms, further experiments were carried out under steady state conditions in both active (+200 mV_{SCE}) and passive (-380 mV_{SCE}) regions, in order to investigate the effect of inhibitor addition on the electrochemical processes occurring in these regions. Current transients in three different systems, a freely corroding system (control sample), the prepassivated system and a remedial corroding situation are compared. Figures 5.6a and b depict changes in the current density vs. time for these systems in the active and passive regions. Table 5.3 shows the current density values at 600 seconds in these regions.

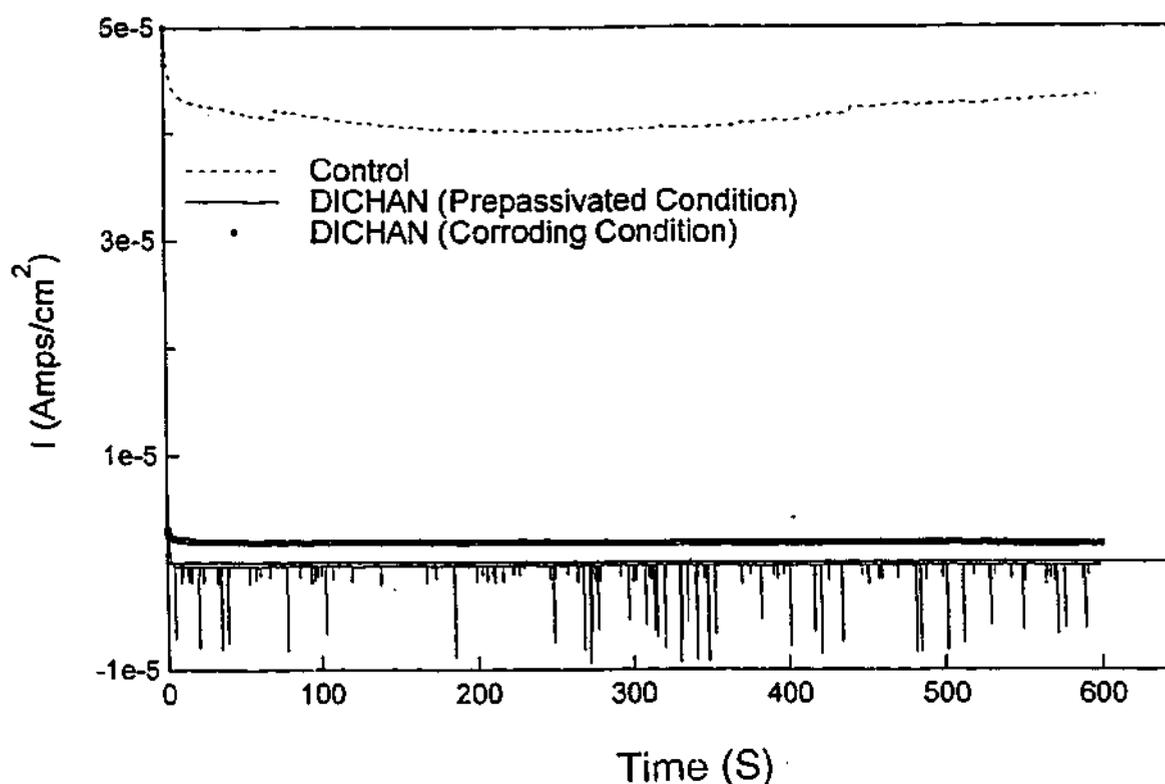


Figure 5.6a – Potentiostatic transients at $-380 \text{ mV}_{\text{SCE}}$ for control and (DICHAN) inhibited specimens having prepassivated and corroding steel surface

Figure 5.6a shows potentiostatic transients resulting from a step in the potential from the open circuit potential (OCP) to $-380 \text{ mV}_{\text{SCE}}$. In the case of the control sample, the current density remained at a level of $0.44 \times 10^{-4} \text{ A/cm}^2$ after 600 seconds. In contrast, the anodic current density of inhibited samples reached a very low constant value i.e. approximately zero when inhibitor prepassivated the steel surface and $0.02 \times 10^{-4} \text{ A/cm}^2$ where inhibitor was added to the corroding surface. This confirms the presence of a 'protective' film on the metal surface in the presence of inhibitor, which acts as a barrier to the passage of electrons and ions and hinders the anodic dissolution process. This is concurrent with the postulation (section 4.3.5) that the efficient protection offered by DICHAN is a result of the combination of synergies of barrier film formation due to chemisorption of the organic amine on the metal surface, and an oxide film formation because of the nitrite portion of the inhibitor. Further marginally lower current values in the case of the prior addition of inhibitor to the system suggests that the inhibitor film formed under these conditions is slightly more protective than when inhibitor was added to the system which was already corroding. This could be due to preconditioning of the metal surface, which facilitates unhindered film formation in the absence of the chloride ions, as discussed earlier.

As the potential is made more positive and the sample is moved into the corroding region (+200 mV_{SCE}) (Figure 5.6b), there is a dramatic increase in the current density to 182.2×10^{-4} A/cm² at 600 seconds for the control sample, 7.4×10^{-4} A/cm² in the case of inhibitor prepassivated surface and 20.8×10^{-4} A/cm² when inhibitor was added to the corroding surface. The current density for the control shows more than two orders of magnitude increase as compared with that in the passive region indicating active dissolution of the metal. The transient curves of the inhibited samples show a slow but uniformly ascending anodic current density. The overall current density values are more than three orders of magnitude higher as compared with the corresponding values for inhibited samples in the passive region at 600 seconds. The higher current density and the ascending anodic current could be due to two processes; the initiation of new pits, and the propagation of the existing pits on the metal surface, resulting in an increase in the anodic area. In the case of inhibited samples the slow increase in the current may also be attributed to the breakdown of the inhibitor film (Hinatsu et al., 1990).

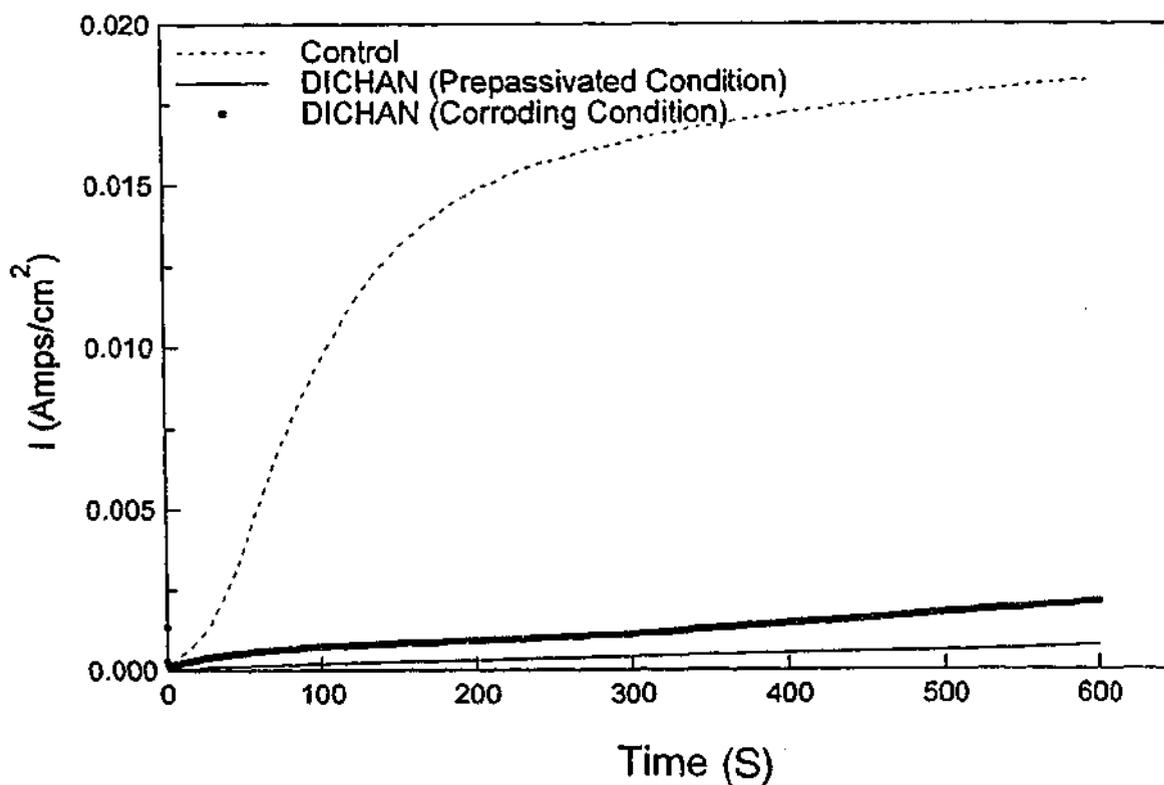


Figure 5.6b – Potentiostatic transients at +200 mV_{SCE} for control and (DICHAN) inhibited specimens having prepassivated and corroding steel surface

Specimen	Passive Region	Active Region
	-380 mV _{SCE}	200 mV _{SCE}
Control	0.44 x 10 ⁻⁴	182.2 x 10 ⁻⁴
DICHAN _{prepassivated}	~0	7.4 x 10 ⁻⁴
DICHAN _{corroding}	0.02 x 10 ⁻⁴	20.8 x 10 ⁻⁴

Table 5.3 – Current densities (A/cm² ± 10%) at 600 seconds in passive and active regions for control and inhibited samples under prepassivated and corroding condition (after 22h)

5.3.2- Comparison of DICHAN with the Other Inhibitor Systems

Cyclic voltammetry

In this section the inhibition mechanism of DICHAN is compared with that of a purely anodic inhibitor sodium nitrite and predominantly cathodic inhibitors dimethylethanolamine (DMEA) and MCI under prepassivated condition using the cyclic voltammetry technique. The resistance to corrosion attack due to the presence of inhibiting film on the steel is examined by comparing the scans for various inhibited systems with those of a freely corroding system (control sample). Figure 5.7 presents the voltammograms for the corroding (control) and the inhibited systems with sodium nitrite and DICHAN. Table 5.4 lists the open circuit potentials and passive current densities displayed by different inhibitor system (Figures 5.7-5.9).

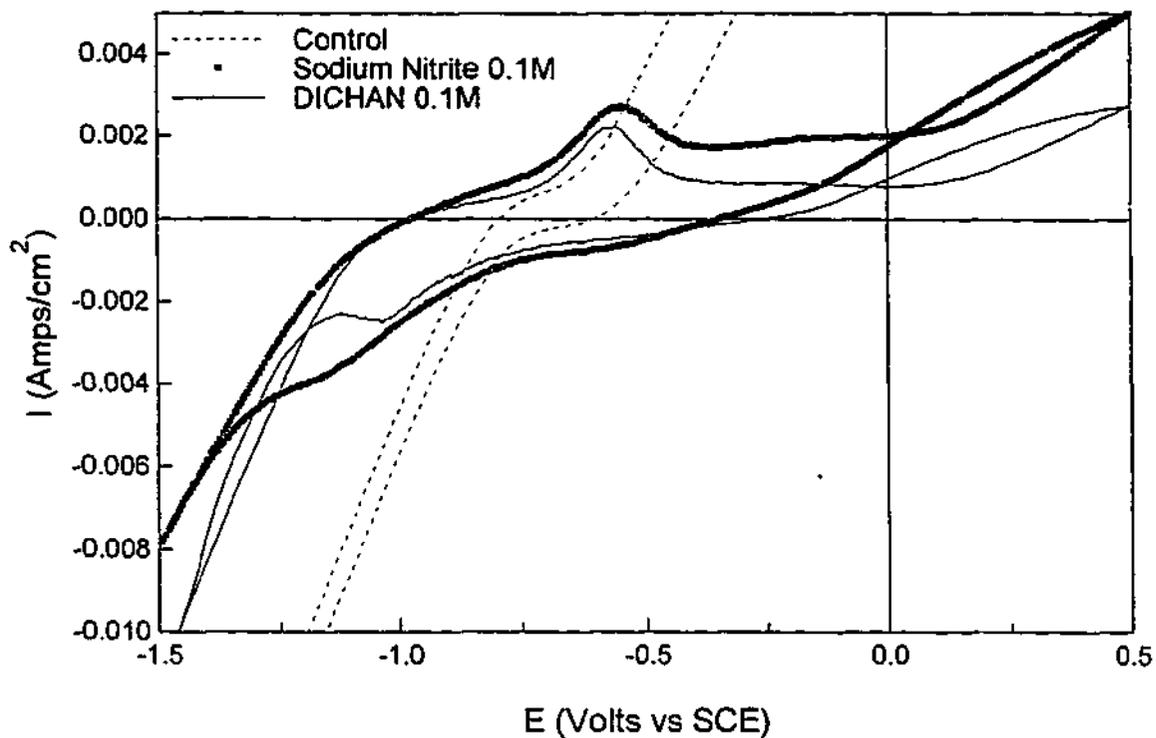
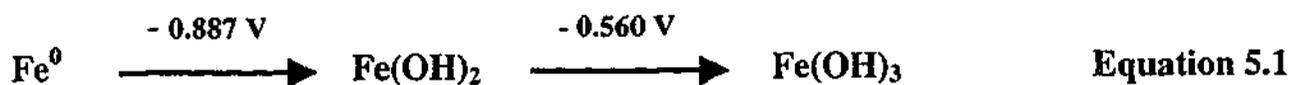


Figure 5.7 – Comparison of cyclic voltammograms of the corroding system (control) and in the presence of sodium nitrite and DICCHAN under prepassivated condition (after 22h)

The voltammogram of steel in the presence of sodium nitrite appears to exhibit anodic/oxidation and a conjugate cathodic/reduction current peak, as were observed in the case of DICCHAN. It is interesting to note that these peaks are observed around the same positions in the case of both sodium nitrite and DICCHAN i.e. at approximately $-1000 \text{ mV}_{\text{SCE}}$ (a poorly defined peak) and $-560 \text{ mV}_{\text{SCE}}$ (a well-defined peak) respectively in the forward sweep and around $-1100 \text{ mV}_{\text{SCE}}$ in the reverse sweep. A review of literature indicates that similar peaks have been observed in the case of oxidation of Fe to Fe^{3+} under potentiostatic control (Latimer, 1952). In an environment having a pH of approximately 14, oxidation of Fe to Fe^{3+} takes place as per the following equation.



This suggests that at the potential of electrochemical passivation (anodic region), the individual properties of the anodic/oxidising inhibitor do not seem to alter the passivation conditions. The likely function of the anodic inhibitor in this case could be to make the oxide film formed during anodic polarisation more protective/resistive against the attack of chloride ions. The role of nitrite ions in this case appears to be

slightly different from that described in Equation 4.2 (in the absence of the potentiostatic control), where it was postulated that the ions act by repairing the weaker spots in the oxide film by converting Fe^{2+} to Fe^{3+} oxide. The protective role of nitrites during anodic polarisation is further confirmed by a comparison of the scans obtained in the presence and in the absence of inhibitor, i.e. control sample. In the control sample the susceptibility of the oxide film to chloride ions is indicated by the disappearance of the oxidation peaks, and in the passive region with a consequent increase in the anodic current density.

Specimen	Potentials (mV _{SCE})		Passive Current Density (A/cm ²)
	OCP	E _B	
Control	-505	.*	.*
DICHAN (0.1M)	-365	100	(8.0 - 9.0) x 10 ⁻⁴
Sodium Nitrite (0.1M)	-430	100	(17.5 - 20.5) x 10 ⁻⁴
MCI (2 wt %)	-775	-55	(34.5 - 36.5) x 10 ⁻⁴
DMEA (0.5M)	-495	-590	.*

* - Cyclic voltammograms appear distorted with very high currents in the passive region

Table 5.4 - Open circuit potentials (OCP), breakdown potential (E_B) and passive current densities for control sample and various inhibited systems

It is appropriate to mention that Rosenfeld (Rosenfeld, 1981), while carrying out the galvanostatic reduction of the iron oxide films, observed that a somewhat larger charge was required to reduce the film in the presence of sodium nitrite than in inhibitor-free electrolyte, suggesting that the oxide film was thicker in the presence of sodium nitrite. It was suggested that sodium nitrite, being a potential oxidising agent, acts as an acceptor of electrons. The interaction of different types of inhibitors with the oxide-

covered metal surface was also discussed by McCafferty (McCafferty, 1978), where he suggested that corrosion inhibitors can interact strongly with a surface even if it is oxide-covered. When the metal surface is oxide-covered, the role of the inhibitor is to maintain a homogeneous oxide film. Thus the results obtained in the presence of the nitrite-based inhibitors are consistent with previous findings of others. Nevertheless, more work is still needed to accurately model the action of nitrite in the case of potentiostatically grown oxide films.

In the case of both sodium nitrite and DICCHAN, a rapid increase in the current density indicating a local breakdown of the film with the nucleation of pits, occurred around the same potential i.e. around $100 \text{ mV}_{\text{SCE}}$. This suggested that the resistance offered to the pit initiation process by the nitrite component of these inhibitors is similar. The passive current density in the presence of sodium nitrite, although it is much lower than that observed for the control sample, is higher than that exhibited in the presence of DICCHAN. The open circuit potential of the steel exposed to sodium nitrite is found to be less anodic than that observed for DICCHAN. These observations indicate that the anodic reaction is suppressed to a lesser extent in the presence of sodium nitrite than in DICCHAN. This could be due to additional protection at the anodic sites in the case of DICCHAN because of the presence of the amine component. These results are consistent with those obtained with the corrosion potential measurements on addition of sodium nitrite and DICCHAN to corroding steel in section 4.3.4.

Cyclic voltammograms for the mild steel immersed in a simulated concrete solution containing chloride ions (control sample) and with chloride and inhibitors, MCI and DICCHAN are shown in Figure 5.8 and their respective potentials and current densities are summarised in Table 5.4. The open circuit potential of the steel when exposed to a solution containing MCI is shifted cathodically to $-775 \text{ mV}_{\text{SCE}}$. This indicates that the possible mechanism of action of this inhibitor is to suppress the cathodic reaction, which is attributed to oxygen reduction as the principal rate limiting reaction.

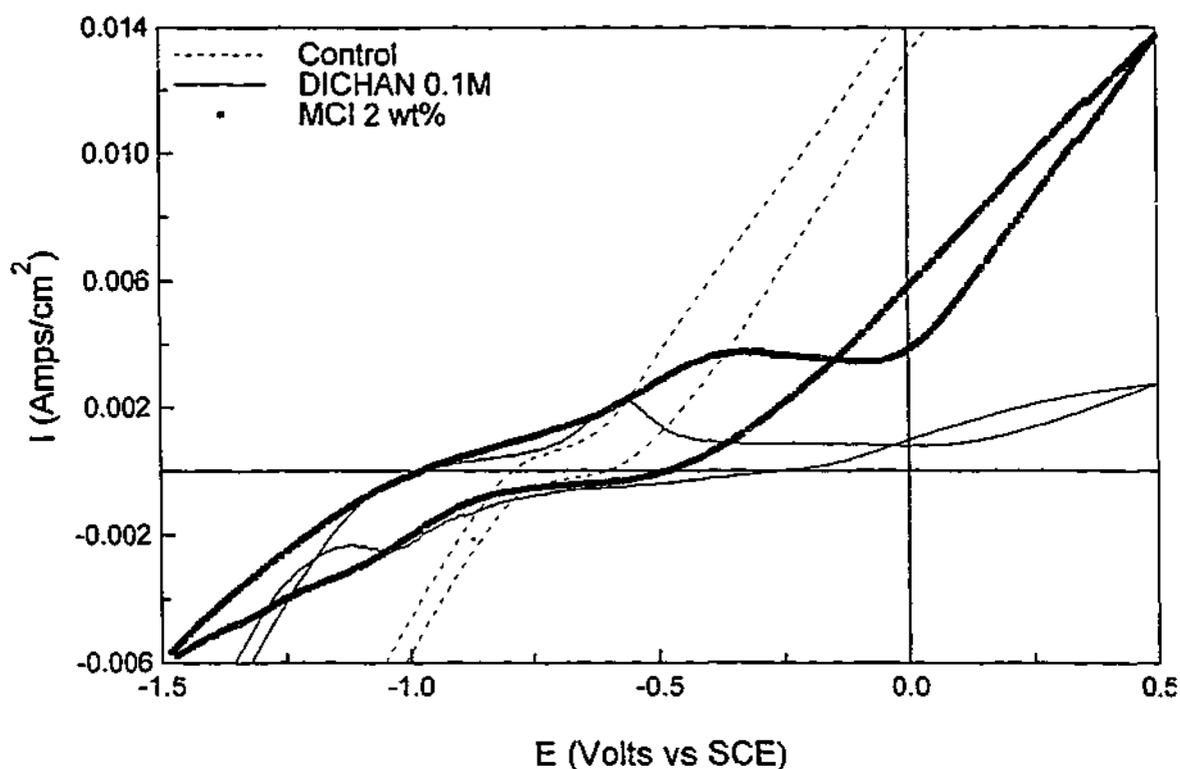


Figure 5.8 – Comparison of cyclic voltammograms of the corroding system (control) and in the presence of MCI and DICHAN under prepassivated condition (after 22h)

An obvious feature of this voltammogram is the absence of oxidation-reduction peaks in the forward and reverse sweeps. The lack of these peaks suggests the absence of oxidising anions such as nitrites in the composition of MCI. It also suggests that MCI inhibitor is not able to protect by promoting oxide formation. It is interesting to note that in spite of the absence of an oxide film, a well-defined passive region extending from $-310 \text{ mV}_{\text{SCE}}$ to $-55 \text{ mV}_{\text{SCE}}$ is observed in the forward sweep of the MCI voltammogram. The passive current density in this case i.e. $(34.5-36.5) \times 10^{-4} \text{ A/cm}^2$ is found to be significantly lower than the high current values observed for the control sample although significantly higher than that in DICHAN case. These observations give indication that MCI does indeed offer some protection at the anodic sites, but to a lesser extent than nitrite containing system. MCI is assumed to contain an alkanolamine as an active ingredient (Martin and Miksic, 1989), hence it is likely that the protection observed at the anodic sites is due to a barrier film formed through chemisorption of the anodic component of the amine molecules.

It is known that organic amines, having an electron donating NH_2 group, adsorb at the metal-solution interface in different configurations depending upon their molecular structure (Hackerman and McCafferty, 1974; McCafferty, 1978; McCafferty and

Hackerman, 1972). The performance of amines, as discussed in section 4.3.5, can be ascribed to the type and strength of bond they form with Fe or FeO at the steel surface through the electron donating nitrogen of NH_2 group. It can also be ascribed to the compactness or the permeability of the barrier layer formed through their hydrocarbon chains. This bonding (adsorption) is likely to lead to the formation of a barrier film on the metal surface. Thus it seems that the amine group, though it limits the growth of an oxide film on the metal, nevertheless helps in forming a better chemisorbed protective species to the metal/metal oxide surface because of an increased availability of electrons at the adsorption centre. The chemisorption at the anodic site causes a reduction in the active centres on the metal surface thereby lowering the passive current density. Similar adsorption is likely to have occurred at the cathodic sites resulting in the suppression of the oxygen reduction reaction.

Indeed the comparison of both DICHAN and MCI suggests that the anodic reaction is suppressed to a greater extent in the case of DICHAN compared to MCI. However LPR results have shown that MCI is a better corrosion inhibitor than DICHAN. This indirectly suggests that the cathodic reaction in MCI must be suppressed to a greater extent. Thus the above observations clearly indicate that MCI is a mixed inhibitor. It protects the steel surface by influencing both cathodic and anodic reactions; however, the dominant inhibition process is cathodic.

Figure 5.9 compares cyclic voltammograms of the mild steel immersed in a saturated calcium hydroxide solution with chloride ions (control sample) and in the presence of DMEA and MCI. The potentials and current densities are presented in Table 5.4. The shape of the voltammogram in the presence of DMEA appears to be similar to that of the control sample with disappearance of the oxidation-reduction peaks and the passive region. Further the open circuit potential ($-495 \text{ mV}_{\text{SCE}}$) appears to be similar to that observed for the control sample suggesting active corrosion. The only difference between the two voltammograms is that the current densities exhibited by steel exposed to DMEA are slightly lower than those observed for the control sample. This suggests that significant corrosion has occurred due to insufficient protection offered by DMEA at this concentration. On increasing the concentration of DMEA by five times i.e. from 0.1 M to 0.5 M, the voltammogram appears to have shifted to lower current densities suggesting the formation of a protective film on the metal surface. The protection mechanism in this case is proposed to be purely through the chemisorption of the amine

molecules at the cathodic and anodic sites. It must be stated that no clear passive region is observed in the case of DMEA suggesting the susceptibility of the barrier film to chloride attack, consistent with long-term LPR measurements discussed in sections 4.3.3-4.3.5.

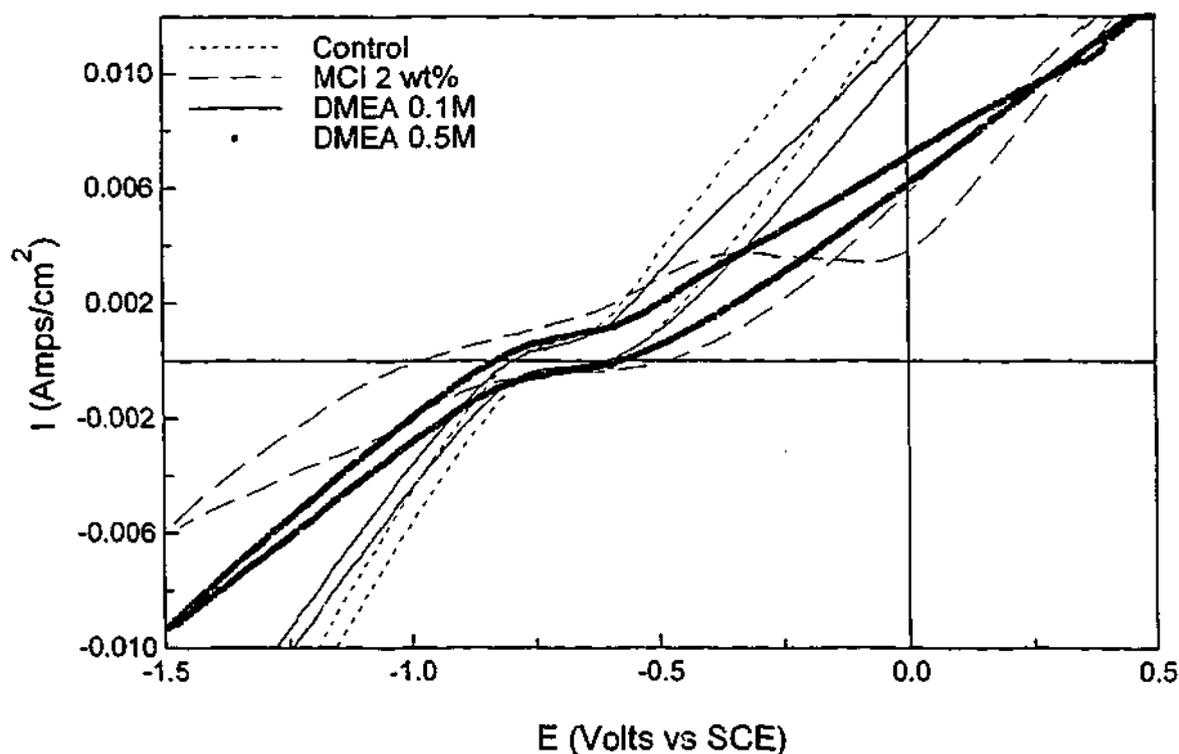


Figure 5.9 –Comparison of cyclic voltammograms of the corroding system (control) and in the presence of DMEA and MCI under prepassivated condition (after 22h)

The difference in the level of inhibition offered by the two amine based inhibitors MCI and DMEA could be attributed to their varied abilities to form a thick impenetrable barrier, which in turn is likely to depend upon size, shape and nature of the inhibitor molecule. This has already been discussed in section 4.3.5. It should, however, be mentioned that the mechanism of action of DMEA described here is different from that postulated by Grunze et al (Grunze et al., 1997), who proposed that DMEA forms a durable passivating film by displacing ionic species from the oxidized steel surface, in particular chlorides which cause corrosion.

Potentiostatic transients

Further investigations on the long-term stability of inhibitors under prepassivated conditions were carried out by stepping the potential of the mild steel, from open circuit potential to the potentials in the cathodic/anodic regions using a potentiostat. Under the

potentiostatic conditions, the growth of a passive oxide/inhibitor film on the steel surface, in contact with the inhibitor containing solution, is controlled and the cathodic/anodic bias caused by the initial growth of the film (i.e. cathodic/anodic potential shift) due to the presence of inhibitors is eliminated (Jovancicevic and Hartwick, 1997).

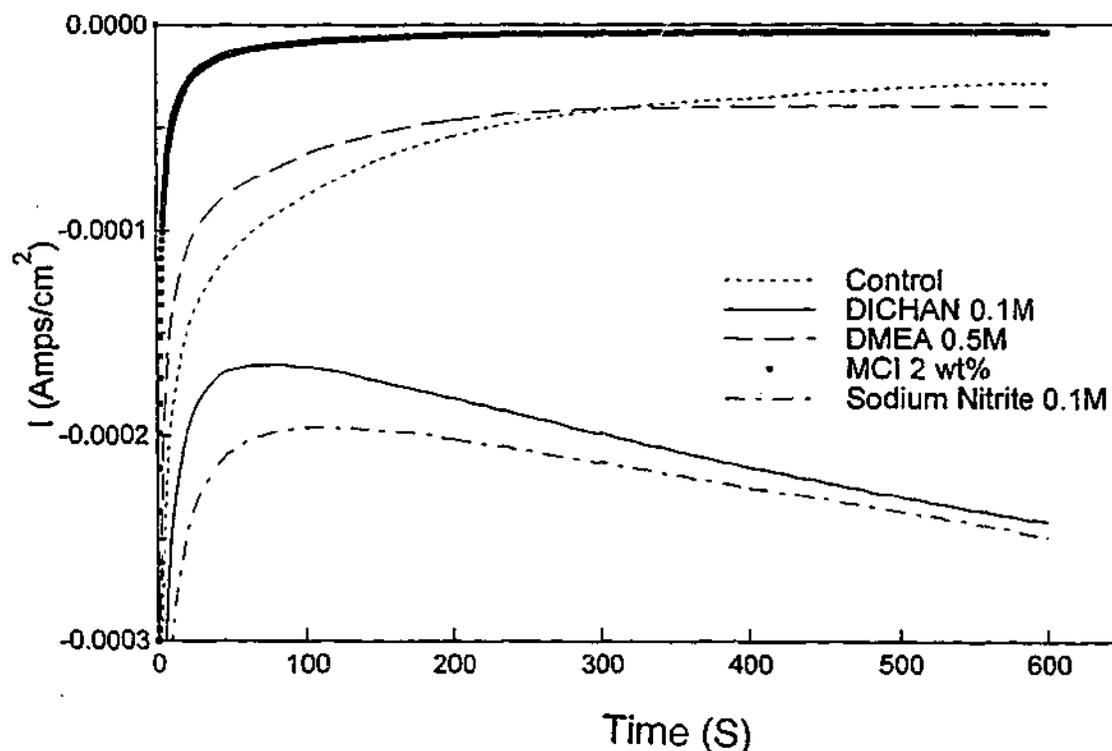


Figure 5.10 – Potentiostatic transients for steel at $-1100 \text{ mV}_{\text{SCE}}$ in the presence of DICHAN, DMEA, sodium nitrite and MCI under prepassivated condition (after 22h)

Figure 5.10 depicts the variations in the current density versus time in the cathodic region ($-1100 \text{ mV}_{\text{SCE}}$) for the steel exposed to different inhibitor systems such as DICHAN, DMEA, sodium nitrite and MCI. Table 5.5 summarises the current densities for these inhibitor systems. At $-1100 \text{ mV}_{\text{SCE}}$, a rapid initial decrease in the cathodic current is observed in the case of all inhibitors irrespective of their mechanism of inhibition. This is likely to be because of either suppression of the cathodic reaction or could be due to hydrogen evolution in some cases e.g. purely anodic inhibitor sodium nitrite. The reduction in the cathodic current is found to be a maximum in the case of the predominantly cathodic inhibitor MCI (from 3.0×10^{-4} to $0.19 \times 10^{-4} \text{ A/cm}^2$ in 35 seconds), followed by DMEA and DICHAN. The current reduction is found to be insignificant in the case of sodium nitrite (from 3.0×10^{-4} to $2.2 \times 10^{-4} \text{ A/cm}^2$ in 35 seconds). These results indicate that the degree of suppression of cathodic reaction is

the maximum in the case of MCI and the least for the anodic inhibitor sodium nitrite at the initial stage. The initial decrease was later followed by different trends for different inhibitors depending upon their dominant mechanism of action. In the case of MCI the current continued to decrease to reach $0.04 \times 10^{-4} \text{ A/cm}^2$ towards the end of the test period (600 seconds). The low cathodic current densities observed in the presence of MCI confirm that the dominant protection mechanism in MCI is by suppression of the cathodic/oxygen reduction reaction. The trend in the current transients obtained in the presence of DMEA was similar to that for MCI, suggesting a similar mechanism of inhibition, however the cathodic current density values for DMEA were found to be higher than those obtained for MCI at the base line. This indicates that the protective film formed in this case is less resistive than that formed by the MCI molecules. The trends in the potentiostatic transients observed for DMEA and MCI are consistent with those obtained using the cyclic voltammetry technique (section 5.3.2) and the linear polarisation resistance technique and corrosion potential measurements (sections 4.3.3 and 4.3.4).

The long-term trend of the cathodic currents in the case of the nitrite containing inhibitors was different from that observed in the case of purely organic inhibitors discussed above. In the presence of the nitrite-based inhibitors, at longer time, the transients show a continuous increase in the cathodic current. It is difficult to attribute this behaviour to a single effect, as such behaviour could be due to different possible reactions occurring at the cathodic sites such as reduction of iron oxide or evolution of hydrogen gas. This effect might also be observed due to a continual anodic inhibition in the cathodic region i.e. the anodic current density may decrease continually due to suppression of the anodic reaction whereas the cathodic reaction rate remains constant. Since $i_{\text{max}} = i_a - i_c$; as i_a decreases, the apparent cathodic current increases. It has been proposed that in the case of an anodic inhibitor, the higher and more stable the cathodic current, the more effective the anodic inhibition is likely to be (Jovancicevic and Hartwick, 1997).

Figure 5.11 compares the transients for the steel in the presence of inhibitors obtained by stepping the potential from the open circuit potential to $-380 \text{ mV}_{\text{SCE}}$ in the passive region. Table 5.5 lists the current densities for these transients. The anodic current density in the case of a control sample, maintained at a constant value seems to be the highest amongst all the transients confirming active dissolution of the metal at the

anode. The current densities for the steel in the presence of DICHAN and sodium nitrite exhibit very low and constant values ($< 0.01 \text{ A/cm}^2$ for DICHAN and $0.03 \times 10^{-4} \text{ A/cm}^2$ for sodium nitrite) suggesting the presence of a thick protective film at the anodic sites, which reduces the active centres on the anode. The current densities in the presence of DICHAN appear to be lower than those for sodium nitrite, suggesting a higher anodic protection, which is consistent with the results obtained in sections 4.3.3 and 4.3.4 using the linear polarisation resistance technique and the corrosion potential measurements. Contrary to these results the current densities exhibited by DMEA are an order of magnitude higher ($0.26 \times 10^{-4} \text{ A/cm}^2$) and are close to those observed for the control sample. These results suggest that the protection offered by DMEA at the anodic sites is insignificant. The current densities for the transients obtained in the presence of MCI appear to be much lower than that observed for DMEA suggesting a better anodic protection as compared with that offered by DMEA, although still lower than DICHAN.

Specimen	Cathodic Region ($-1100 \text{ mV}_{\text{SCE}}$)		Passive Region
	50 s	600 s	600 s
Control	–	–	0.4×10^{-4}
DICHAN (0.1M)	-1.7×10^{-4}	-2.4×10^{-4}	$< 0.01 \times 10^{-4}$
DMEA (0.5M)	-0.8×10^{-4}	-0.40×10^{-4}	0.26×10^{-4}
Sod. Nitrite (0.1M)	-2.1×10^{-4}	-2.5×10^{-4}	0.03×10^{-4}
MCI (2 wt %)	-0.14×10^{-4}	-0.04×10^{-4}	0.14×10^{-4}

Table 5.5 – Current densities ($\text{A/cm}^2 \pm 10\%$) in cathodic and anodic (passive) regions for steel in the presence of DICHAN, DMEA, sodium nitrite and MCI under prepassivated condition (after 22h)

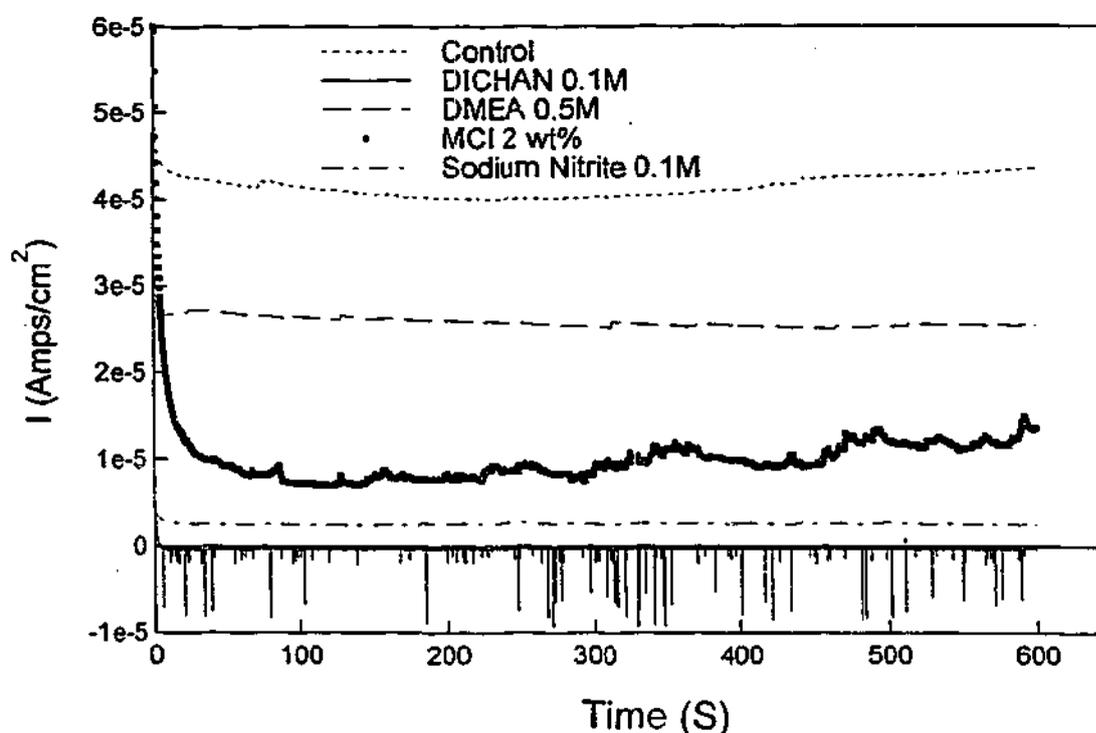


Figure 5.11 – Potentiostatic transients for mild steel at $-380 \text{ mV}_{\text{SCE}}$ in the presence of DICHAN, DMEA, sodium nitrite and MCI under prepassivated condition (after 22h)

5.4 - CONCLUSIONS

The results obtained using different polarisation techniques confirm the hypothesis that the amine-based inhibitors protect the metal by a pure adsorption mechanism, whereas the nitrite-based inhibitors function by either forming an oxide layer or reinforcing the electrochemically-formed passive oxide film (when the system is under the potentiostatic control). The multivariant effects of these inhibitors at the steel surface are related to their electron structure and mechanism of action. While the nitrite-containing inhibitors reinforce the oxide film by accepting electrons and themselves being reduced, the amine-based inhibitors function through the electron donating $-\text{NH}_2$ group. The amine group is also shown to result in better bonding (chemisorption) to the metal/metal oxide surface because of an increased availability of electrons at the adsorption centre. This leads to the build up of a thick barrier layer, on the metal surface thereby hindering both cathodic and anodic reactions. Amongst the inhibitors, DICHAN and sodium nitrite appear to have a greater effect on the anodic reaction, whereas MCI and DMEA primarily affect the cathodic reactions. The varied inhibition capacities of the amine-based inhibitors MCI, DMEA and DICHAN in the presence of chloride ions could be attributed to the difference in the strengths of the chemisorptive

bonds they form with the steel surface. This in turn depends upon the electron density at the nucleophilic (electron donating) nitrogen of the amine group and the stereochemistry surrounding it.

It is also observed that the effectiveness of inhibitor depends on the corrosion-state of steel at the time of inhibitor addition. A higher level of protection is offered by inhibitor DICHAH in the case of a prepassivated situation as compared with that observed for the corroding condition. Inhibitor efficiency is also found to be dependent on the relative concentrations of chloride and inhibitor species at the steel/solution interface. The efficiency of inhibitor is further shown to be time dependent as the waning of inhibition is observed with the passage of time. All these observations confirm the postulations made on the basis of the earlier results obtained using the linear polarisation resistance technique and corrosion potential measurements.

Under the controlled potentiostatic conditions, in the cathodic region the dominant protection mechanism of MCI and DMEA is via the decrease in the rate of the oxygen reduction reaction. Whereas for DICHAH and sodium nitrite, results suggest that inhibition is by suppression of anodic dissolution of steel. The most important information obtained from cyclic voltammetry and potentiostatic transients is possibly the partial anodic characteristics of DMEA and MCI, which were not obvious from the earlier experiments.

CHAPTER 6

DIFFUSION MECHANISM OF MIGRATORY CORROSION INHIBITORS IN CONCRETE

6.1 – INTRODUCTION

The use of surface applied migratory corrosion inhibitors (MCIs) based on organic amines, for corrosion mitigation of new and existing reinforced concrete structures has been discussed in chapter 2. These MCIs, when applied at the surface of a corroding structure, are claimed to migrate through concrete to access the corroding area and form a protective film on the reinforcement (Bjegovic et al., 1993; Fear, 1996; Phanasgaonkar et al., 1996; Phanasgaonkar et al., 1997). The effectiveness of these inhibitors to protect the steel surface depends upon their ability to migrate through the concrete cover to achieve/maintain an adequate concentration in the vicinity of the steel-concrete interface in addition to their capacity to form a protective film on the steel surface. The latter aspect, i.e. the ability of these inhibitors to offer protection to the steel immersed in a saturated calcium hydroxide solution, has already been discussed in chapter 4. However, in order to define an inhibitor's effectiveness in mitigating the corrosion of reinforcement embedded in concrete, its capacity to diffuse through concrete needs to be investigated. This becomes all the more relevant in the rehabilitation application of these inhibitors in the case of a deteriorating structure, where the ability of the surface applied inhibitor to perform its function will depend upon its diffusion properties.

Three potential organic amine-based inhibitor systems, which were found to possess good inhibition capacity in solution experiments in chapter 4, were selected for investigating their diffusion characteristics through concrete. These systems included a mixed (organic-inorganic) inhibitor dicyclohexylamine nitrite (DICHAN), an individual organic amine dimethylethanolamine (DMEA) and a commercial migratory corrosion inhibitor (MCI). Diffusion coefficients were calculated using a Fickian diffusion model

for both steady state and non steady state conditions. The effect of water/cement ratio, thickness of concrete cover, and the concentration of the inhibitor on the diffusion kinetics of these inhibitors were examined.

Inhibitor diffusion in concrete is only a part of the overall transportation processes affecting the corrosion rate, and needs to be evaluated in the context of the other processes, such as chloride penetration, oxygen diffusion and water sorptivity. The combined effect of all these individual transportation processes in concrete determines the rate at which degradation processes can proceed. A general comparison of diffusion coefficients of inhibitors with those of chloride and oxygen is carried out. This work on inhibitor diffusion through concrete, forms a basis for the further studies described in chapter 7 and 8, which include application of these inhibitor systems to the surface of concrete specimens under natural and accelerated diffusion conditions respectively. It also assists in subsequent correlation of the inhibition data obtained in calcium hydroxide solution experiments in chapters 4 and 5, with the results in the actual concrete specimens in chapters 7 and 8.

6.2 - THE FACTORS INFLUENCING THE DIFFUSION PROCESS

The mechanism of inhibitor diffusion in concrete is complex and possibly involves different steps that are mutually interdependent; hence it is necessary to make a careful review of the likely factors which can influence this process. The transport of diffusing species is known to depend upon various factors such as the pore structure of the concrete, the characteristics of the diffusing substance and the exposure conditions (Saetta et al., 1993). Porosity, as determined primarily by the water/cement ratio of concrete, is important in developing the knowledge of the transport properties of various chemical species through concrete. Most of the models used today to describe the properties of concrete are based on the assumption that the pore structure of cement paste is continuous and homogeneously distributed and diffusion occurs most readily within the largest continuous channels (Garboczi, 1990; Nilsson et al., 1996; Page et al., 1981).

It must be recognised, however, that in the hardened concrete, which is generally considered as a two-phase material composed of hydrated cement paste and aggregates,

the coarse aggregate particles exercise an important influence on the permeability characteristics of concrete. The porosity of the hydrated cement paste in the transition zone surrounding the coarse aggregate particles is higher than that of the cement paste in the bulk mortar (Mehta, 1991). This may lead to development of paths that are favourable to transport (called percolation). Hence the diffusion rate of the species in concrete is likely to be higher than in the cement paste of the same composition. Besides water/cement ratio and aggregate size, permeability of concrete also depends upon consolidation, curing and good concreting practice. For instance normal cycles of heating and cooling in climates in which the temperature differences between air and seawater, or between night and day, are high can considerably affect the permeability of concrete. Also sometimes there are cracks/microcracks present in concrete which can "short-circuit" diffusion paths. Diffusion resistance within the crack is negligible to the diffusion resistance of the cover itself; hence transportation rates of the diffusant through the cracks are likely to be faster than for bulk diffusion.

The level of water saturation of the pores in the concrete is also likely to influence the transport mechanism of various diffusing species. Under non-saturated conditions, there is a possibility of transport due to the capillary action driven by the moisture gradient, together with ionic diffusion of the species. In the case of migratory corrosion inhibitors there is also a possibility of a vapour phase transport through the partially empty pores because of their high vapour pressure. In fully saturated conditions, however, transport of diffusing species is restricted to the relatively slow process of diffusion, the concentration gradient being the driving force (Andrade, 1993).

Besides the host material and the level of saturation in its pores, the transportation rate through concrete is also likely to be influenced by the nature of the diffusing species such as chloride, oxygen and inhibitors. Several studies have been published on the rate of diffusion of chloride ions through cement and concrete (Collepari et al., 1972; Gjørv and Vennesland, 1979; Goto and Roy, 1981; Nilsson et al., 1996; Page et al., 1981), where researchers have mainly concentrated on the ionic diffusion as the primary process. These studies have also investigated the likely physico-chemical interactions between the chloride and the cement matrix that affect the apparent "diffusion" rate. A number of researchers (Gjørv et al., 1976; Yu and Page, 1979) have undertaken the study of oxygen diffusion in the water-saturated concrete and cement paste and have found that in comparison with chloride diffusion, oxygen diffusion is relatively faster.

Further, the thickness and the quality of concrete have only a small effect on the flux of oxygen. In recent years some efforts have been made to examine diffusion characteristics of migratory corrosion inhibitors. Bjegovic and coworkers (Bjegovic et al., 1993) have developed a method for monitoring the process of diffusion of migratory corrosion inhibitors based on volatile amines through concrete, and have determined the diffusion coefficients using Fick's first law. Diffusion of corrosion inhibitors based on amino-alcohols, has also been studied by Fear and the results are presented in their report (Fear, 1996). Other experiments were carried out as a part of the Strategic Highway Research Program (SHRP-S-666) to examine the penetration of amino-alcohols from a repair material through to the parent concrete (Al-Qadi et al, 1993). The findings of the studies on the penetration of chloride, oxygen and inhibitors in concrete have been detailed previously in sections 2.5.1 and 2.5.2.

6.3 - EXPERIMENTAL PROCEDURE

6.3.1 - Materials

Preparation of concrete

Two mixes with water/cement ratios 0.45 and 0.60 were used. The mix design for both water/cement ratios with the types of aggregate, sand and cement used, is presented in Table 6.1. Concrete cylinders of 75mm diameter and 150mm length were cast in PVC moulds and compacted by vibration. The specimens were demoulded after 24 hours and fog room cured for 28 days. Test samples of 10mm and 30mm thickness were cut from these cylinders using a distilled water cooled diamond saw.

W/C Ratio: Proportions:	0.60 by mass (kg)	0.60 kg/m ³	0.45 by mass (kg)	0.45 kg/m ³
Aggregate (9 mm) – kg/m ³	1.8	880	1.8	910
Sand (Clayton coarse) – kg/m ³	1.7	830	1.7	860
Water - L/m ³	0.6	294	0.45	17
Cement (gen. purpose) – kg/m ³	1.0	490	1.0	490

Table 6.1 - Proportions of the concrete mix

Diffusion cell

The Diffusion cell used in this work was a two-compartment cell made of an outer PVC body (Figure 6.1). The compartments were separated by a cylindrical concrete membrane, having different thickness (10 and 30mm) and water/cement ratios (w/c: 0.45 and 0.60), mounted at the center using a neutral cure silicone sealant. Compartment A (upstream compartment/cell) contained aqueous (0.1M) inhibitor solution and compartment B (downstream compartment/cell) contained water. Both these compartments were provided with sealable openings from which aliquotes can be added or withdrawn. The seals also helped in preventing any losses due to evaporation.

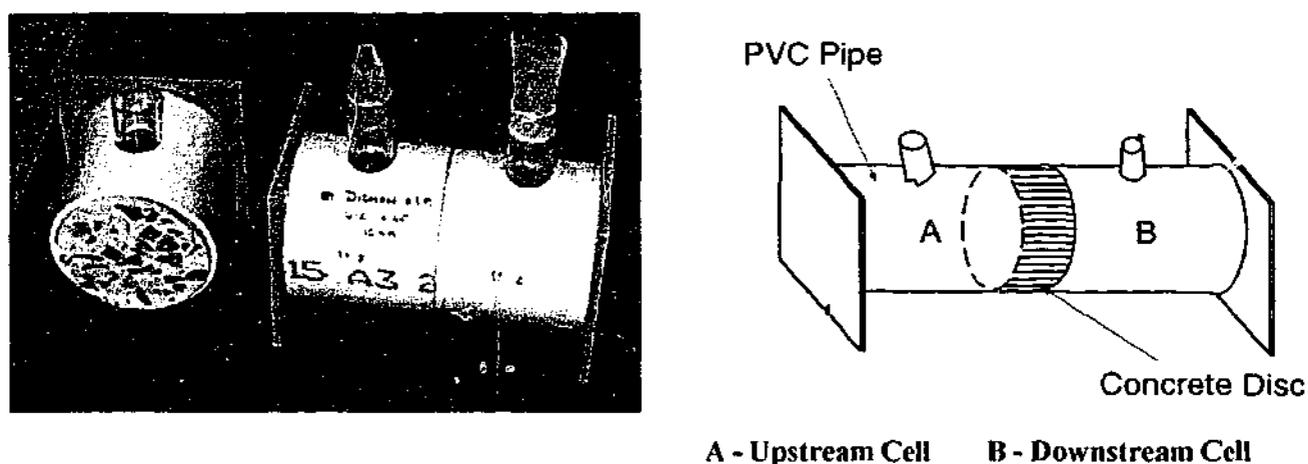


Figure 6.1 –Diffusion cell used to determine inhibitor diffusion.

Inhibitor solutions

Inhibitor concentrations used were 0.1M for DICHAN and DMEA and 5 wt % for the commercial MCI, which is assumed to contain a hydroxyalkylamine having molecular weight between 50 to 500 as an active ingredient (Martin and Miksic, 1989). The concentration was considered in % terms since the exact amount of active ingredient present in this formulation was unknown. The influence of variation in the upstream concentration on the level of diffusion was also studied by using higher concentrations of DMEA (1M) and MCI (20 wt %) in the upstream compartment. DICHAN was excluded from the concentration studies because of its limited solubility in water. All of the tests were conducted in duplicate at a temperature of 25 ± 1 degrees C.

6.3.2 - Determination of Unknown Inhibitor Concentration

The amount of inhibitor diffusing through the concrete membrane was monitored by temporarily withdrawing 25 mL aliquots of solution from the downstream compartment at different intervals over a period of up to 470 days, and analysing them using an amine-sensitive ORION 95-12 electrode (Figure 6.2). The measurements were made in a magnetically stirred thermostatted cell. The pH was adjusted to >12 using sodium hydroxide and the ionic strength was adjusted using an ionic strength adjustment buffer. After each measurement the aliquots containing the additives were returned to the cell in order to maintain the concentration of the inhibitor and solution volume in the downstream compartment.

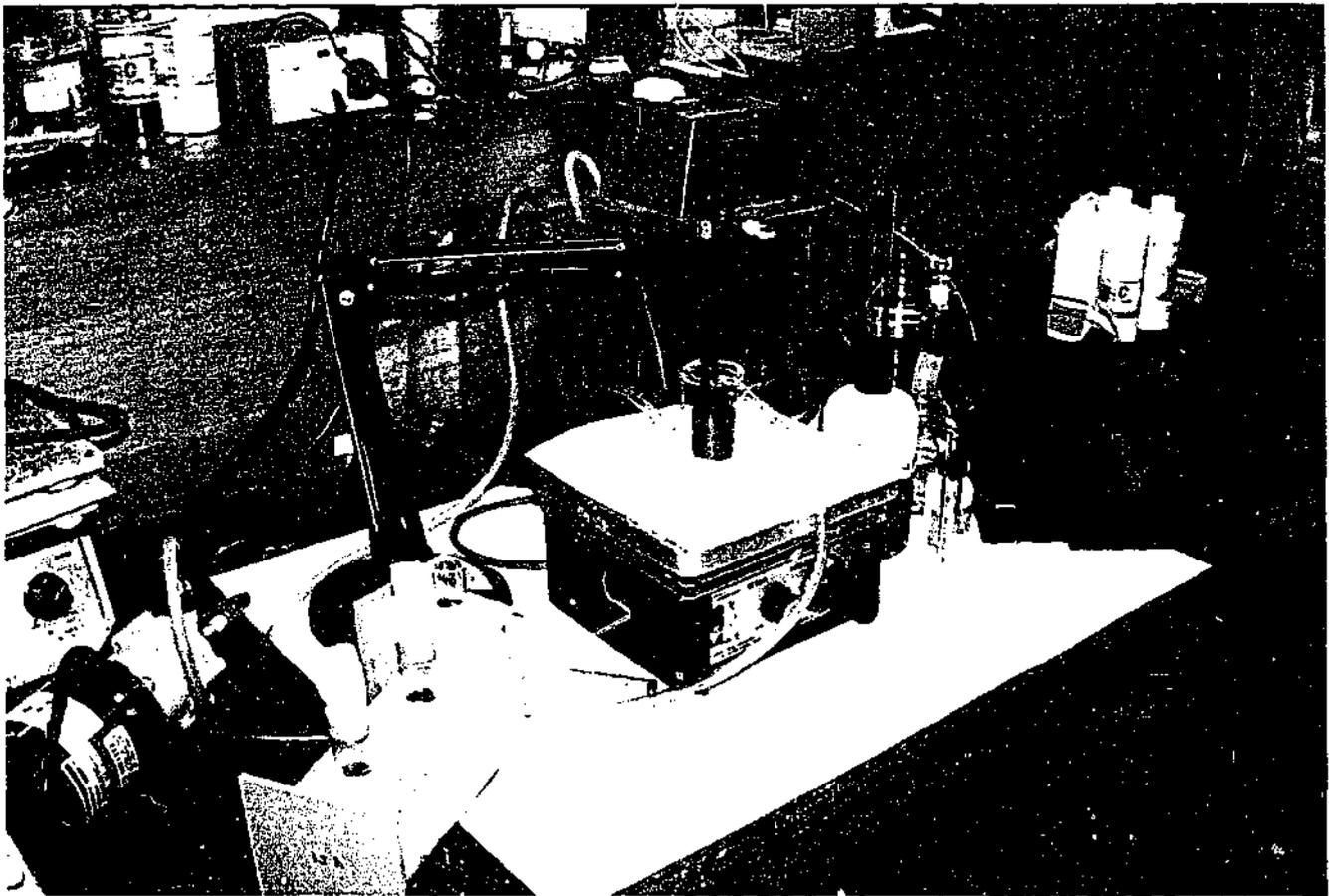


Figure 6.2 – Experimental set up for analysing unknown inhibitor concentration

Theoretical basis for measurement of inhibitor concentration

The specific amine sensitive electrode, used for analysing the solution, contains a hydrophobic gas permeable membrane to separate the sample solution from the electrode internal solution, 0.1 M NH_4Cl . Dissolved amine in the sample diffuses through the membrane until the partial pressure of the amine is the same on both sides

of the membrane. In any given sample the partial pressure of amine is proportional to its concentration, and this is related to potential, E via the Nernst equation.

$$E = E_0 - S \log \{NR_3\} \quad \text{Equation 6.1}$$

Where $\{NR_3\}$ is the (unknown) amine concentration, E_0 is the reference potential, which is partly determined by the internal reference element and S is the electrode slope, which is defined as the change in millivolts observed with every tenfold change in concentration. Since E_0 and S are constants, the calibration curve could be plotted for a range of known concentrations and the corresponding measured electrode potentials and the unknown concentrations for different inhibitors can be determined from the respective calibration curves.

A representative calibration curve for DICHAN is presented in Figure 6.3. The unknown downstream concentrations of inhibitors over different periods, obtained from the calibration curves, were plotted as a function of time. The optimum period to measure the concentration changes due to diffusion of amines was previously shown to be a 7-10 day interval (Bjegovic et al., 1993).

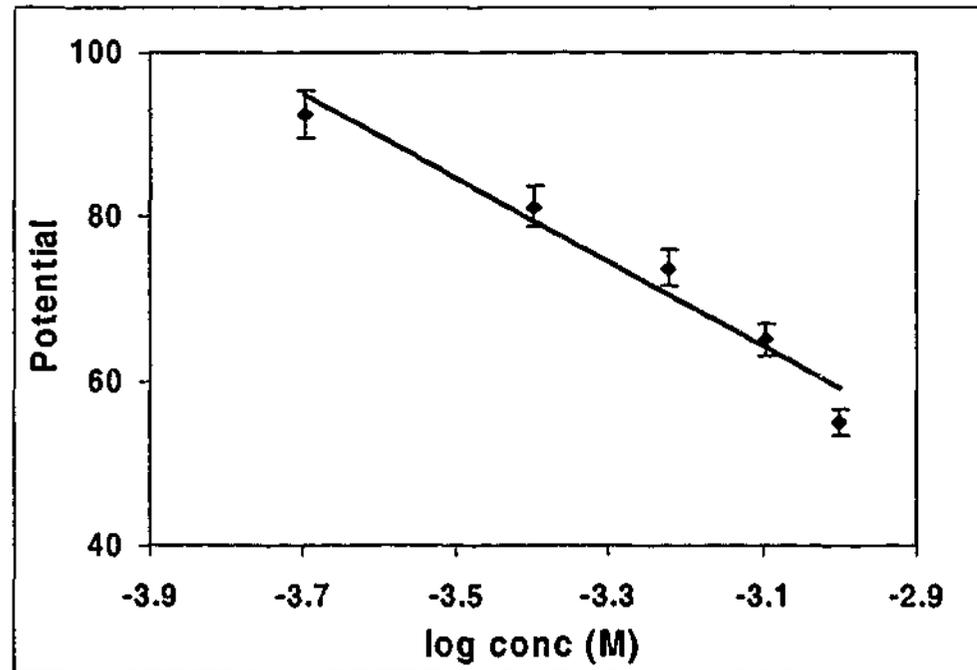


Figure 6.3 – Calibration curve for DICHAN

6.3.3 - Determination of Diffusion Coefficients

The theoretical basis for the estimation of inhibitor diffusion coefficients under both steady state and non steady state conditions of fickian diffusion have been discussed and the respective equations have been derived in section 2.5.3. Hence, in this section, only the final equations used in the determination of diffusion coefficients will be presented.

Steady state conditions

The effective diffusion coefficient D_{eff} (in m^2/s) assuming the steady state conditions of flow was calculated using the following equation, where V is the volume of solution in the downstream cell in m^3 , A is the cross-sectional area of the concrete membrane in m^2 , l is the thickness of the membrane in m and C_1 and C_2 , are the diffusant concentrations in the upstream and downstream cells respectively. Since C_1 , A , V and l are known, D_{eff} can be estimated by calculating the slope of the C_2 vs t plot.

$$C_2 = D_{\text{eff}} C_1 \frac{(t - t_0)A}{Vl} \quad \text{Equation 6.2}$$

Non steady state conditions

Non-steady-state diffusion coefficients or the apparent diffusion coefficients D_{app} were estimated using a finite difference solution to Fick's Second Law of Diffusion (Crank et al., 1981) as per the equation

$$\frac{C(x,t)}{C_0} = \text{erfc} \frac{x}{2\sqrt{Dt}} \quad \text{Equation 6.3}$$

where C is concentration, t is time, x is the distance and erfc is the error function complement, equal to the 1- the error function. Boundary Condition: $C(0,t) = C_0$ Initial condition: $C(x,0) = 0$

An iterative approach is then employed to determine the value of D which best fits the experimental data. In the present work the concrete membrane thickness is divided into a number of increments and the diffusant concentration profile within the concrete membrane at time ' t ' is calculated. The flux emerging from the downstream face over time is integrated to yield a predicted concentration–time plot for the downstream half-

cell. Assumed boundary conditions are; that the upstream concentration remains essentially constant, and that the downstream concentration is negligible by comparison, throughout the period of interest. The diffusion coefficient is estimated by iterative comparison of the measured and predicted concentration-time plots.

6.4 – EVALUATION OF DIFFUSION BEHAVIOUR OF DIFFERENT INHIBITORS IN CONCRETE

The primary assumption made in these studies is that the transportation of inhibitor molecules takes place by ionic or molecular diffusion through the concrete pore water. Diffusion of inhibitors is studied here as a function of concrete porosity (as deduced from the w/c ratio), cover-depth and inhibitor concentration.

6.4.1 - Effect of Water/Cement Ratio and the Physico-Chemical Characteristics of Inhibitor Molecules

Figures 6.4 and 6.5 show plots of inhibitor concentration versus time, where the amount of inhibitor, which has migrated through the concrete membrane (having w/c ratio 0.45 and 0.6), is plotted as a percentage of concentration in the upstream cell. The concentration diffused as a ratio of the original upstream concentration (percentage diffusion) was presented instead of the absolute value of inhibitor concentration. This is mainly because of different starting (upstream) concentrations of commercial MCI (5 wt %) and the individual amines DICHAN and DMEA (0.1M), which makes the comparison of diffusivity of different inhibitors, based on their diffused concentrations emerging out into the downstream compartment, very difficult. Additionally, the lack of accurate knowledge of the amine component and its percentage in the finished commercial product MCI makes the comparison more complex. Table 6.2 presents representative data for the time dependent diffusion characteristics of DICHAN, summarising the electrode potentials and the corresponding downstream concentrations.

The most striking features of Figures 6.4 and 6.5 are that the concentration-time plots for all the inhibitors do not follow fickian case I diffusion for the full range. It is evident that these plots can be divided into two distinct regions. The initial part extending up to around 150days, which approximately follows fickian diffusion and

where inhibitor concentration in the downstream cell increases as a function of time, and the latter part, which cannot be fitted into a fickian model. In this part of the plot the amount diffused reaches a maximum value and starts to level off as defined by the diffusion plateau. Attempts are made here to treat the initial and the latter parts separately. The early and intermediate, apparent linear regions, have been fitted to Fick's first and second laws for steady state and non steady state conditions and diffusion coefficients are calculated, whereas the diffusion plateau is interpreted in terms of a "diffusion anomaly", discussed further below.

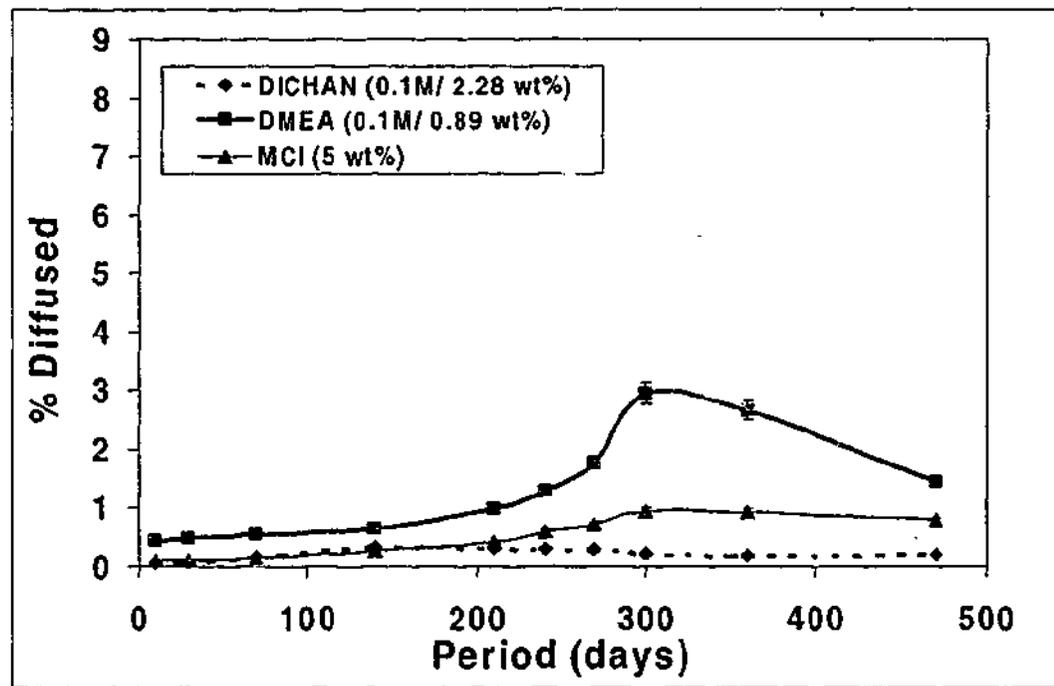


Figure 6.4 - Inhibitor % diffused through 30mm concrete w/c ratio 0.45

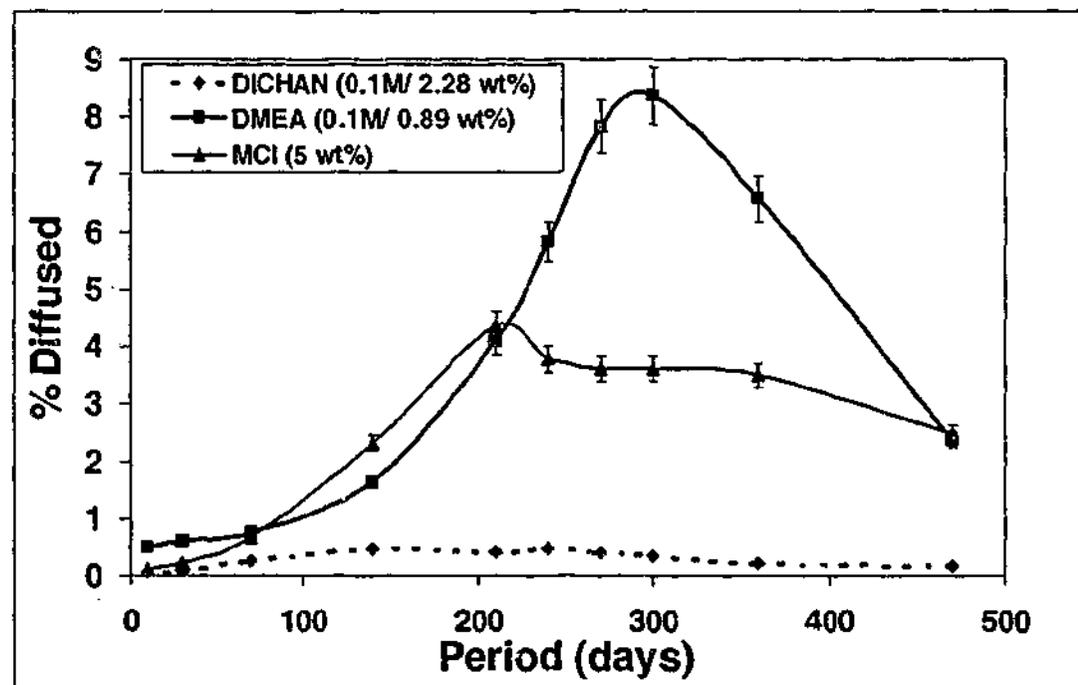


Figure 6.5 - Inhibitor % diffused through 30mm concrete w/c ratio 0.6

DICHAN Upstream Cell Concentration / 0.1 M (2.28 wt%)														
Period Days	Specimen I					Specimen II					Average		Std Dev	Std Dev (%)
	Potential (mV)	Conc in B log C* (M)	Conc in B C (M)	Conc in B (wt%)	% Diffused (I)	Potential (mV)	Conc in B log C* (M)	Conc in B C (M)	Conc in B (wt%)	% Diffused (II)	DICHAN (wt%)	DICHAN % Diffused		
10	131	-4.178	0.0001	0.0015	0.066	129	-4.133	0.0001	0.0017	0.074	0.0016	0.070	-0.00008	-5.00
30	121	-3.998	0.0001	0.0023	0.101	124	-4.044	0.0001	0.0021	0.090	0.0022	0.096	0.00012	5.50
70	96	-3.564	0.00027	0.0062	0.273	100	-3.632	0.00023	0.0053	0.233	0.0058	0.253	0.00046	7.96
140	73	-3.264	0.00055	0.0124	0.545	79	-3.391	0.00041	0.0093	0.406	0.0109	0.476	0.00158	14.55
210	79	-3.381	0.00042	0.0095	0.416	80	-3.407	0.00039	0.0090	0.392	0.0092	0.404	0.00027	2.93
240	74	-3.285	0.00052	0.0118	0.518	78	-3.362	0.00044	0.0099	0.435	0.0109	0.477	0.00096	8.77
270	77	-3.350	0.00045	0.0102	0.447	80	-3.416	0.00038	0.0088	0.383	0.0095	0.415	0.00073	7.65
300	83	-3.459	0.00035	0.0079	0.347	84	-3.489	0.00032	0.0074	0.324	0.0077	0.336	0.00026	3.39
360	100	-3.641	0.00023	0.0052	0.229	101	-3.663	0.00022	0.0050	0.217	0.0051	0.223	0.00013	2.55
476	106	-3.739	0.00018	0.0042	0.183	110	-3.804	0.00016	0.0036	0.157	0.0039	0.170	0.00029	7.47

* - The diffused concentration of inhibitor in the downstream compartment B (i.e. log C) is calculated using a linear regression method for the (E vs log C) calibration curve plotted with the known concentrations of the same inhibitor

Table 6.2 - A typical example of a diffusion profile for DICHAN through a concrete membrane having 30mm thickness and w/c ratio 0.6

On comparing the trends exhibited by different inhibitors in these graphs it appears that, in the case of water/cement ratio 0.45, (Figure 6.4) both MCI and DICHA show a much slower rate of diffusion than DMEA. A similar trend is observed in the case of concrete having a water/cement ratio 0.6 (Figure 6.5), with MCI diffusing measurably faster than DICHA. The rate of diffusion of all the inhibitors in this case is significantly higher than that observed in the specimens with w/c ratio 0.45, which is consistent with the greater porosity of the concrete.

Application of steady-state conditions to the starting/intermediate region

The steady-state diffusion coefficients derived using Fick's first law are presented in Table 6.3, along with the solubilities and the molecular formulae of the inhibitors. From Figures 6.4, 6.5 and Table 6.3 it is evident that an increase in the water/cement ratio results in an increase in the rate of penetration of inhibitor molecules. The effect of water/cement ratio is quite apparent in the case of DMEA and MCI where diffusion coefficients show a significant increase on increasing w/c ratio from 0.45 to 0.60. This is likely to be due to both an increase in the volume of the capillary pores and the reduction in pore segmentation that accompanies an increase in the w/c ratio above a value of 0.4-0.45 (MacDonald and Northwood, 1996). Water/cement ratio is also likely to influence the tortuosity of the diffusion path, with lower values resulting in a more tortuous diffusion path around aggregate particles.

These results agree well with values previously reported for chloride ions (Midgley and Illston, 1984; Page et al., 1981). The results are also consistent with those obtained for the amino-alcohol-based migratory corrosion inhibitor Sika "Ferrogard" 903 (Wolfseher and Partner, 1997), where an increase in the capillary porosity or the water/cement ratio from 0.45 to 0.6 has been shown to increase the penetration capacity of the inhibitor. e.g. the "Ferrogard" content at a depth between 25 to 37.5 mm in the case of water/cement ratio 0.45 was found to be 0.9 $\mu\text{g/gm}$ of concrete as against 8.0 $\mu\text{g/gm}$ of concrete for the same depth with the water/cement ratio 0.60.

In the case of DICHA the effect of water/cement ratio on the diffusion coefficient is found to be relatively small. This is likely to be related in large part to a combination of relatively high molecular size and the very small concentration gradient allowed by the limited solubility of this inhibitor.

Inhibitor	30 mm		10 mm	Molecular Formula	Solubility per 100 g Water
	W/C :0.45	W/C : 0.6	W/C :0.45		
DICHAN					
(0.1M/2.28 wt%)	0.5×10^{-12} ($\pm 0.1 \times 10^{-12}$)	0.4×10^{-12} ($\pm 0.06 \times 10^{-12}$)	0.2×10^{-12} ($\pm 0.01 \times 10^{-12}$)	$(C_6H_{11})_2NH_2NO_2$	3.9
DMEA					
(0.1M/0.89 wt%)	1.8×10^{-12} ($\pm 0.07 \times 10^{-12}$)	4.6×10^{-12} ($\pm 0.4 \times 10^{-12}$)	0.8×10^{-12} ($\pm 0.02 \times 10^{-12}$)	$HOCH_2CH_2N(CH_3)_2$	Completely miscible
(1M/8.91 wt%)	0.5×10^{-12}				
MCI					
(5 wt%)	0.8×10^{-12} ($\pm 0.1 \times 10^{-12}$)	4.4×10^{-12} ($\pm 0.7 \times 10^{-12}$)	1.0×10^{-12} ($\pm 0.1 \times 10^{-12}$)	$R_1R_2R_3^*NOH$	Completely miscible
(20 wt%)	0.5×10^{-12}				

* hydrogen or alkyl group

Table 6.3 - Diffusion coefficients (m^2/s) (calculated by fitting Fick's first law to early/intermediate apparent linear regions), molecular formulae and solubilities of inhibitors

As mentioned in the introduction, the diffusivity is not only an intrinsic property of the membrane material, but it also depends upon the nature of the diffusant (Saetta et al., 1993). For a given porosity of concrete, different diffusion rates are observed for different inhibitors (Table 6.3) e.g. DICHAN is shown to have the lowest diffusion rate, MCI slightly higher, and DMEA the highest. The differences in the diffusion rates of inhibitor molecules could be ascribed to differing mobilities of the inhibitor molecules resulting from differences in their physico-chemical characteristics such as solubility, vapour pressure, molecular size, polarity and the chemical makeup of the molecules. The polarity (ionic nature) and the chemical structure are important, as they might have some influence on inhibitor binding with the surrounding concrete ingredients. Vapour pressure is also included here since, in the case of organic inhibitors with substantial vapour pressure, there is always a possibility of transport via gas permeation through the partially filled/empty pores. However, it should be remembered that high vapour pressure, which may result in faster migration of the inhibitor through concrete towards the steel reinforcement, can also cause heavy inhibitor losses to the atmosphere.

Elsener et al (Elsener et al., 1999) have shown that the volatile constituent of inhibitor evaporates through the porous mortar resulting in a loss of inhibiting properties. Similarly, high solubility of the inhibitor in water might lead to leaching out of the inhibitor.

For a given concrete thickness and porosity, transport of DICHAN is likely to be restricted due to its sparing solubility (3.9 g per 100 g of water), which would limit the concentration gradient between exposed surface and embedded rebar. DICHAN also has a higher molecular size compared with DMEA and MCI, which may limit diffusion in concrete. The inhibitor has a molecular weight of 228 g/mol, and the structure includes two cyclohexane rings. The size of the DICHAN molecule may be quite large as compared with the size of capillary pores (of the order of 1.3 μ m) and the gel pores (between 15-20 Å) (Neville, 1982). By comparison, DMEA is a relatively small molecule with a molecular weight of only 89 g/mol. From the similarities observed between the behavior of MCI and DMEA, it appears that the active amine constituent in MCI is also a relatively small molecule.

The possibility of binding (immobilisation) of organic/inorganic components of DICHAN, to the concrete pore surface in a concentration dependent equilibrium also cannot be denied. In fact the higher contribution of binding in limiting the mobility of DICHAN is consistent with the observation that changes in the water/cement ratio have a relatively small effect on the diffusion coefficient. The limited effect of w/c ratio on binding is consistent with the work on chloride binding by Goto and Roy (Goto and Roy, 1981), who studied the effect of water/cement ratio on the diffusivity of sodium and chloride ions through the hardened cement paste. They observed that the effect of w/c ratio on diffusion of these ions was relatively small, ascribing this to a strong interaction of these ions with the cement paste.

DICHAN is an alkyl-substituted quaternary ammonium salt of the nitrite anion. Although steric factors and deprotonation of free alkyl-ammonium ions to simple substituted amine molecules by the alkaline pore water would be expected to inhibit binding of the cation, binding of free nitrite ions would be expected to be quite strong. Calcium nitrite solution has previously been found to be ineffective as a migrating inhibitor (Tomosawa et al., 1992). Recent studies by Li and coworkers (Li et al., 1999), while studying the nitrite content in the concrete pore water by in situ leaching method,

have identified strong binding characteristics for this inorganic group. Similarly, it was shown by Tritthart et al (Tritthart et al., 1999) that the inorganic component of an amino-alcohol based migratory inhibitor had been completely bound or had precipitated in concrete and could not be detected in the pore solution. Thus these factors are all likely to result in a very slow DICHAN transport process.

Unlike DICHAN, MCI and DMEA are completely miscible with water and appear not to have the binding characteristics of DICHAN with concrete, at least during the initial period. This is indicated by significant variation in their diffusion coefficients as a function of the water/cement ratio. Hence the difference in diffusion rate of DMEA and MCI is considered to be primarily related to their relative molecular size. It was found (see Table 6.3) that diffusion coefficient of DMEA increased by two and a half times, whereas that of MCI exhibited in excess of a five times increase on raising the water/cement ratio from 0.45 to 0.60. The reason for this may be ascribed to the fact that MCI could be either a slightly larger or more polar molecule than DMEA. At a w/c ratio equal to 0.6 the available migration paths are sufficient to render any differences in the molecular size of these two chemical species negligible. The effect of water/cement ratio on the permeability coefficient of the hydrated cement paste was investigated in earlier research (Woods, 1954). It was found that the permeability coefficients were considerably lower for water/cement ratios below about 0.6 and would increase by orders of magnitude when water/cement ratio was increased from 0.3 to 0.7. Where the water/cement ratio was below 0.6, the lower permeability coefficient was attributed to the segmentation of the capillary pores due to blocking by the cement gel. This is again consistent with the earlier explanation about the influence of w/c ratio on the diffusion coefficients. Further, the data presented for MCI suggests that it is likely to contain only one amine-based migrating active ingredient, otherwise the concentration-time plot would be expected to be distorted by separation of the ingredients during passage through the concrete.

At longer times, it was observed that, the amount of inhibitor diffused reached a maximum value and started to level off as seen in Figures 6.4 and 6.5. The accurate modeling of this effect may not be possible in the absence of further investigation using other methods such as the analysis of concrete pore water or concrete resistivity measurements. However, it is evident that this is not a case I diffusion and hence application of fickian laws is not possible in this case. The plateau effect was observed

consistently, and its timing showed certain trends with respect to membrane thickness and the upstream inhibitor concentration. This suggests that there exists some "anomalous effect" which is mechanistically quite different from the initial ionic/molecular diffusion.

One of the effects that may explain this non fickian diffusion mode may be the binding or interaction between the permeating inhibitor solution and concrete, given the extended contact period (between 150 and 300 days) between the two. The inhibitor-concrete interaction may result in progressive immobilization of the diffusing molecules and effectively reduce their participation in the diffusion process and hence the ionic transport. On the other hand there may be a reduction of pore volume and or the average size of the pore diameter due to the formation of a precipitate which blocks the pores partially or fully. This in turn can change the effective permeability and hence diffusivity directly. Similar reactions have been observed in the case of chlorides (Collepari et al., 1972; Goto and Roy, 1981) and inorganic components of an amino-alcohol based inhibitor by other researchers (Elsener et al., 2000; Tritthart et al., 1999).

There could be different possible inhibitor/concrete interactions. One possibility is physical adsorption of inhibitor molecules onto the concrete pore walls, which may provide a site for inhibitor attachment ("binding site"). This could occur in a similar manner to that occurring at the inhibitor/steel interface. Since the non-polar tails of the inhibitor molecules are likely to form a hydrophobic barrier, it may help in reducing the transport of the other aggressive species such as chloride, oxygen or water, which aid corrosion. Also concrete is a highly ionic material and may act as a stationary phase in an ion exchange column. Since the inhibitors are likely to be protonated on hydrolysis, the possibility of attachment of some of the ionic components of the mobile phase, i.e. of the permeating inhibitor solution, to the ionic sites in concrete cannot be denied. A further possibility could be chemical complexation of the inhibitors with the constituents of cement paste. e. g. the spectroscopic analysis of commercial MCI inhibitor had indicated that one of the components of this inhibitor is the ammonium salt of carboxylic acid (benzoic acid) (section 4.3.3). Hence the chemical reaction between the constituents of the cement paste (such as calcium and the carboxylic group) resulting in the formation of calcium carboxylate is also possible. Also microstructural modifications resulting from precipitation and/or hydration/recrystallization phenomena related to extended immersion "curing" cannot be ruled out.

It is worthy of note that the possible interactions between the organic inhibitor and concrete postulated here are contrary to the observations of Tritthart et al (Tritthart, et al et al., 1999). These workers found that the active organic ingredient (the amino-alcohol) of the migratory corrosion inhibitor formulation FG 903 remained dissolved in the pore solution and was not bound by cement. However, it must also be recognised that Tritthart's observations, as well as other laboratory investigations, reported on diffusion studies through concrete are based on the short-term (up to 30-60 days) results. Observation of the plateau effect in this work has eventuated due to the long-term nature of the experiments i.e. around 300 days. Further, the chemical nature of the other components in the commercial formulations might also affect the binding characteristics of the individual inhibitor. It is relevant to note here that, an inhibitor having a similar make up to the commercial inhibitor (i.e. a blend of amino-ethanol and carboxylic acid) was investigated for its diffusion behaviour through mortar by Elsener et al (Elsener, et al et al., 2000). It was found that the non volatile component of the inhibitor i.e. the carboxylic acid reacted with the calcium ions present in the concrete pore solution leading to the precipitation of the carboxylate. This further resulted in a pore blocking effect reducing the permeability of the concrete surface. One possible technique to investigate this binding or precipitation phenomenon could be to press out and analyse the pore solution containing unbound inhibitor from the concrete. The bound inhibitor portion can then be extracted using a suitable solvent from the concrete membrane for further analysis.

In some cases it was also observed that the downstream concentration started decreasing towards the end of the test period. The likely explanation for this decrease could be that there are two processes likely to be occurring concurrently in the downstream compartment - diffusion of inhibitor through the concrete membrane from the upstream compartment and loss of volatiles from the downstream cell. Based on the design of the diffusion cell, some losses or leakages are always possible from both the compartments. During the initial stages, the factor of inhibitor losses is not a major issue, as they are well compensated by the relatively higher flux of inhibitor emerging from the downstream face of the concrete membrane. However, at a later stage the flux decreases significantly, due to one of the possibilities described above. The rate of loss of the diffusant through evaporation from the downstream side may exceed its rate of arrival, leading to a net decrease in the downstream concentration. Again contribution from the changes to the chemical environment, due to returning the measurement

aliquots to the downstream cell during the monitoring period, or even the chemical degradation of the amine, or its interaction with concrete, cannot be ruled out here.

6.4.2 - Effect of Concrete Cover Thickness

Table 6.4 and Figures 6.6a, b, c show a comparison of diffusion characteristics of the three inhibitor systems through 10mm and 30mm thick concrete membranes. As expected the concentration increase was more rapid for the thinner membrane. As noted previously, at longer times the amount diffused in the downstream cell appeared to peak to a certain value and then became relatively stable. This effect was observed much earlier for a 10mm membrane i.e. between 100 to 200 days as compared with 300 days in the case of a 30mm membrane. This is likely to be due to faster occupation of the lesser number of "binding sites" available in a 10mm concrete membrane (because of the smaller area of the pore walls) as compared with the 30mm membrane. Assuming that an equivalent flux passes through the upstream face of both 10 and 30 mm concrete, the plateau effect can be considered to be related to the ratio of the "flux" to "the number of binding sites". As the number of binding sites in a particular concrete membrane is likely to depend upon the volume (or the thickness, all the other parameters being equal) of the membrane, the leveling off of inhibitor could be regarded as a function of the concrete thickness.

Also for DICHA and DMEA, the concentration at which the plateau effect was observed for the 10mm membrane (0.0065 wt % for DICHA and 0.0203 wt % for DMEA) was slightly lower than that for the 30mm membrane (0.0077 wt % for DICHA and 0.0263 wt % for DMEA). This is consistent with the lower number of binding sites in a 10mm thick membrane, resulting in the earlier leveling off of the concentration, due to saturation of these sites. In the case of MCI, however, the plateauing of the concentration in the case of a 10mm membrane appears to be similar or slightly higher than that for a 30mm membrane. The reason for this is not clear at this time.

Upstream Conc -		DICHAN / 0.1 M (2.28 wt%)				DMEA / 0.1 M (0.89 wt%)				MCI 2005 / 5 wt%			
Period	10 mm membrane		30 mm membrane		10 mm membrane		30 mm membrane		10 mm membrane		30 mm membrane		
Days	wt%	% diffused	wt%	% diffused	wt%	% diffused	wt%	% diffused	wt%	% diffused	wt%	% diffused	
30	0.0017	0.074	0.0014	0.060	0.0047	0.529	0.0043	0.479	0.0098	0.196	0.0056	0.112	
60	0.0034	0.147	0.0016	0.069	0.0057	0.635	0.0045	0.500	0.0155	0.310	0.0056	0.112	
90	0.0052	0.230	0.0039	0.169	0.0064	0.716	0.0049	0.546	0.0511	1.022	0.0079	0.158	
150	0.0065	0.285	0.0077	0.337	0.0142	1.588	0.0058	0.654	0.0616	1.233	0.0138	0.276	
210	0.0045	0.198	0.0072	0.317	0.0203	2.278	0.0089	0.997	0.0633	1.267	0.0212	0.424	
310	0.0036	0.158	0.0053	0.230	0.0193	2.169	0.0263	2.954	0.0572	1.143	0.0478	0.955	
430	0.0025	0.111	0.0049	0.216	0.0149	1.666	0.0203	2.272	0.0497	0.995	0.0400	0.799	

Table 6.4 - Comparison of inhibitor concentration in downstream cell in wt% and its conversion to % diffused in the case of 10mm and 30mm concrete membrane having w/c ratio 0.45

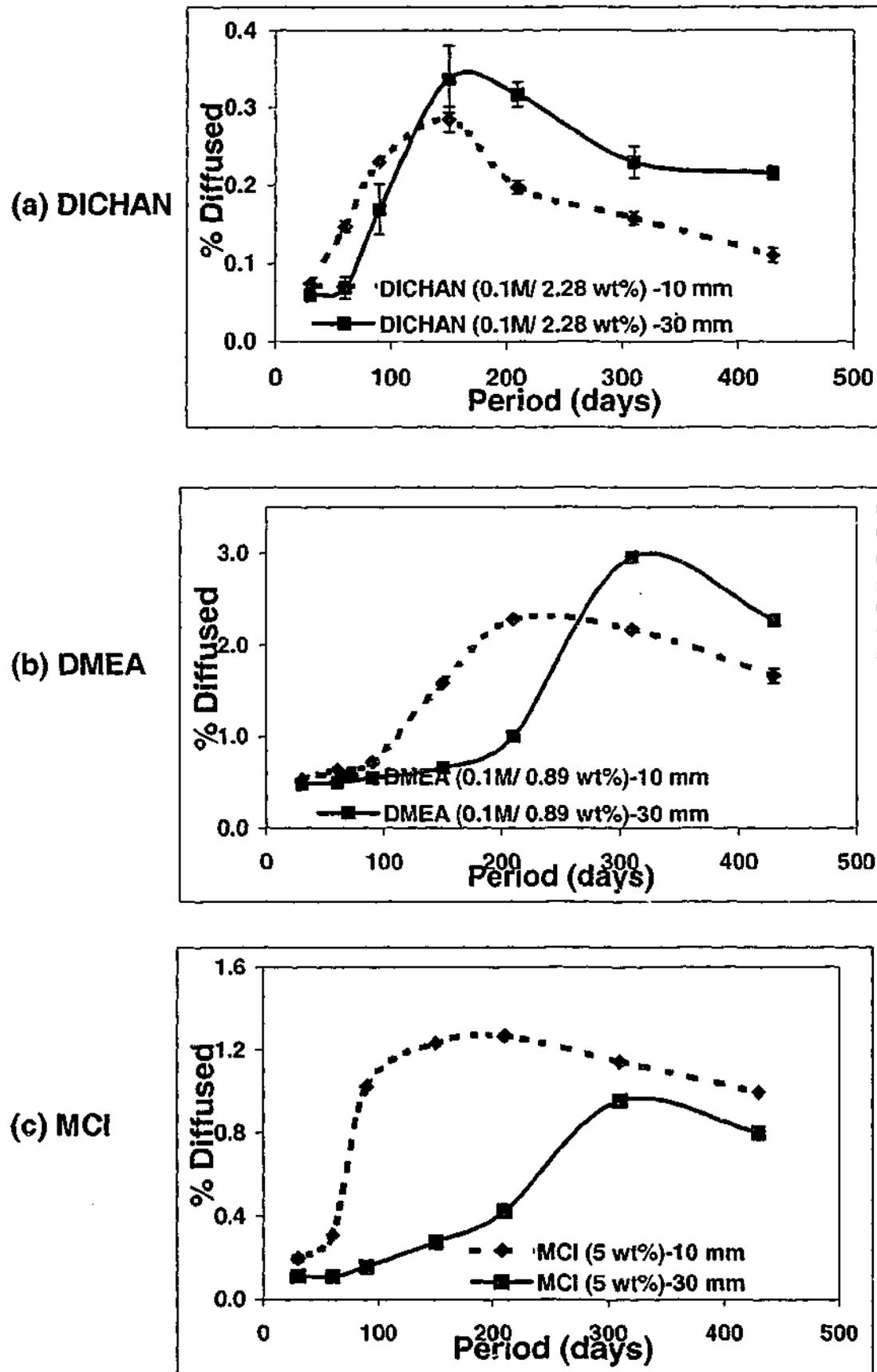


Figure 6.6 - Inhibitor % diffused through 10mm and 30mm concrete membrane having w/c ratio 0.45

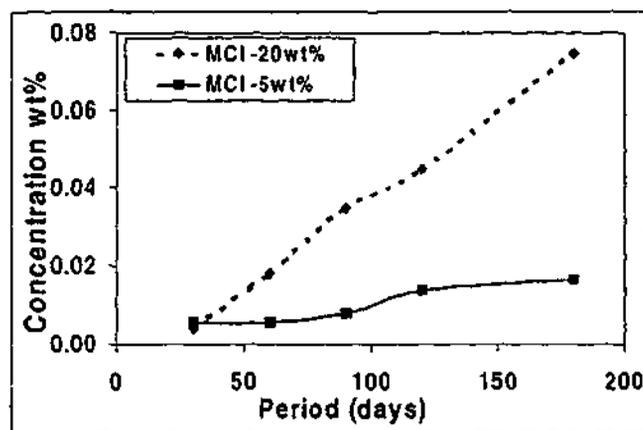
On comparing the diffusion coefficient values for both thicknesses (Table 6.3), the coefficients for 10mm thick concrete are found to be smaller than 30 mm for DICHAN and DMEA. One of the possible reasons for this could be that the application of the

steady-state technique to a 10mm membrane does not adequately reflect the actual diffusion process in concrete. As is known (Benz et al., 1994), the interfacial zone between the aggregate particles and the cement matrix of the concrete plays a significant role in the movement of ions in concrete. Hence in such a case the use of larger segments, with thickness in the range of two to three times the maximum coarse aggregate size i.e. 30mm, may be more appropriate as it would closely simulate the actual conditions in concrete (MacDonald and Northwood, 1996). Alternatively, use of mortar specimens could be an alternative option for achieving steady state conditions, as has been observed by Page et al (Page et al., 1981) in their study of chloride diffusion.

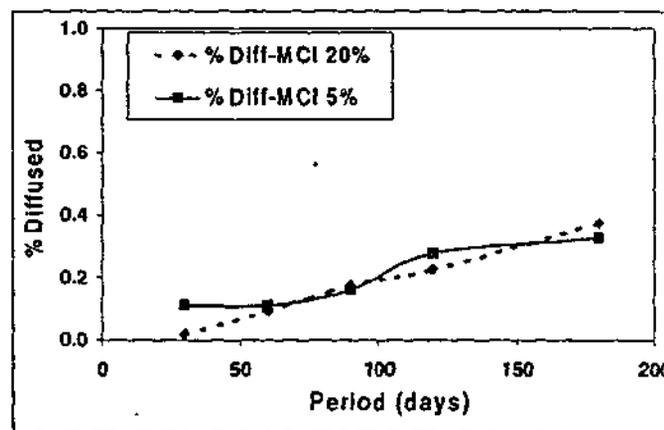
6.4.3 - Effect of Change in Inhibitor Concentration

Figures 6.7a and b and Figures 6.8a and b show the effect of concentration on diffusion of MCI and DMEA respectively through a 30mm concrete membrane having w/c ratio 0.45. In the case of MCI an increase in the upstream concentration from 5 wt % to 20 wt % resulted in an equivalent increase in the flux through the concrete membrane and a proportionate increase in the downstream concentration (Figure 6.7a). This resulted in comparable diffusion coefficients (Table 6.3) and a similar ratio of downstream to upstream concentration (Figure 6.7b), well within the repeatability expected in chloride diffusion testing (Taywood Engineering Limited). This indicates that there is no significant binding between this inhibitor and concrete at least during the initial period, thus allowing more inhibitor molecules to be transported through the concrete membrane as the inhibitor concentration is increased. This observation is consistent with our earlier results where a five times increase in the diffusion coefficient was observed on increasing the water/cement ratio from 0.45 to 0.60. Also it is interesting to note that leveling off was not observed in the case of the higher concentration until the end of the monitoring period (180 days), which again supports the postulation concerning the insignificant binding during this period. This behaviour is in contrast to the case of DMEA, where a ten times increase in the upstream concentration i.e. from 0.1M to 1M, resulted in only about a three times increase in the flux/downstream concentration (Figure 6.8a and b). Also the plateau effect was observed much earlier i.e. around 120 days as against 300 days in the case of 0.1M concentration (Figure 6.4). It is interesting to note that, in the case of both 0.1M and 1M concentrations, the leveling off of the inhibitor diffusion occurs after reaching approximately 0.02 wt % concentration in the downstream cell. The time taken to reach this level is considerably

shorter for the higher concentration. This suggests that there are a limited number of interaction sites available on the concrete pore walls. Once these sites are occupied by inhibitor molecules, further binding does not occur even on increasing the upstream concentration.

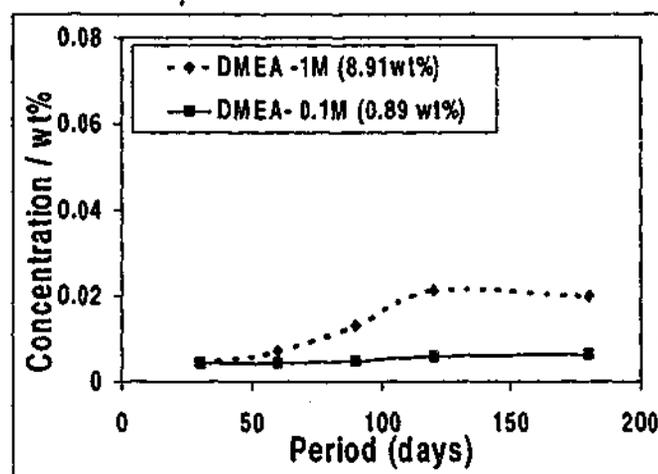


(a) in terms of concentration wt %

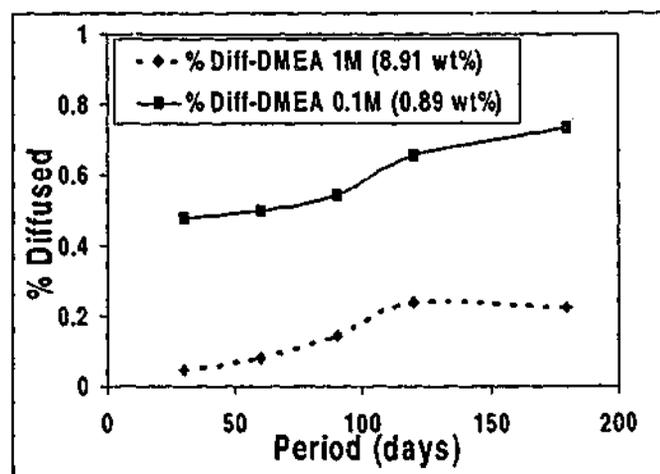


(b) in terms of % diffused

Figure 6.7 - Comparison of downstream inhibitor concentration on varying the upstream concentration of MCI in the case of 30 mm concrete membrane having w/c ratio 0.45



(a) in terms of wt %



(b) in terms of % diffused

Figure 6.8 - Comparison of downstream inhibitor concentration on varying the upstream concentration of DMEA in the case of 30 mm concrete membrane having w/c ratio 0.45

The diffusion coefficients obtained here using steady state kinetics are comparable with those reported by Bjegovic and coworkers (Bjegovic et al., 1993) for a commercial migratory corrosion inhibitor, MCI 2020 ($1.5 \times 10^{-12} \text{ m}^2/\text{s}$). It must, however, be stated that compared to the diffusion coefficients obtained in the current work and those estimated by Bjegovic and coworkers, the values obtained by Elsener et al (Elsener et al., 2000) in the case of mortar appear significantly higher i.e. $3.0 \pm 0.5 \times 10^{-10} \text{ m}^2/\text{s}$. It needs to be emphasised that Elsener and coworkers used a higher w/c ratio (0.75) for the mortar (higher porosity) and maintained the cure conditions at 80% RH for the samples. This action possibly facilitated other modes of inhibitor transport such as the capillary action or gas permeation.

The present results suggest that attempts to fit the Fick's first law model to the apparent linear regions in the early and intermediate part of concentration-time plots do not provide a perfect linear fit. As can be seen from the shape of the concentration time plot, the early age data points are likely to result in an underestimation of the coefficient. There is also evidence suggesting this occurred in some of the data reported by Miksic et al (Bjegovic et al., 1993). It was, therefore, felt that a description of the flow of inhibiting species in concrete by applying Fick's first law is an oversimplification, as steady state conditions are unlikely to simulate the actual transport conditions in concrete. As mentioned earlier, the interfacial zone between the coarse aggregate and the cement matrix may play an important role. Further, the parameters such as the composition and the porosity of concrete may vary as concrete matures with time. These variables are likely to affect the constant concentration gradient, required to be maintained under the conditions of a steady state. Hence it appears to be more appropriate to apply non-steady-state kinetics as described by the Fick's second law. These results can then be compared with those calculated using steady state conditions.

6.4.4 - Application of Non Steady-State Conditions

Modeling of inhibitor penetration using procedures well established for assessment of chloride ingress and lifetime prediction using the diffusion coefficients obtained above shows that the measured downstream concentrations cannot have been reached within the duration of the experiments. Hence the data, especially during the initial period, could not be made to match theoretical concentration-time curves for any value of D

using Fick's second law over a longer period. As fog room curing does not saturate the concrete, it must be assumed that the test pieces were not saturated at commencement of the test, and that absorption of inhibitor into the concrete membrane by capillary action driven by moisture gradient, or the transport by vapour phase during the early stage of the experiments has significantly shortened the induction period. The induction period is the time taken for the diffusing species to penetrate through the thickness of the test piece and reach a detectable concentration in the downstream cell. Figure 6.9 shows a typical data set and the resulting theoretical concentration-time plot for diffusion of DICHAN in 10mm concrete membrane, w/c 0.45. Given the influence of the initial absorption phase, the estimated result should, perhaps more accurately, be called a "penetration coefficient" rather than a diffusion coefficient.

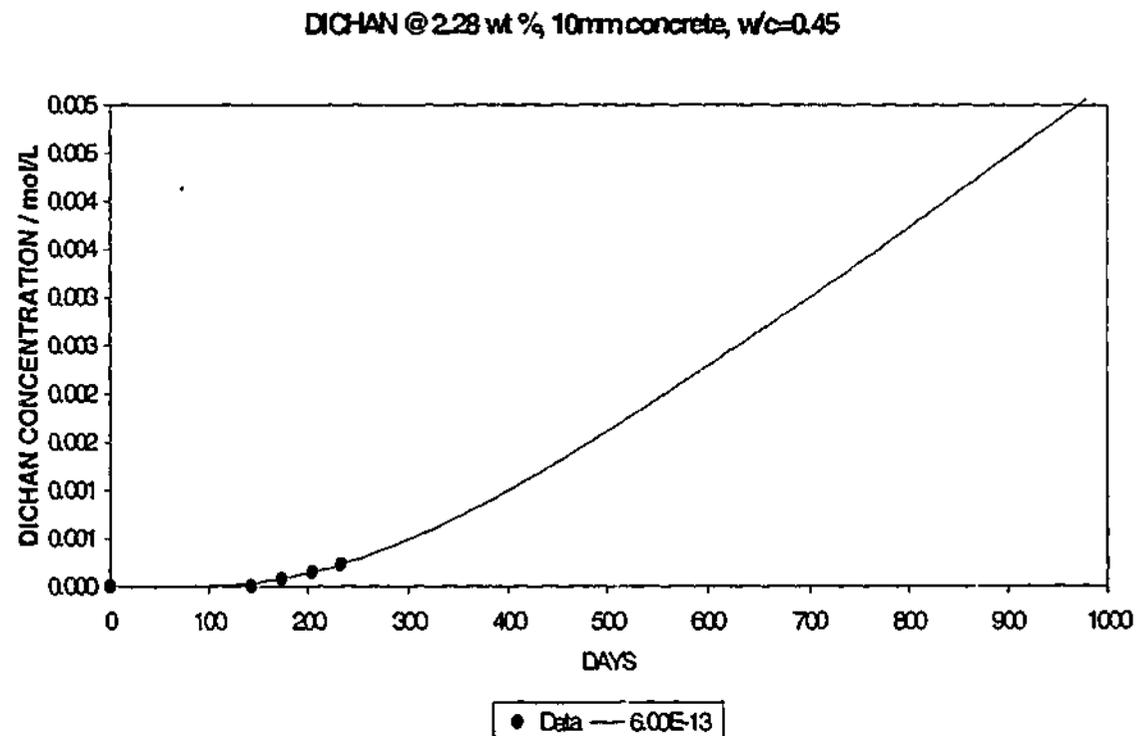


Figure 6.9 - Typical data set and estimated theoretical concentration-time plot for diffusion of DICHAN in a 10 mm concrete membrane having w/c ratio 0.45

The penetration coefficients estimated by assuming non-steady-state conditions for the above experiments are presented in Table 6.5. As the predictive model used was originally written for chloride migration tests and works with molar quantities, for the purpose of this exercise MCI has been assumed to be ethanolamine (m.w. 61.10 g/mol). This compound is known to be used in some commercial migrating inhibitor formulations. In application of the model it has been assumed that the majority of the data reflects essentially diffusive transport, and that the net practical effect of the initial absorption phase has only been to reduce the induction period.

Inhibitor	30 mm		10 mm
	W/C : 0.45	W/C : 0.6	W/C : 0.45
DICHAN (0.1M/2.28 wt%)	1.0×10^{-12}	2.5×10^{-12}	0.6×10^{-12}
DMEA (0.1M/0.89 wt%) (1M/8.91 wt%)	3.0×10^{-12} 2.7×10^{-12}	7.2×10^{-12}	1.5×10^{-12}
MCI (5 wt%) (20 wt%)	1.6×10^{-12} 3.2×10^{-12}	7.0×10^{-12}	1.0×10^{-12}

Table 6.5 - Penetration coefficients (m^2/s) for inhibitors using Fick's second Law

Several important features emerge from the non-steady state analysis conducted here. Diffusion coefficients estimated by the non-steady state equation showed similar trends to those calculated by using the steady state equation. e.g. amongst the three inhibitors, DICHAN exhibited the lowest diffusion coefficient and DMEA the highest. Similarly, increase in the porosity of concrete resulted in higher penetration of all the inhibitors under non-steady state conditions. The effect of concentration variation showed that the diffusion coefficient of MCI increased by two times on increasing the upstream concentration four times. This observation suggests that on increasing the upstream concentration there was more than an equivalent increase in the diffused amount of inhibitor. This is different from the equivalent increase in the diffused amount obtained under the steady state conditions, which helped to maintain comparable diffusion coefficients for MCI under those conditions. Diffusion coefficient values in the case of DMEA were maintained when the concentration was increased by 10 times. This is again different from a marked decrease observed in diffusion coefficients of DMEA under steady state conditions. The above observations may be attributed partially to insignificant binding on concrete pore walls in the case of both DMEA and MCI over the initial time period for which this fit is performed. However, this needs to be supported by more evidence.

In the case of experiments using a 10mm thick concrete membrane, with the exception of the MCI, the penetration coefficients obtained for the other inhibitors are

significantly higher than the corresponding diffusion coefficients reported for assumed steady-state conditions in Table 6.3. Hence it is evident that the test systems were not, with the exception of the MCI test mentioned above, at a complete steady-state during most or all of the measurement period.

It may be noted here that the diffusion coefficient values shown in Table 6.5 may be slightly optimistic in comparison with true diffusion coefficients. This could be due to the nature of the assumptions made regarding the effects of an initial absorption phase on the test results. The initial absorption phase is likely to distort the concentration profile, and hence the effective concentration gradient, within the membrane during the early part of the measurement period. If the membrane is saturated (with water) at the commencement of the experiment, the initial concentration gradient is defined by the bulk concentration of diffusant (inhibitor) in the upstream cell at one face, the diffusant (inhibitor) free water at the downstream face, and the geometric thickness of the membrane. An initial absorption phase possibly results in a quantity of inhibitor containing water from the upstream side being absorbed into one half of the membrane thickness, the other half being occupied by absorbed water from the downstream cell. Depending upon the degree of binding between the inhibitor and the concrete membrane, there may be a front of inhibitor at some distance behind the advancing water front. The concentration profile thus developed by the absorption phase results in effectively reducing the geometric distance between the upstream and downstream inhibitor concentrations. Finally over a period of time the diffusion process is likely to take over and remove the distortion. The effect of the initial inhibitor adsorption is shown schematically in Figure 6.10.

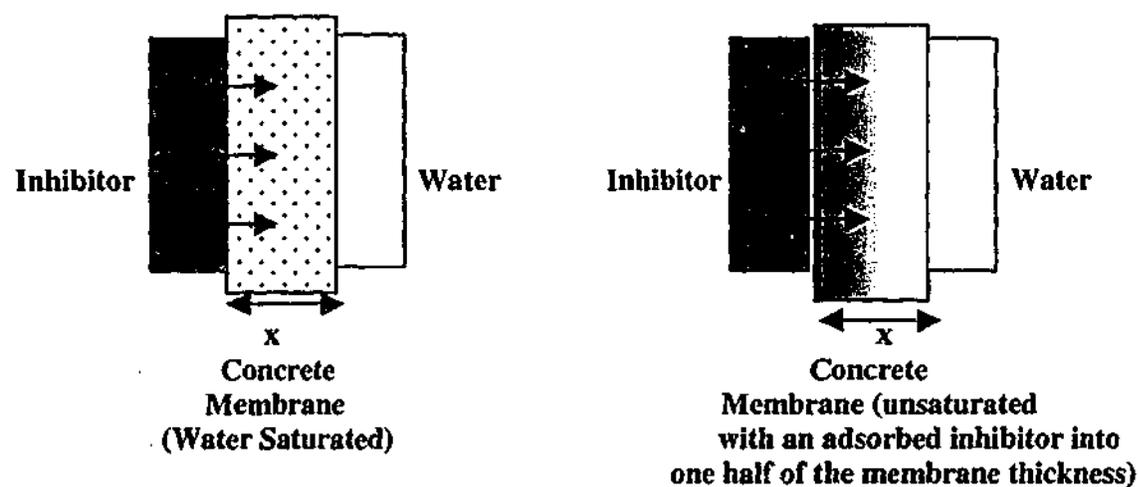


Figure 6.10 - A schematic of inhibitor concentration profile in a concrete membrane developed by an initial absorption phase

The penetration coefficients calculated under such circumstances will be larger than pure diffusion coefficients for otherwise identical saturated systems. As previously noted, diffusion coefficients obtained in the case of mortar samples stored in 80% RH were found to be significantly higher $3 \pm 0.5 \times 10^{-10} \text{ m}^2/\text{s}$ suggesting more capillary action due to unsaturated mortar (Elsener et al., 2000).

As stated earlier, inhibitor penetration is only a part of the overall transport processes in concrete, which include diffusion of chloride, oxygen and moisture. Table 6.6 shows comparative values of the penetration coefficients for all the above species. It must, however, be acknowledged that the values reported in the table for chloride and oxygen diffusion coefficients are taken from the published literature and may be applicable for a specific concrete mix design and cover depth. Hence a direct comparison of these coefficients and modeling of the corrosion/inhibition kinetics based on their relative concentrations at the steel/concrete interface should be done with care. Nevertheless it is evident that the penetration coefficients obtained for inhibitors are of comparable order of magnitude to those obtained for oxygen and chloride ions, especially for structural concretes in marine exposures. Such environmental exposures usually require years of migration before a significant concentration of chloride accumulates at typical depths of cover. It is therefore evident that a short-term topical application of a volatile species to saturated/near saturated concrete could not be expected to yield effective inhibitor concentrations at the reinforcement by liquid phase/ionic diffusion within a useful timeframe. It therefore follows that surface applied inhibitors are most likely to provide corrosion inhibition in circumstances that favour capillary absorption of the solution or vapour phase diffusion, both of which are significantly rapid mass transport mechanisms than liquid phase diffusion.

Chloride	Oxygen	Inhibitors					
		←			→		
W/C : 0.5	W/C : 0.5	W/C : 0.45			W/C : 0.6		
		DICHAN	MCI	DMEA	DICHAN	MCI	DMEA
1.65×10^{-12} (*)	5×10^{-10} (**)	0.5×10^{-12}	0.8×10^{-12}	1.8×10^{-12}	0.4×10^{-12}	4.4×10^{-12}	4.6×10^{-12}

(*) - (Collepari et al., 1972) (**) - (Gjorv et al., 1976)

Table 6.6 - Diffusion coefficients of chloride, oxygen and inhibitors (m^2/s)

6.5 – DIFFUSION MODEL AND CONCLUSIONS

Our investigation of different inhibitor systems primarily suggests that inhibitor penetration through concrete is a complicated process and all the aspects of this process can not be well understood with the currently available data. Nevertheless, based on the current results, efforts are made to summarise the transport behaviour of inhibitors in concrete using a simplified diffusion model. On closer examination of the concentration–time plots, two regions featuring possibly two different transport processes are observed. The initial Fickian diffusion region, characterised by an apparent linear relation between the amount diffused and time, and the latter time-dependent anomalous diffusion region, where inhibitor concentration in the downstream cell peaks to a certain value and starts to level off (or decrease) showing a "diffusion plateau". Diffusion behaviour in the early part of the curve has been investigated by attempting to fit the data to Fickian diffusion kinetics using both steady state and non steady state conditions. Diffusion coefficients thus calculated do show specific trends depending upon physico-chemical characteristics of the diffusant (inhibitor) and the properties of the host material (concrete) such as porosity and the cover-depth. The results with different water/cement ratios have indicated that lower porosity of concrete exhibits higher degree of resistance to inhibitor penetration. However, for a given porosity, the rate-limiting process governing the diffusion of inhibitors involves factors such as molecular size, solubility, vapour pressure and some form of surface interactions with concrete.

Attempts to fit Fick's second law of diffusion by iterative comparison of the measured and predicted data have shown a poor fit, especially at early times. This has been attributed to initial absorption of inhibitor due to capillary action because of partial saturation of fog room cured concrete. Also, an additional possibility of gas permeation of inhibitor because of its high vapour pressure through partially empty or dried concrete pores cannot be ruled out. With the exception of the MCI experiments using a 10mm thick concrete membrane, all of the penetration coefficients obtained using Fick's second law are significantly higher than the diffusion coefficients reported for assumed steady-state conditions. The reason for this is assumed to be an application of the steady state kinetics to a system, which may not have developed a time-independent concentration profile. The optimistic values of the penetration coefficients could also be partially due to the effect of the initial absorption phase.

It appears from the concentration-time graphs that at longer times the amount diffused starts to level off, or there is a discrete discontinuity in the concentration increase in the downstream compartment. The behaviour is quite complicated and appears to be mechanistically different than the Fickian diffusion. It gives rise to what is recognised as a non-fickian diffusional anomaly, where the dominating transport is the reaction-controlled transport. These diffusion anomalies can result from a concurrent reaction between the penetrant (inhibitor) and the reactive groups or components of concrete. The sequence of the steps, which possibly follows these irreversible reactions is: immobile product, reduction of the pore size and finally decrease in the amount of diffusant. It will be interesting to study the influence of this plateau effect on the corrosion/inhibition behaviour of rebar. As we have seen in chapter 4, inhibition of the rebar takes place by the adsorption of inhibitor contained in the surrounding electrolyte. In the case of concrete, the adsorption will be facilitated by the portion of the inhibitor that will be in the unbound state and will be dissolved in the pore solution.

The above considerations defining the shape of the diffusion curves have individual limitations. The first hypothesis needs accurate data on the downstream concentration as a function of time. Whereas the second approach requires a specific knowledge of the physico-chemical factors involved in the actual binding processes in order to accurately model the likely inhibitor-concrete interactions. Further work, such as examination of the actual inhibitor concentration profiles in concrete, using some of the advanced techniques e.g. radioactive isotope technique combined with the microscopy would help in better understanding the possible inhibitor interactions with concrete.

6.5.1 - Limitations

One of the limitations in application of the above model to real structures is that it is based on the assumption that inhibitor transportation takes place purely by the liquid phase (ionic) diffusion process only. This is possible only in the case of fully saturated conditions, which could be expected in submerged concrete structures. Such an approach usually assumes that D is a material constant. However, in the present experimental conditions the concrete pores were not fully saturated to begin with, and hence there may have been some inhibitor transport due to capillary action. This was evident during the application of Fick's second law to the data, where the predicted curves could not be fitted to the early age data points. In actual structures the

splash/spray zones, are likely to undergo periodic wetting and drying, which will involve an additional inhibitor transportation route in the form of capillary action due to moisture movement. In such cases inhibitor transportation will take place much faster than by ionic or molecular diffusion. Also, there will be a possibility of gaseous permeation of volatile inhibitors through partially filled concrete pores where the vapour pressure of the inhibitor is likely to play an important role. These other transport mechanisms can result in much more rapid penetration of inhibitors in concrete than due to diffusion alone. In such cases the model based on pure ionic diffusion will not be able to adequately represent the inhibitor transport in concrete.

Another limitation of the model is the consideration that concrete is a homogeneous material and the existence of pores is a continuous and simple function of the pore radius. However, in real structures concrete generally has a certain number of defects such as microcracks, paste separation and voids as well as macrocracks especially if the structure is already corroding. All these defects are likely to increase the permeability and diffusivity of the concrete matrix, as the diffusion front in such cases will follow the crack surface. Inhibitors will then be able to penetrate much faster into the interior of concrete via cracks than they would do through uncracked concrete. It must be borne in mind that these defects will also result in an increase in the penetration rate of chloride. The microclimate at the steel surface at the tip of the crack will change much faster than that surrounding of the steel away from the crack (Bakkar, 1988). In such a situation the overall corrosion kinetics will be governed less by the diffusion kinetics but it will be dictated more by the electrochemical kinetics involving the relative amounts of chlorides and inhibitors at the steel-concrete interface.

Further, the vapour pressure and the solubility of inhibitor in water are the other two critical factors determining the transport of these surface applied migratory inhibitors through concrete. As high vapour pressure and a high solubility may result in faster migration of the inhibitor towards the reinforcement, however, it may lead to losses or leaching out of inhibitor from concrete. Further, the higher vapour pressure or solubility is likely to reduce the residence time of the inhibitor molecules in the barrier film formed over the steel surface, thereby adversely affecting the long term inhibition properties. A detailed investigation of all these factors is necessary in order to predict the success rate of migratory inhibitors.

The inhibitor diffusion model, which is developed using a diffusion cell in this chapter, is combined with the inhibition model for different inhibitors from chapter 4, and a combined model for the corrosion inhibition of rebar in reinforced concrete specimens will be developed in chapter 7. Such a model can be used when designing a corrosion mitigation system for a reinforced concrete structure. Further, the possibility of enhancing the extremely slow process of ionic diffusion by an application of electric field to the reinforced concrete specimen will be explored in chapter 8.

CHAPTER 7

PERFORMANCE OF INHIBITORS IN REINFORCED CONCRETE SPECIMENS

7.1 - INTRODUCTION

In the earlier stages of this work the effectiveness of various inhibitors was evaluated in a saturated calcium hydroxide solution by employing different investigative electrochemical techniques. The results obtained using the relatively short accelerated laboratory testing have shown that these inhibitors offer excellent protection in saturated calcium hydroxide solution, and the level of protection is dependent upon the concentrations of both chloride and inhibitors at the steel-solution interface. However, it should be recognised that the extrapolation of these results directly to the concrete environment is not possible. This is mainly due to the complex electrochemistry of iron in alkaline media of solid concrete and very low volume of concrete pore water in contact with the steel. Besides, the lack of homogeneity in concrete makes the environment in contact with the steel less predictable and therefore subject to variation from region to region (Slater, 1983). Also the circumstances in the bulk aqueous solution and in the concrete environment are significantly different. This is especially true in relation to the diffusion properties of the species involved such as inhibitor, water, oxygen and the corroding species such as chloride ions. The net result is a slower reaction kinetics at the steel/solution interface.

Besides these major differences, there is a slight difference between the pH of both the media. In the case of the concrete pore solution, due to the presence of dissolved potassium and sodium hydroxides (Gouda, 1970), the pH is slightly higher i.e. approximately 13.5, whereas in the case of calcium hydroxide solution, the pH does not exceed 12.5 (Hausman, 1967). An increase in the pH on changing from the solution to solid concrete may affect the threshold chloride ion concentration for the breakdown of the passive film as a result of changing the limiting ratio of Cl^-/OH^- .

Despite these differences, the experiments described in chapter 4 have been a useful guide for screening the more active inhibitors from a bigger group down to only four to be discussed in this part of the work. In addition, these inhibitors were also investigated for their diffusion characteristics as discussed in chapter 6. The results described in these previous chapters have indicated that the systems having good inhibition characteristics do not necessarily show good transport behaviour. The kinetics governing inhibitor penetration through concrete were distinctly different from the electrochemical kinetics of inhibitor film formation. Hence the next logical step in this research program is to study the combined effect of electrochemical behaviour and transport rates on the overall kinetics of the corrosion inhibition in reinforced concrete.

Four inhibitor systems, selected from the saturated calcium hydroxide solution experiments and the diffusion measurements, are investigated further using long-term exposure tests in actual reinforced concrete specimens. These included the nitrite-based commercial inorganic inhibitor DAREX, an individual organic amine dimethylethanolamine (DMEA), a mixed inhibitor dicyclohexylamine nitrite DICHAN and an amine-based commercial migratory corrosion inhibitor (MCI). DAREX is assumed to have a similar mechanism of action to that of sodium nitrite used earlier in the solution experiments. The influence of these inhibitors, particularly on a prepassivated sample as well as under corroding conditions was assessed in order to give consideration to the design of the application system; i.e. as a newly built structure or as an already damaged structure. A comprehensive testing program will be carried out by preparing reinforced concrete specimens with and without addition/surface application of inhibitors and monitoring the corrosion behaviour of reinforcement using the linear polarisation resistance technique and corrosion potential measurements discussed earlier. The results obtained on the concrete specimens are correlated and discussed in the context of the results obtained from previous experiments (chapters 4-6).

7.2 - PREPARATION OF REINFORCED CONCRETE SPECIMENS

Reinforced concrete specimens were designed as per the following considerations and were subjected to inhibitor treatment using two different inhibitor application methods i.e. either by mixing with concrete at the time of casting the specimens - "admixture

application" or by "surface application" of inhibitor on the concrete specimen having the corroding rebar. These experiments were designed to simulate the approximate service conditions in a new versus an old corroding structure, with the exception that Cl⁻ ions were precast into the concrete. This of course would not be true for a new structure.

7.2.1 - Concrete Quality Considerations

The issue of concrete quality, its permeability to inhibitors as well as chlorides is extremely important when it comes to laboratory testing. It has been observed that the penetration coefficient of inhibitor molecules in concrete having a lower water/cement ratio is low (Bjegovic et al., 1993). Researchers have found that the diffusion coefficient of chloride ions in high quality concrete is also very low and, all conditions being equal, time to corrosion of the reinforcing steel is exceptionally long (Yunovich and Thompson, 1998). Water/cement ratios mentioned in connection with laboratory trials show considerable difference: from 0.28 to 0.65 or even 0.9 (Arya and Ofori-Darko, 1996; Nmai and Krauss, 1994; Pfeifer et al., 1986). It is also proposed that if inhibitor admixtures are used, they should be evaluated under conditions simulating the real world application, which for practical purposes means concrete with a maximum w/c ratio of 0.4, which would be in compliance with ACI 318 code for concrete for corrosive environments (ACI Committee 318, 1992). In the present work, in order to reduce time-to-corrosion and time-to-inhibitor diffusion i.e. to accelerate the testing procedure, compromise was made with regard to the concrete quality. This was achieved by making a poor concrete with high water/cement ratio (0.6) and sand/cement (3:1) ratio. From the point of view of reinforcement corrosion this is likely to lead to a rapid diffusion of chloride ions to the steel surface, easier ingress of oxygen and lower electrical resistivity. Increase in the water/cement ratio was also expected to enhance inhibitor penetration.

Despite the poor quality of concrete used and the expected rapid degradation due to chloride, this research protocol was adopted in order to establish whether or not the inhibitors will withstand these extreme conditions (quite likely in a cracked structure) and whether the inhibitor is able to diffuse. It is accepted that the absolute corrosion rate obtained will not be relevant to real structures; however, it would be true to say that all situations in real life are unique and so an absolute corrosion inhibition rate is not

achievable. This work establishes that if the inhibitors can be transported to the steel surface, they can inhibit corrosion in the aggressive environments.

Concrete cover thickness is another factor, which can affect the transport of chloride/inhibitors and hence time-to-corrosion/protection. Cover thickness for the minibeam specimens recommended by researchers range from 19 –38 mm (Berke and Hicks, 1990; Nmai et al., 1994; Nmai et al., 1992): Berke and coworkers (Berke et al., 1994) suggested that for screening type tests concrete with higher (0.5) water/cement ratio and a cover thickness less than 30 mm could be used. Some researchers, while citing the ACI building codes, which recommend a minimum cover thickness of 38 mm for concrete exposed to aggressive environments, suggest that the minimum cover thickness of the concrete test specimen be at least in the range of 25 mm to 38 mm (ACI Committee 318, 1992; ACI Committee 357, 1984; Tourney and Berke, 1993). Since concrete cover of 38 mm would require prohibitively long testing time for the laboratory studies, the rule was adopted that concrete cover twice the maximum aggregate size is sufficient for laboratory evaluations (Yunovich and Thompson, 1998). The aggregate size used in the test specimens under study was 10-14 mm hence the concrete cover used was 30 mm.

7.2.2 - Specimen Design

The reinforced concrete specimens prepared were square prisms of dimensions 200 x 100 x 72.5 mm. A 300 mm length reinforcing bar having 12.5 mm average diameter was axially embedded in the concrete leaving a 50 mm length out of the concrete at both ends. The specimen design is shown schematically in Figure 7.1. Both ends of the bar (60 mm length on each side) were covered with epoxy coating to reduce the possibility of corrosion occurring at the steel/concrete/air interface. One end of the reinforcing bar was silver-soldered to PVC insulated copper wire. An internal anode (platinum coated titanium) was embedded in concrete parallel to the reinforcing bar at a distance of 15 mm from the top surface of the specimen. The internal anode forming a part of the three-electrode cell, was expected to act as an auxiliary electrode providing a uniform current distribution during the electrochemical measurements in concrete. A hole was drilled from the lateral side of the concrete specimen for inserting a Luggin probe; the tip of the Luggin probe was adjusted in the vicinity (within approximately 1-2 mm) of the rebar whereas the other end was immersed in a cup containing a saturated potassium

chloride solution and a saturated calomel electrode. This arrangement was put in place to minimise the concrete resistance (IR drop) while measuring the potential of the rebar. Concrete specimens were maintained in a constant temperature (22 degrees Celsius) and humidity laboratory and placed over a sponge, which was semi-immersed in salt-water (3.5 wt % NaCl), simulating a marine environment. This approach also avoids drying out of the concrete and hence maintains constant corrosion conditions at the steel surface.

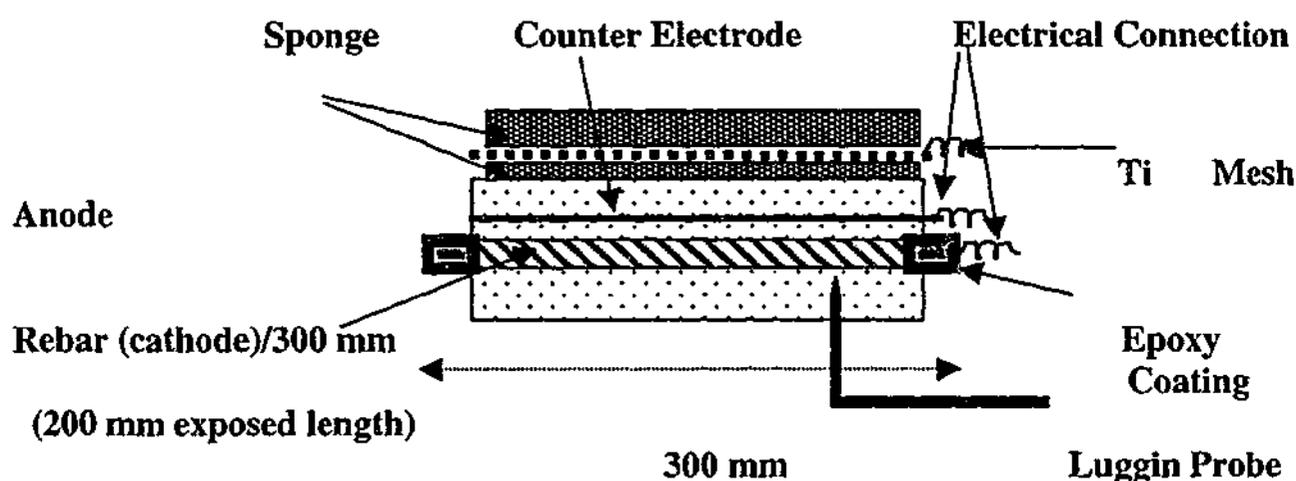


Figure 7.1 – Schematic diagram of a reinforced concrete specimen

7.2.3 - Specimen Preparation

The preparation of the reinforced concrete specimens involved three main steps. The preparation of the reinforcing bars, design and preparation of the wooden moulds and the casting and curing of the specimens.

Reinforcing bar

Low carbon steel ribbed bars having an average diameter 12.5 mm were used in "as received" conditions ie. with a black oxide layer covering the metal surface. The bars were cut to a length of 300 mm and one end of the reinforcing bar was silver soldered to PVC insulated copper wire. Both ends of the rebar (60 mm) were covered by an epoxy resin. This was found to be not completely successful, since in some cases the epoxy coating was found to be scratched during the demoulding of the specimens, leading later to localised corrosion of the specimens. The length of the bar exposed to the concrete was approximately 180 mm. Figure 7.2a shows the rebar used as reinforcement.

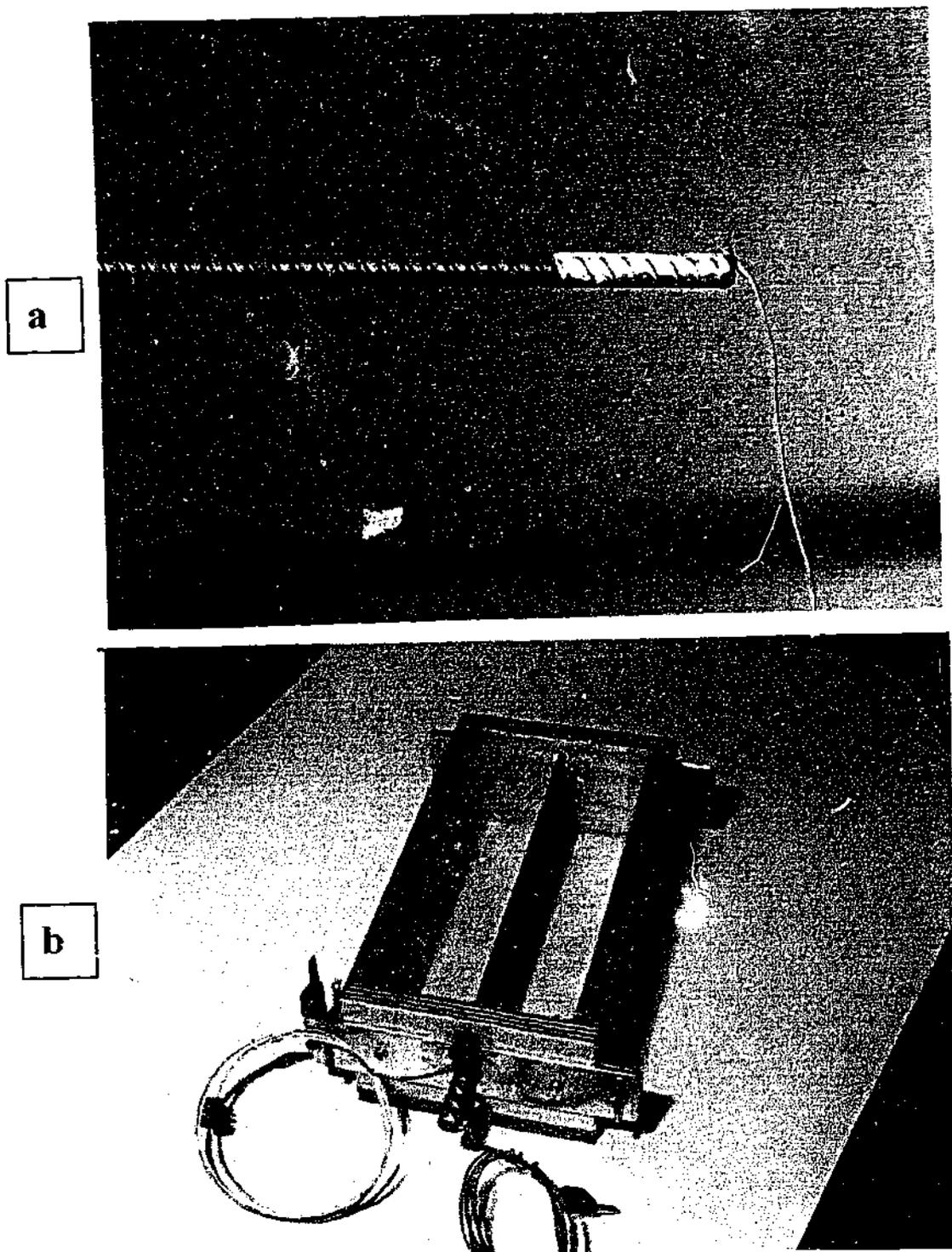


Figure 7.2 – (a) A representative rebar and (b) a wooden mould containing a rebar and an internal anode

Wooden moulds

The moulds were specifically manufactured wooden rectangular boxes with appropriately drilled holes for inserting the rebar and the titanium internal anode. The boxes consisted of five pieces (base plus four lateral faces). The lateral faces were fixed together with wing nut screws. This enabled the easy positioning of the reinforcing bar and the internal anode in the box and also facilitated demoulding. The rebar as well as

the internal anode were mounted in the wooden box prior to concrete pouring. Figure 7.2b shows a wooden mould with a rebar and an internal anode inserted in the mould.

Specimen casting and curing

The concrete specimens were prepared using a mixture of cement, sand, coarse aggregate and water in the proportion of 1:3:4:0.60 respectively. The mix design/proportions are summarised in Table 7.1. This mix was selected mainly with a view to make a poor quality concrete having w/c ratio 0.6 and sand/cement ratio 3:1. The cement used was portland cement type D to avoid complexing of the chloride with C₃A. The coarse aggregate was 10-14mm size. Sand (Clayton coarse) was used as fine aggregate. Sodium chloride 5 % (chloride 3 %) by weight of cement was admixed to induce rapid corrosion and to simulate a contaminated structure. The critical level of chloride, expressed in terms of weight of chloride per unit volume of concrete (as is generally mentioned in the case of existing structures), was 8.4 kg/m³ of concrete. It must be recognised that the guidelines of the building research establishment (Anon, 1982) suggest that for good quality concrete, a chloride ion content of less than 0.2% of the cement used presents a low risk of steel corrosion and that greater than 1% presents a high risk. However, most specifications and recommendations specify that the chloride content be less than about 0.2% or at the most 0.2 to 0.4% of the cement content (Bentur et al., 1997). This means that the quantity of chloride added in these specimens was approximately ten times higher than the threshold chloride level i.e. 0.2% of the cement or 0.8kg/m³ concrete (Table 7.1). Concrete specimens with two different mix designs, with and without admixed inhibitors, were cast. This also allowed a comparison with the earlier experiments in the calcium hydroxide solutions.

Thirty-four concrete specimens were cast using the same mix design and materials, but with or without addition of different inhibitors. In the first group, specimens were cast in duplicate (2x1) without addition of chloride or inhibitor to simulate the conditions of a new structure without salt/chloride contamination ("plain concrete"). Another group was designed with the presence of chloride (no inhibitor) in duplicate (2x1) to evaluate the effect of chloride addition on the corrosion behaviour of steel. The presence of chloride and the absence of inhibitor created accelerated corrosion conditions simulating a "corroding structure". These samples were treated as "control samples" and were used for comparing the corrosion behaviour of the remaining specimens discussed below.

Proportions:	Chloride Contaminated mix		Plain Concrete	
	by mass	kg/m ³	by mass	kg/m ³
Cement (gen. purpose)	1.0	277	1.0	277
Sand (Clayton course)	3.0	832	3.0	832
Aggregate (9 mm)	4.0	1110	4.0	1110
Water	0.6	166	0.6	166
Sodium Chloride (as Chloride)	0.05 (0.03)	14 (8.4)	-	-

Table 7.1 – Concrete mix design

The four pairs of specimens (2x4) that constituted the third group were cast by admixing the predetermined quantities of four different inhibitors, e.g. dicyclohexylamine nitrite (DICHAN), dimethylethanolamine (DMEA), DAREX (calcium nitrite) and MCI. This was done to simulate the “admixture situation” or “prepassivated condition” as discussed in section 4.2.2. The only difference with the present situation being that the rebar was exposed simultaneously to chloride and inhibitor at the time of casting whereas in the solution experiments the metal surface was allowed to equilibrate in the presence of inhibitor two hours prior to the addition of chloride ions. The quantities of admixed inhibitors in the case of DAREX (28.7 kg/m³) and MCI (0.84 kg/m³) inhibitors were as per the dosages recommended by the manufacturers for a given level of chloride. The quantities of the individual amines (DMEA and DICHAN) were equivalent to the recommended concentration of amine based commercial inhibitor (0.84 kg/m³ concrete). Table 7.2 summarises the actual quantities of the inhibitors added to the mix and Figure 7.3 presents a flow chart for the specimens investigated in this chapter.

After mixing, the blends were carefully poured into the prepared boxes containing the reinforcing bar-internal anode systems. The specimens were vibrated as the concrete

was poured on a vibrating table until the rise of bleeding water occurred. The specimens were demoulded 24 hours after casting and placed in a fog room for four weeks. Thereafter the specimens were maintained in the laboratory and placed over a sponge semi-immersed in a 3.5wt% salt solution. This arrangement was designed to minimize the IR drop and make concrete ionically conductive during measurements. It also simulated the type of conditions expected in a marine environment.

Chemicals	Concentration	kg/m ³
Sodium Chloride (as chloride)	5 wt% of Cement	13.87 (8.42)
DICHAN	0.01M	2.28
DMEA	0.01M	0.89
MCI	0.7 L/m ³ (Sp. Gr.: 1.14-1.26)	0.84
DAREX [Ca(NO ₂) ₂]	22.25 L/m ³ (Sp. Gr.: 1.29)	28.70

Table 7.2 – Table of proportions for the admixed inhibitors

The fourth group of reinforced concrete specimens (2x3), contaminated with chloride but without admixed inhibitors, was subjected to inhibitor treatment by topical (surface) application of inhibitors in order to simulate the “remedial/rehabilitation application” in the case of a real structure. Three inhibitors, DICHAN, DMEA and MCI were selected for surface application. The neat solutions of DMEA and MCI and a saturated solution of DICHAN were applied to the top surface of the concrete specimen and a piece of sponge saturated with the calcium hydroxide solution containing inhibitor was placed to cover the entire top surface of the specimen. The sponge was kept moist in order to avoid the losses due to evaporation and to have an optimal inhibitor penetration. The specimens were treated with inhibitors every 3 weeks for a period of 300 days. The inhibitor application was stopped after 300 days, however, the corrosion behaviour of the rebar was monitored up to 450 days. This was done mainly to assess the persistency

of inhibitor film to chloride attack especially in the absence of fresh supply of inhibitor molecules.

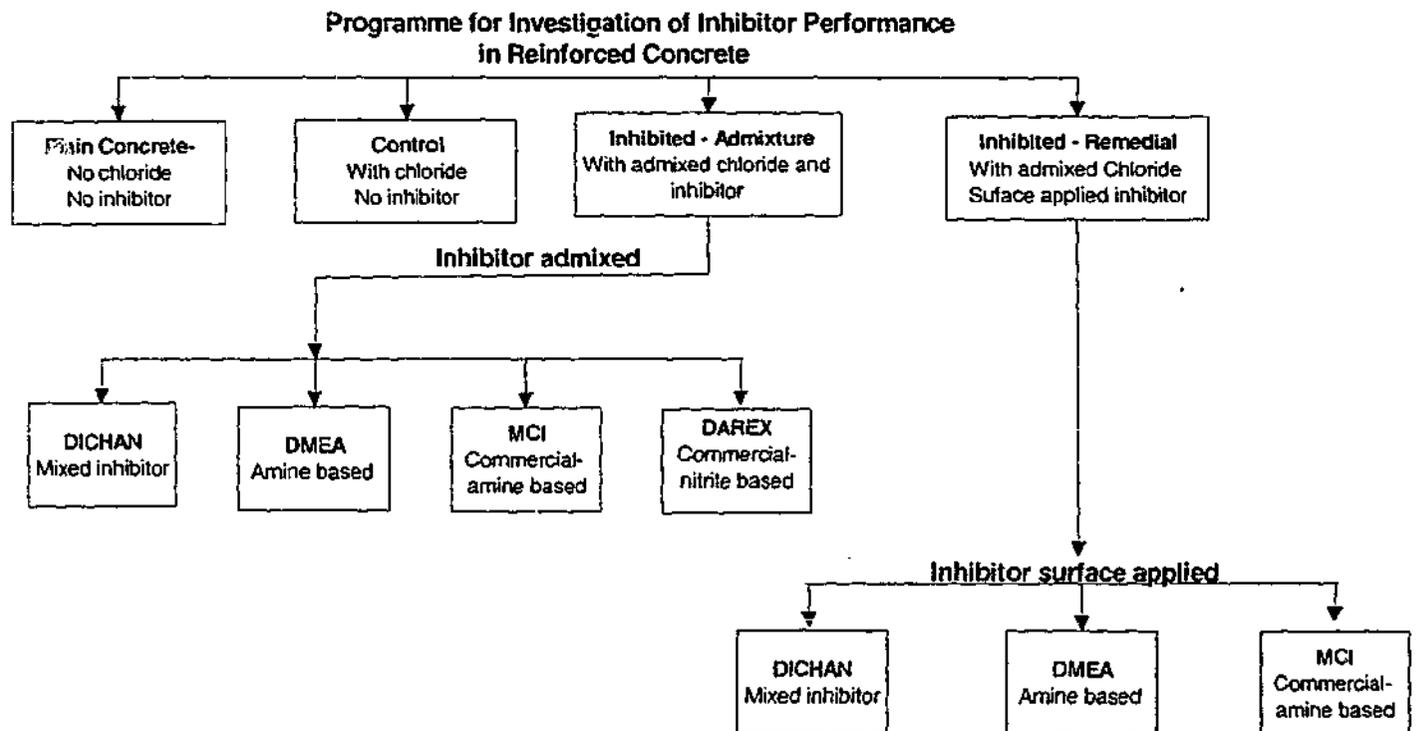


Figure 7.3 – Flow chart for concrete specimens prepared with "admixture" and "remedial" application systems

7.2.4 - Monitoring Corrosion Behaviour of Steel Using the Linear Polarisation Resistance Technique and Corrosion Potential Measurements

The issue of monitoring corrosion of the reinforcement embedded in concrete is intrinsically important when it comes to testing on a small concrete square prism in the laboratory. The standard test generally used for predicting the inhibitive properties of admixtures to be used in concrete in the laboratory is described in the ASTM G109 (ASTM G109-99, 1999). Some researchers have used the linear polarisation resistance technique for monitoring corrosion behaviour of reinforcement. It has been observed that, when appropriately interpreted, corrosion rate measurements using polarisation resistance can be a good indication of the corrosion activity, at least under laboratory conditions (Berke and Hicks, 1990; Gonzalez et al., 1985b; Sagues, 1989), where the area of the steel surface affected in the test is known.

In the present work % inhibition (based on the polarisation resistance R_p) was monitored instead of the absolute corrosion rate. Further, the LPR results were also

supplemented with the corrosion potentials E_{corr} measurements. The monitoring was carried out at regular intervals over a period of 450 days. Figure 7.4 shows a typical reinforced concrete specimen (with a Luggin probe) and a set up (Solartron equipment) used for carrying out LPR measurements.

The linear polarisation resistance technique

The theoretical basis for LPR measurement and its limitations have been previously discussed in section 2.4.4. Application of this technique to determine relative inhibition capacities of inhibitors has also been described in section 4.2.3. The corrosion cell in the concrete specimens consisted of a rebar acting as a working electrode and the platinum coated titanium rod as a counter electrode. Linear polarisation resistance measurements were performed using a Solartron 1280 b potentiostat and the data was plotted and analysed using Corrware and Corrview softwares. All the potentials were measured using a Luggin probe and reported with respect to a saturated calomel electrode (SCE). The polarisation resistance was measured for both inhibited and control sample and % inhibition was calculated using Equation 2.4.

Corrosion potential measurements

The open circuit potentials/corrosion potentials (E_{corr}) of the reinforcement in the case of passivated, control and inhibited concrete specimens were measured against a saturated calomel electrode (SCE) using a high input impedance (10^{10} ohm) voltmeter. The shifts in the potentials on the addition of chloride and inhibitors were monitored in order to examine the probability of corrosion or inhibition. The nature of the shifts in the measured potential values was used to postulate the mechanism of action of different inhibitor systems.

It should be mentioned that the specimens were prepared in duplicate, with a view to obtain the average of the two sets of readings (R_p as well as E_{corr}) and to fit the resulting data in a standard deviation. However, in the cases where one of the two specimens was found to display a considerable scatter in the data, the results obtained by monitoring only one specimen were reported.

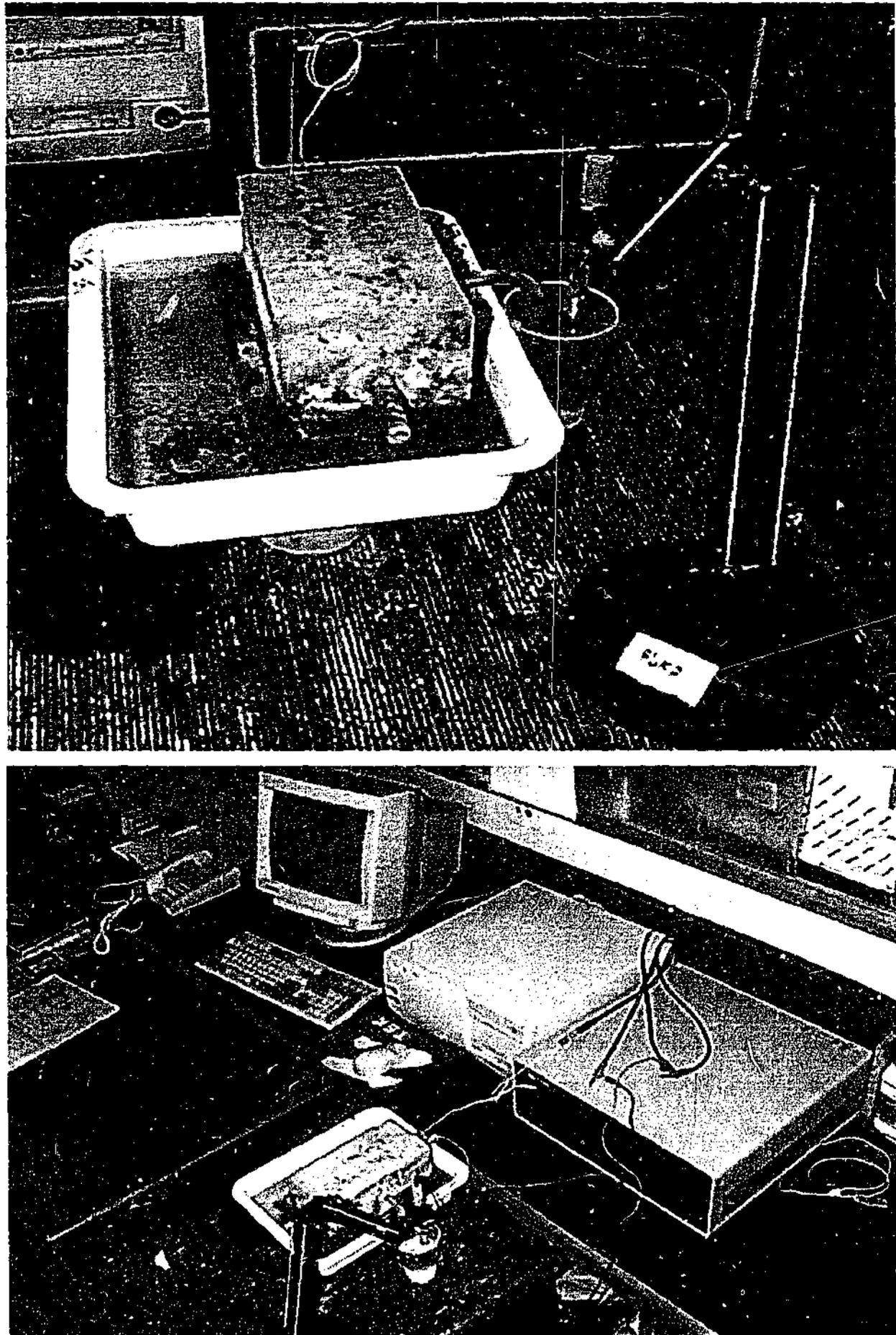


Figure 7.4 - A reinforced concrete specimen (with a Luggin probe) and the Solartron equipment used for carrying out LPR measurements.

7.3 – EVALUATION OF THE PERFORMANCE OF INHIBITORS IN CONCRETE SPECIMENS UNDER ADMIXTURE AND SURFACE APPLIED CONDITIONS

In the beginning of this chapter it was discussed that the conclusions drawn on the basis of a comparative evaluation of inhibitors in aqueous solutions may not be directly applicable to rebars in concrete because of the complex electrochemistry at the steel-concrete interface. It is relevant to note that in the solution experiments, the level of inhibition reflects the ability of the inhibitor to form a resistive film on the steel surface. However in the case of concrete, % inhibition is a combined effect of the ability of inhibitor molecules to penetrate through concrete and the capacity of the inhibitor to form a barrier film. Further, in the case of concrete, since the replenishment kinetics of inhibitors at the steel surface is dependent on the slow process of ionic diffusion (chapter 6), one requires much longer periods of monitoring compared with the solution studies. In the present chapter the corrosion behaviour of concrete specimens is monitored for 450 days using LPR and corrosion potential measurements.

7.3.1- Comparative Study of % Inhibition (based on R_p) and Corrosion Potentials

Admixture situation

Table 7.3 summarises the R_p and E_{corr} values versus time for reinforced concrete specimens in group 3, where DICHA, DMEA, MCI and inorganic commercial nitrite (DAREX) were added as admixtures in the concrete mix. Plain concrete, having the same mix design but without the addition of chloride or inhibitor, is also included in the same table for comparison purposes. Figure 7.5 shows the % inhibition (based on R_p obtained from equation 2.4) as a function of time for the same group. Figure 7.6 depicts corrosion potentials of the plain concrete and the influence of admixed chloride and inhibitors on these potentials. The specimens were kept in a fog room for 28 days and the monitoring started only after the specimens were removed from the fog room. Hence the inhibition level observed on the "zeroth day" in the figure corresponds to the first measurement performed after the 28 days fog room period. As expected, steel is well passivated in the case of plain concrete (in the absence of chloride) and thus shows near 100% inhibition, i.e. high R_p values relative to the control sample (Table 7.3) throughout the test period. The corrosion potential moved from -123 mV_{SCE} to -8 mV_{SCE} . This is indicative of a low probability of corrosion, as a result of the formation

of a stable passive oxide film on the rebar surface due to the highly alkaline environment provided by concrete and as predicted by the Pourbaix diagram (Pourbaix, 1966). In the absence of chloride, this passive film remains intact throughout the measurement period (450 days).

The control sample (in the absence of inhibitor) in this case is considered to be the baseline or the x-axis, as the % inhibition values for the plain concrete as well as inhibited samples were calculated on the basis of the polarisation resistance of the control sample. A distinct drop in the corrosion potential from $-123 \text{ mV}_{\text{SCE}}$ (plain concrete) to $-448 \text{ mV}_{\text{SCE}}$ (control sample) was observed on addition of chloride to the concrete mix indicating the onset of the corrosion activity. This behaviour was found to be consistent with the decreasing trend observed in the case of polarisation resistance R_p of control (from 24 kohm.cm^2 to 15 kohm.cm^2).

In the case of concrete specimens admixed with inhibitors, the overall inhibition levels were found to be in the following order: DAREX (calcium nitrite) \gg MCI $>$ DMEA $>$ DICHAN. This order is significantly different from that observed under solution conditions (DICHAN \equiv MCI $>$ sodium nitrite $>$ DMEA) in chapter 4.

The calcium nitrite based commercial anodic inhibitor DAREX showed the best corrosion inhibition properties amongst all inhibitors. The initial trend of high inhibition of DAREX started showing a downturn after approximately 180 days, which is consistent with the behaviour expected of an anodic inhibitor. The % inhibition ultimately decreased to approximately 70% at the end of 450 days test period. This trend is consistent with the time dependent behaviour observed in the case of sodium nitrite in saturated calcium hydroxide solution, although the level of protection was still higher than that observed in the solution experiments. The inhibition mechanism in the case of DAREX (in concrete) and sodium nitrite (in solution) is proposed to be by oxidation of Fe^{2+} to Fe^{3+} thus forming an oxide film resistive to chloride attack. However, once the concentration of nitrite ions drops below a critical level due to their chemical consumption in the passivation process, decrease in % inhibition occurs.

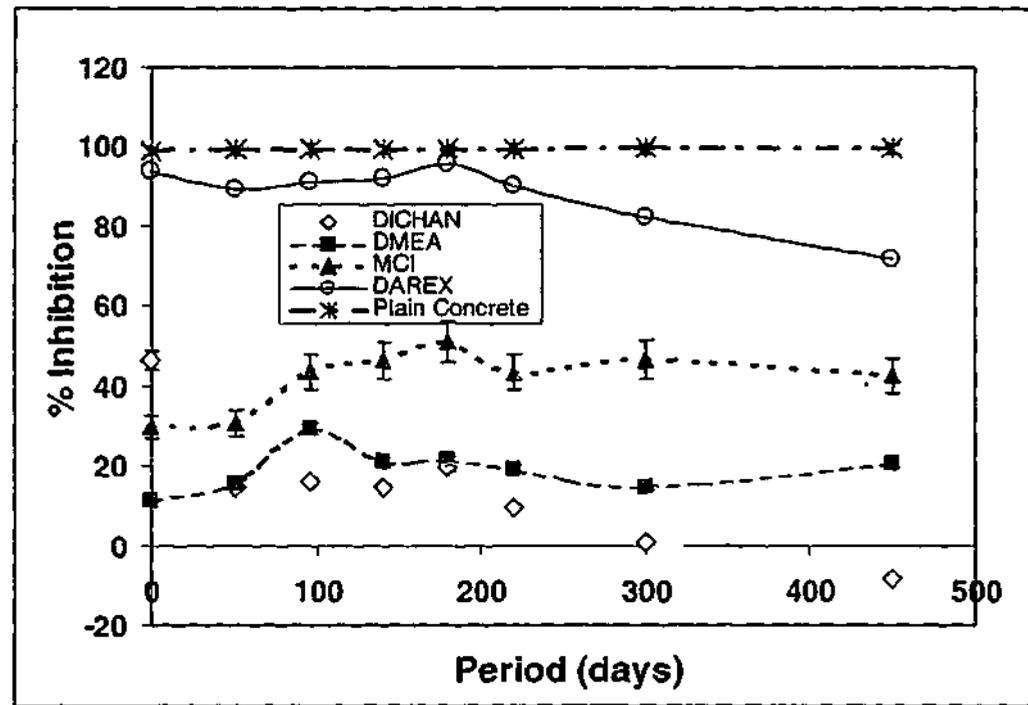


Figure 7.5 – Comparative study of % inhibition vs time for different inhibitors admixed in concrete

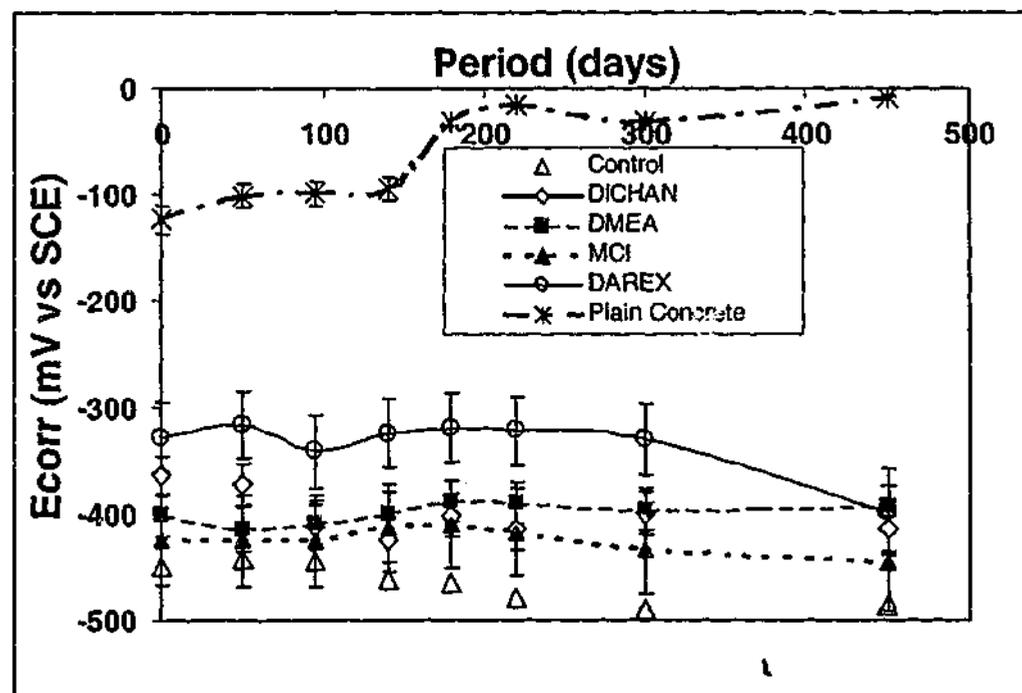


Figure 7.6 – Comparative study of corrosion potential (E_{corr}) vs time for different inhibitors admixed in concrete

Period Days	Control		DICHAN			DMEA			MCI			DAREX			Plain Concrete		
	R_p kohms.cm ²	E_{corr} mV _{SCZ}	R_p kohms.cm ² (±5%)	%Inhn	E_{corr} mV _{SCZ} (±5%)	R_p kohms.cm ² (±5%)	%Inhn	E_{corr} mV _{SCZ} (±5%)	R_p kohms.cm ² (±10%)	%Inhn	E_{corr} mV _{SCZ} (±10%)	R_p kohms.cm ² (±10%)	%Inhn	E_{corr} mV _{SCZ} (±10%)	R_p kohms.cm ² (±11%)	%Protn	E_{corr} mV _{SCZ} (±11%)
0	23.7	-448	44.1	46	-364	26.7	11	-401	33.7	30	-425	598	94	-328	1974	99	-123
50	21.6	-442	25.3	15	-373	25.5	15	-414	31.1	31	-426	248	89	-317	2431	99	-101
95	15.3	-444	18.3	16	-413	21.7	29	-409	27.2	43	-426	181	91	-341	2918	99	-99
140	15.7	-459	18.4	15	-425	19.8	21	-400	29.4	46	-413	218	92	-325	2687	99	-95
180	14.7	-462	18.3	20	-402	18.5	20	-388	30.3	51	-410	429	96	-320	2667	99	-33
220	15.4	-477	17.1	9	-414	20.1	23	-390	28.3	45	-417	168	90	-322	3021	99	-17
300	14.2	-488	14.2	1	-400	17.0	17	-395	28.9	51	-433	79	82	-361	3327	100	-31
450	14.5	-485	13.4	-8	-414	18.2	21	-394	25.2	42	-447	51	71	-399	3078	100	-8

* - Significant variation in the R_p values because of the highly resistive passive film formed at the rebar surface

Table 7.3 - Comparative study of polarisation resistance (R_p) and corrosion potential (E_{corr}) for concrete specimens with admixed inhibitors

Corrosion potentials in the case of specimens admixed with DAREX, exhibited a distinct positive shift to $-328 \text{ mV}_{\text{SCE}}$ as compared with that of the control sample ($-448 \text{ mV}_{\text{SCE}}$) thus confirming the anodic nature of the inhibitor action. The potential $-328 \text{ mV}_{\text{SCE}}$ was sustained for up to 300 days, and then shifted cathodically to $-399 \text{ mV}_{\text{SCE}}$ towards the end of the test period. Maintaining of the potential value is likely to be because of the stabilisation of the oxide film at the steel surface, whereas a drop in the potential towards the end of the test period may indicate a rupture of the oxide film due to chloride attack. The trend observed in the potential is consistent with that obtained with the LPR measurements.

DICHAN exhibited time dependent inhibition properties in concrete as observed in the case of DAREX, but the inhibition level obtained was much lower. The inhibition observed on the "zeroth day" (Figure 7.5) was a moderate level (approximately 45 %), which suggests the presence of a less protective film at the outset. The susceptibility of this film to chloride attack in the aggressive environment is further confirmed by a sudden drop in inhibition to ~15% observed around 50 days. The inhibition level was sustained at this low value for up to 180 days, and then dropped to the level of the actively corroding control sample around 300 days. After 300 days negative inhibition was observed indicating a lower polarisation resistance of the inhibited sample than that of the control. This may be due to an acceleration of the corrosion process caused by the depletion of nitrite ions, resulting in an inhibitor concentration below the threshold level. A similar behaviour was observed with (a purely anodic inhibitor) sodium nitrite at 0.01M concentration (chloride:nitrite ratio 26.4) in the solution experiments of section 4.3.8.

The Corrosion potential of the reinforcement embedded in DICHAN admixed concrete (Figure 7.6) displayed a positive shift to $-364 \text{ mV}_{\text{SCE}}$ as compared with that in the control sample, consistent with the results obtained in the case of DAREX indicating dominant anodic inhibition. However, the absolute potential in the case of DICHAN was less positive as compared with that observed in the case of DAREX suggesting a lower degree of the anodic protection offered by DICHAN in concrete. The potential dropped to $-413 \text{ mV}_{\text{SCE}}$ within 95 days and was maintained between -400 to $-425 \text{ mV}_{\text{SCE}}$ until the conclusion of the test period. The dropping of potential from $-365 \text{ mV}_{\text{SCE}}$ to $-415 \text{ mV}_{\text{SCE}}$ indicated the breakdown of the passive film and onset of corrosion. Thus the overall trend in the movement of corrosion potential is consistent

with that observed in the case of the % inhibition experiments and it also compares well with that observed in the saturated calcium hydroxide solution.

In the case of amine-based inhibitors, both DMEA and MCI exhibited low/moderate inhibition levels as compared with those displayed by DAREX, and these levels were maintained throughout the test period. In the case of DMEA, the inhibition level was found to fluctuate between 15-25% over the duration of the experiment i.e. 450 days. The insignificant level of inhibition in this case indicates the susceptibility of the passive film at the rebar surface. The corrosion potential of rebar subjected to an admixed DMEA, fluctuated between -390 and -415 mV_{SCE} throughout the test period (Figure 7.6). It is possible that the maintenance of the potential level in this case could be due to either mixed /dominant cathodic inhibition (Harrop, 1988) or it could also be due to an increase in the corrosion activity. However, low but persistent inhibition observed throughout the test period (Figure 7.5) for the corresponding low potential values observed in Figure 7.6 may support the possibility of mixed/cathodic nature of action of this inhibitor. This behaviour is different from the results obtained in a DMEA containing saturated calcium hydroxide solution, where potential exhibited a significant cathodic shift with time. In the case of DMEA, if one takes into consideration the fact that the concrete specimens were kept in the fog room for the first 28 days, then it is quite likely that the protective film formed initially at the steel surface by this inhibitor was destabilised by chloride ions during this curing period, resulting in a lower inhibition level on the "zeroth day" of measurement. Thus this inhibitor behaves similarly in both solution and concrete systems, despite the significant physical differences between the two media. This may be due to a high solubility of DMEA in water and an equally high penetration coefficient in concrete (Table 6.3). This can possibly result in an equivalent inhibitor concentration at the steel surface in both cases.

In the case of MCI the inhibition began at a low level of 30%, however, it increased to approximately 50% during long-term measurements. This behaviour is consistent with a cathodic inhibition mechanism. The general inhibition trend exhibited here for the MCI inhibitor in concrete is once again similar to that observed in the saturated calcium hydroxide experiments; albeit the inhibition levels between the two sets of experiments differ considerably (30-50 % in the case of the concrete against 90 % for the solution). The E_{corr} in the case of specimen admixed with MCI, exhibited a cathodic shift to -433 mV_{SCE} after around 300 days, which decreased further to -447 mV_{SCE} towards the end

of the test period of 450 days (Figure 7.6). An observation of the negative shift in corrosion potentials combined with the moderate level of persistent inhibition for the corresponding period (Figure 7.5) is consistent with the cathodic nature of inhibition.

Thus the trend and level of inhibition in the case of amine-based inhibitors are clearly different from the decreasing inhibition trend with time displayed by nitrite-based anodic inhibitors. The difference in the behaviour is probably associated with the different inhibition mechanisms – nitrite ions function by oxidising ferrous to ferric thus repairing the protective film by inducing repassivation at the anode (Rosenberg et al., 1977); whereas amines function by forming a barrier film through chemisorption of organic amines at cathodic and anodic sites thereby hindering both cathodic and anodic reactions (McCafferty, 1978; Nathan, 1973). The barrier film formed by the amine group is resilient to chloride attack. More importantly, its protecting capacity does not require a minimum inhibitor concentration to obtain meaningful inhibition. Further, the replenishment of these molecules at the steel/concrete interface is possibly facilitated by their comparatively high diffusion rates through concrete.

Another observation made from the above results is that with the exception of the nitrite-based purely anodic inhibitor DAREX, inhibition trends exhibited by all the inhibitors in the concrete specimens are distinctly poorer from those displayed in saturated calcium hydroxide solution. The difference in the inhibition efficiency observed in the two situations may be partly attributed to the physical differences between the two electrolytes leading to different transport rates of inhibitor molecules in two media. In addition, the heterogeneity at the steel/concrete interface could be another factor which could add to the complexity (Slater, 1983). These factors are further supplemented by the low penetration coefficients for these inhibitors in saturated concrete (chapter 6). Besides this, in the case of inhibitors such as DICHAN, solubility could be another limiting factor which could drastically restrict the concentration of $(R_2NH_2)^+$, (or simple substituted amine molecules in the case of deprotonation of the alkylammonium ion by the alkaline pore water - sections 4.3.5 and 6.4.1) and NO_2^- species at the steel surface. It should also be mentioned that, contrary to the solution experiments, in the case of concrete specimens both chloride as well as inhibitor were added to the concrete mix at the same time. Hence there is probably a competition between inhibitor molecules to form a protective film and chloride ions to rupture the film at the outset. The 28 days fog room curing may further enhance this problem.

Thus a weaker or less resistive film at the rebar surface is obtained in concrete as against a prepassivated surface observed (in the absence of chloride ions) in the solution system. In future work it would be more reasonable to accelerate the chloride induced corrosion through wet/dry cycling with salt water rather than addition of chloride to the initial mix.

Surface applied condition

Figure 7.7 refers to plots of % inhibition vs time for reinforced concrete specimens under corroding condition where inhibitor is applied to the surface of the concrete specimens after corrosion has already been initiated (group 4). Figure 7.8 shows the corrosion potentials for the corresponding period. The effect of surface application of three inhibitors DICHAN, DMEA and MCI has been examined. Corrosion potentials of control sample are also included in the same figure. Table 7.4 summarises R_p and E_{corr} values versus time for reinforced concrete specimens with surface applied inhibitors.

As previously noted the inhibition level observed on the "zeroth day" under the remedial conditions corresponds to the first measurement performed after 28 days in the fog room. Therefore at this stage, specimens without any surface applied inhibitor behaved similar to the control samples. Inhibition levels measured on the "zeroth day", ranging from 2 to 10%, indicate the starting corrosion levels for different concrete specimens (in the absence of inhibitor treatment). Inhibitor was then applied to the top surface of the specimens and allowed to penetrate to the rebar to form a protective film on the rebar surface. The next measurement was performed six weeks after the "zeroth day" measurement. The polarisation resistance R_p of these specimens after six weeks, was found to increase gradually to different levels depending upon the nature of inhibitors.

In the case of specimens subjected to surface application of DICHAN, the inhibition level went up to only 14% within approximately 95 days of testing and, at longer times, the level of inhibition decreased to a zero level around 200 days in spite of the periodic application of the inhibitor. After this period the concrete specimens exhibited accelerated corrosion as was observed in the solution experiments. A steady loss in the corrosion mitigation capacity followed by an accelerated corrosion exhibited by DICHAN in both solution and actual concrete experiments is typical of anodic action and is likely to be due to a decrease in the concentration of DICHAN molecules at the steel surface.

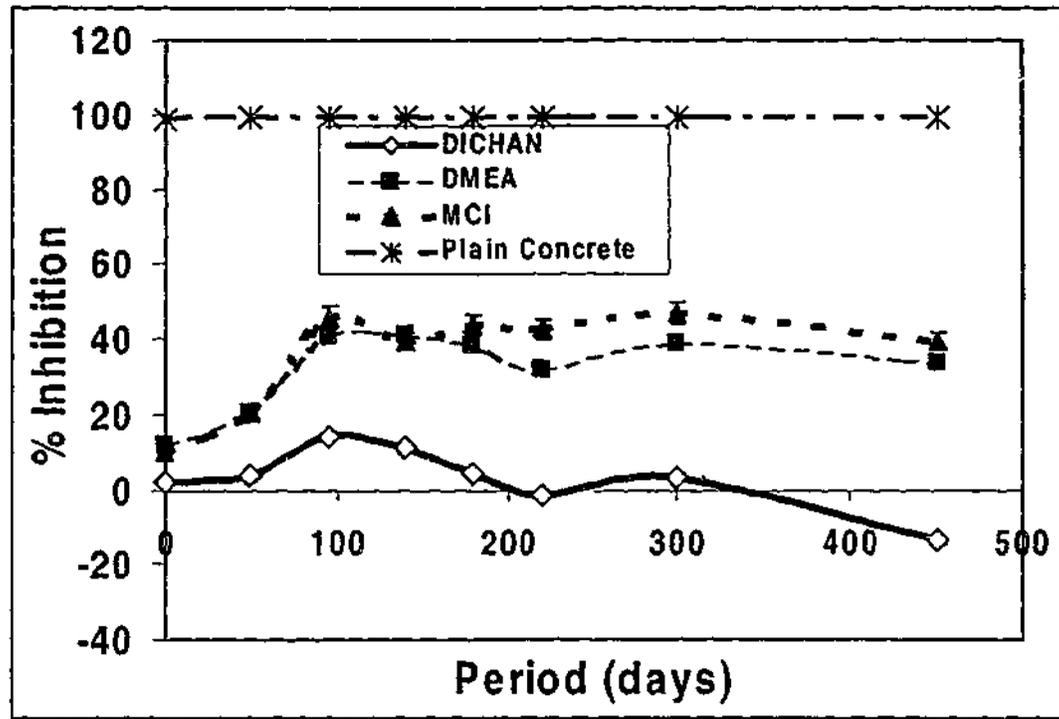


Figure 7.7 – Comparative study of % inhibition vs time for different inhibitors with surface application

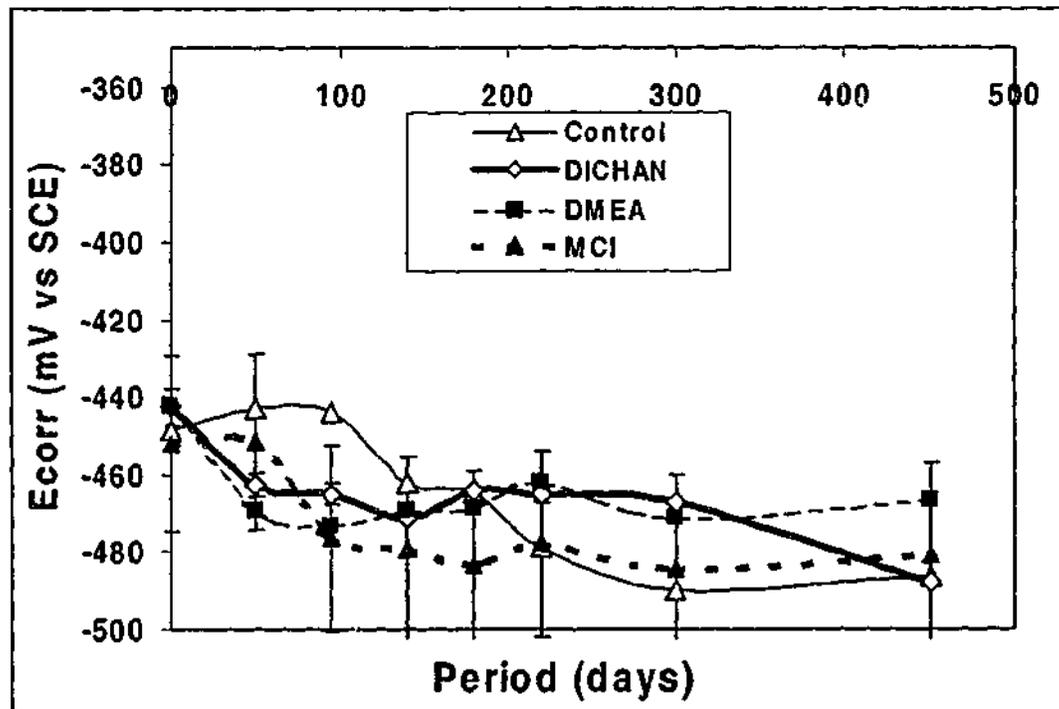


Figure 7.8 – Comparative study of corrosion potential (E_{corr}) vs time for different inhibitors with surface application

Period Days	Control		DICHAN			DMEA			MCI			Plain Concrete		
	R_p kohms.cm ²	E_{corr} mV _{SCE}	R_p kohms.cm ² (±6%)	%Inhn	E_{corr} mV _{SCE} (±5%)	R_p kohms.cm ^{2*}	%Inhn	E_{corr} mV _{SCE} *	R_p kohms.cm ² (±6%)	%Inhn	E_{corr} mV _{SCE} (±5%)	R_p kohms.cm ^{2**}	%Protn	E_{corr} mV _{SCE} (±11%)
0	23.7	-448	24.2	2	-443	26.8	12	-443	26.4	10	-452	1974	99	-123
50	21.6	-442	22.5	4	-463	27.0	20	-469	27.3	21	-452	2431	99	-101
95	15.3	-444	17.9	14	-465	25.8	41	-473	28.3	46	-477	2918	99	-99
140	15.7	-459	17.7	11	-471	26.8	41	-469	26.1	40	-480	2687	99	-95
180	14.7	-462	15.4	5	-464	23.8	38	-467	26.2	44	-484	2667	99	-33
220	15.4	-477	15.2	-2	-465	22.7	32	-460	26.9	43	-478	3021	99	-17
300	14.2	-488	14.7	3	-467	23.2	39	-469	26.7	47	-485	3327	100	-31
450	14.5	-485	12.8	-14	-488	21.8	34	-465	24.0	40	-481	3078	100	-8

* - Readings on one specimen were considered because of the considerable scatter obtained with the second specimen

** - Significant variation in the R_p values because of the highly resistive passive film formed at the rebar surface

Table 7.4 - Comparative study of polarisation resistance (R_p) and corrosion potential (E_{corr}) for concrete specimens with surface applied inhibitors

The corrosion potential of the reinforcement subjected to DICHAN treatment showed a negative shift from -443 to -463 mV_{SCE} within 50 days; and after maintaining around this value for 300 days, it finally dropped to -488 mV_{SCE} at the end as was observed in the case of control sample (Figure 7.8). The decrease in the potential with the corresponding decrease in the % inhibition for the same period (observed in Figure 7.7) indicates insignificant anodic inhibition resulting in an active corrosion.

DMEA showed moderate remedial inhibition properties. Approximately 40% inhibition, based on the $R_{p\text{control}}$ value, was attained in 95 days and the level kept fluctuating between 35-40% even after discontinuing the surface application of inhibitor. The persistence of a 40 % inhibition level until the conclusion of the test period in the case of DMEA in concrete is indeed different from the time dependent declining characteristics observed in the case of experiments in saturated calcium hydroxide solution. The decline in the inhibition capacity of this inhibitor at longer time in solution experiments could be attributed to a low persistency of the barrier film especially in the presence of aggressive chloride ions. It was also possible that some loss due to volatilisation of this inhibitor from the vicinity of steel/solution interface might have occurred because of its high vapour pressure. The diffusion characteristics of DMEA in concrete being different from that in the solution, it is likely that the amount of DMEA already transported to the rebar was possibly being retained for longer time. The E_{corr} values (Figure 7.8) displayed by the rebar exposed to DMEA, showed an initial drop from approximately -445 to -470 mV_{SCE} in 50 days. The potential then kept fluctuating around this value until the conclusion of the test period. The decrease followed by the stabilisation of E_{corr} , when considered with the % inhibition values, may (Figure 7.7) indicate that cathodic inhibition is likely. Similar cathodic shift was obtained when DMEA was added to the calcium hydroxide solution containing corroding steel coupon.

MCI exhibited a slightly better performance in remedial application than DMEA. Corrosion inhibition levels in this case, even though were found to be low initially, increased gradually up to about 45% within 95 days of testing, suggesting formation of the inhibitor film. Beyond 95 days, the concrete specimen treated with this inhibitor continued to show higher R_p values as compared with that of the control sample. This is postulated to be due to the stabilisation of the passive film at the steel surface. The inhibition was persistent even beyond 300 days, a period after which surface application

of inhibitor was discontinued. On comparing these results with those obtained in the solution experiments, it may be noted that even though a consistent inhibition throughout the test period was observed in both cases, the level of protection obtained in solution was much higher than that observed in the concrete experiments. The possible reasons for this have been discussed previously. The negative shift in the rebar potential (E_{corr}) exhibited by surface application of MCI was similar to that observed in the case of DMEA and is consistent with the cathodic inhibition process. In the case of MCI, however, corrosion potentials were found to be more negative (between -475 to -485 mV_{SCE}) as compared with those obtained with DMEA application, suggesting a distinctly higher degree of cathodic inhibition. Again the trend in the E_{corr} values obtained in the case of concrete is consistent with that in the remedial experiments in saturated calcium hydroxide solution.

It has been observed that in the case of both MCI and DMEA, the level of inhibition under admixture as well as remedial applications is similar. This confirms that these inhibitors indeed diffuse through concrete and attain a significant concentration level at the surface of the steel reinforcement, thus inhibiting corrosion. These can, therefore, be used just as effectively in the rehabilitation of an existing structure, or as an admixture for a new structure, or in a concrete patch repair situation.

It is pertinent at this point to recall that diffusion results in the case of 30mm thick concrete (having 0.6 w/c ratio), exhibited leveling off of the inhibitor concentration in the downstream cell, suggesting the likely blocking of the pores due to inhibitor-concrete interaction. This seems to have occurred after approximately 300 days in the case of DMEA and around 200 days for MCI. The inhibition data as summarised in Figure 7.7, when considered in view of the above diffusion results, it is noteworthy that the protection levels once achieved were maintained even after discontinuing the supply of inhibitor molecules. This observation is consistent with the postulation of formation of a persistent inhibitor film at the steel surface due to a stronger chemisorptive bond between the amine molecules and the steel surface (McCafferty, 1978). Further, the performance of organic amine-based inhibitors is less concentration dependent as compared with that of nitrite-based inorganic inhibitors. The long-term protection is also suggestive of the dominant cathodic nature of inhibitor action.

7.3.2 - Inhibition Model in Reinforced Concrete

It is hypothesised that in any inhibitor application in concrete, the formation and maintenance of the protective inhibitor film depends upon attaining equilibrium between two processes. Firstly, the chemical process, responsible for the formation of the passive film at the steel surface and secondly the diffusion process responsible for the transport and subsequent replenishment of the consumed inhibitor molecules at the steel concrete interface. In the remedial situation, the performance of the inhibitor is more likely to be controlled by the diffusion kinetics, as the inhibitor applied at the surface of the concrete specimen needs to be transported to the rebar, whereas under admixture condition the inhibitor is already present in the vicinity of the rebar from the time of the casting of the concrete.

The model which can possibly describe the action of inhibitor e.g. DICHAN in concrete is as follows: Initially a small number of DICHAN molecules manage to diffuse through concrete to the rebar and provide some protection, possibly through a repassivation process at the anodic sites, due to the nitrite part of the inhibitor. However, once the nitrite ions get consumed, they are not replenished at the same rate by fresh inhibitor because of its sparing solubility and extremely slow process of diffusion. The above process disturbs the equilibrium at the steel/concrete interface and leaves it with a deficiency of inhibitor molecules. As DICHAN is a predominantly anodic inhibitor, once the quantity of nitrite ions gets depleted, corrosion is accelerated, which is indicated by a downturn in % inhibition as shown in Figures 7.5 and 7.7. In this case even if the cathodic component of the amine from DICHAN, is expected to provide some inhibition, the overall effect seems to be dominated by the anodic amine and the nitrite components. It is interesting to note that the downturn in % inhibition for concrete specimens treated with DICHAN is observed around the same time as the observation of blocking of pores in the diffusion experiments, which indeed is supportive of the above postulation.

Similar models can be applied to describe the action of amine-based inhibitors (DMEA and MCI). The amine-based inhibitors act predominantly via the formation of an organic barrier film through chemisorption of the amine molecules. This process of chemisorption probably occurs at both cathodic and anodic sites, but the dominant protection in this case is offered mainly at cathodic sites. Other factors which could

contribute to the better performance of DMEA and MCI as compared with DICHAN is probably their higher solubility in water and higher diffusion coefficients in concrete, which considerably increase their availability at the steel/concrete interface. The significantly lower inhibition levels observed in concrete in the case of the MCI as compared with those obtained in the solution experiments, could be possibly attributed to the likely precipitation of some of its components in concrete pores leaving only the amine as a real active component for inhibiting corrosion, as in the case of DMEA. The decrease in the inhibition capacity of MCI observed in concrete is consistent with Elsener and coworkers' results (Elsener et al., 1999; Elsener et al., 2000), who observed a significant decrease in the inhibitor efficiency due to precipitation of the non volatile fraction of the inhibitor.

7.4 – CONCLUSIONS

The results in the plain concrete confirm that in the absence of corrosion initiator (chloride ions), steel rebar embedded in concrete would indeed remain in a pristine condition and corrosion would not occur. However in the presence of chloride ions noticeable corrosion activity occurs with the progressive deterioration of the structure. The results have also demonstrated the ability of amine based migratory corrosion inhibitors to reduce corrosion by diffusing through concrete and forming a protective film at the steel surface regardless of the method of application/treatment. The absolute corrosion inhibition capacity and the time over which inhibitor is active, depend on the thickness and resistivity of the film formed by the inhibitor at the steel surface and its persistency against the attack of chloride, which is in turn dependent upon the nature of the inhibitor.

As an admixture DAREX exhibits the best performance in the presence of chloride ions. However, over an extended period its behaviour appears to be concentration dependent resulting in a gradual decrease in the protection level as the nitrite ions are consumed, which is consistent with its anodic nature. The effectiveness of DICHAN in the concrete specimens seems to be limited as it shows a dramatic decrease in corrosion inhibition properties, either as an admixture or in surface application, which is contrary to its performance in saturated calcium hydroxide solution experiments. This is associated with DICHAN's poor solubility and poor diffusion properties through the

concrete. Organic amine-based inhibitors DMEA and commercial MCI appear to be quite effective especially at longer time as inhibition levels in the case of these inhibitors stabilise with time. The difference in the inhibition levels of amine-based and nitrite-based inhibitors under short-term and long-term application can be attributed to different inhibition mechanisms. The amines work predominantly via a chemisorption mechanism to form a protective film rather than acting as oxidants to form ferric oxide to repassivate the ferric oxide film.

The overall lower inhibition in concrete specimens as compared with the previously reported solution experiments is due to the fact that the actual concentration of inhibitor species at the steel/concrete pore water interface is significantly lower than that at steel/calcium hydroxide solution interface in the earlier experiments. Since the concentration of inhibitor species at the steel/concrete interface is decided primarily by inhibitor diffusion characteristics, it can be concluded that the performance of inhibitors in concrete is controlled more by its diffusion kinetics in concrete rather than the electrochemical kinetics at the steel/concrete interface. This hypothesis is further confirmed under remedial conditions where the capacity of inhibitors to perform their function depends upon their rate of penetration through concrete. The influence of diffusion characteristics becomes apparent at longer times in admixture situations as well, since the depletion in the inhibitor quantity at the steel/concrete interface needs to be replenished by a fresh supply of inhibitor molecules from the surrounding concrete areas. The initial period in admixture application, however, seems to be dominated by inhibition kinetics.

Thus in conclusion these studies have shown that nitrite-based DAREX is an effective inhibitor when applied as concrete admixture in higher quantities or the quantities prescribed by the supplier. Organic amine based DMEA and MCI can extend the life of a structure by protecting the steel surface not only when used as admixtures but also when applied to the surface as migrating inhibitors. The level of protection offered by these inhibitors at shorter time period is slightly lower than the ones offered by the nitrite based inorganic inhibitors. However, at longer time they provide much better protection and their performance is not concentration dependent.

The above study has indicated that the comprehensive testing program carried out on the reinforced concrete specimens using accelerated testing under the controlled

conditions of the laboratory can be used to predict the level of protection offered by a particular inhibitor system to the concrete structure. This should enable engineers to design an appropriate inhibitor application system for the corroding or newly built reinforced concrete structure, which would provide much longer service life.

CHAPTER 8

PROTECTION OF REINFORCEMENT BY COMBINING INHIBITORS AND ELECTRIC FIELD

8.1 - INTRODUCTION

The work presented under chapters 4, 5 and 6 has clearly underlined the fact that even though the protective action of inhibitors, once they are in the contact with steel surface, could be very promising, their transport through concrete is restricted. Further in chapter 7 we developed a model of inhibitor behaviour in reinforced concrete under different conditions of inhibitor application. The main feature of the model stated that even though the overall inhibitor performance depends on both its inhibition ability and the penetration capacity, it is mainly the transport kinetics of these molecules through concrete, which control their behaviour in concrete. It was therefore thought that both the transport process and the protection capacity of inhibitors could be enhanced by application of electric field between the reinforcement and an external anode.

The main consideration in this case was that amine-based inhibitors are likely to become protonated when mixed with water. When an electric field is applied between cathode and anode, it would make the metal surface negatively charged (cathodic) and facilitate the movement of the positively charged/protonated molecules towards the charged cathode. This may result in the acceleration of the inhibitor transport through concrete and may also enhance the adsorbability of the charged inhibitor molecules on to the metal surface. Increase in the adsorption of cation active inhibitors on the metal by moving the potential of the metal away from the potential of zero charge (E_{pzc}) has been explained in terms of ϕ potential scale concept in section 2.7.2. The beneficial effect of cathodic polarisation/electric field on inhibitor performance in the case of different metal-inhibitor combinations on application of different current densities has been reviewed by Kuznetsov (Kuznetsov, 1996). A marked increase in the protective action of certain corrosion inhibitors (chromates, zinc and calcium salts) was also

observed by Rosenfeld in 1953 (Rosenfel'd, 1953) in soft water when cathodic polarisation having comparatively low current densities was applied to the steel. Cathodic protection is often applied for corrosion mitigation of reinforcement in concrete. Hence the next obvious step is to combine the two protection methods to explore the possibility of the conjoint action of the two. Corrosion inhibitors under the influence of high current densities (0.46-1.24 mA/cm²) have been shown to provide corrosion protection to the embedded rebars by electrically injecting the inhibitors into the concrete matrix under the Strategic Highway Research Program (Asaro et al., 1990; Hettiarachchi and Gaynor, 1992).

In the present work the corrosion behaviour of the concrete specimens subjected to either electric field or inhibitor treatment or both was monitored over time, using the linear polarisation resistance technique and corrosion potential measurements. Additionally, in the case where cathodic protection was applied, depolarisation tests were carried out at the end of each cathodic polarisation test in order to examine the effectiveness/protection mechanism of cathodic polarisation.

8.2 - EXPERIMENTAL PROCEDURE

Reinforced concrete specimens admixed with chloride, similar to those used in the case of remedial application in chapter 7, were used for simultaneous application of electric field and inhibitors. Specimen design, preparation, concrete mix design and quantity of admixed chloride have already been described in chapter 7. Inhibitor was applied to the surface of the concrete specimen and a thin piece of sponge/thick cloth saturated with inhibitor containing calcium hydroxide solution was placed to cover the surface of the specimen as was described in chapter 7. To simulate the cathodic protection/electrical inhibitor injection system, a titanium mesh was laid on the sponge to serve as a temporary anode enabling application of electric field between the temporary anode and cathode/rebar. The function of the thin sponge/cloth kept on the surface was to provide an inhibitor-containing electrolyte maintaining a contact between the anode and the cathode. Also a thick piece of sponge saturated with inhibitor containing calcium hydroxide solution was kept on the top of the titanium mesh to minimise inhibitor losses due to evaporation. The concrete specimens were placed over a sponge semi-immersed in a 3.5 wt % salt solution in order to avoid the drying out of the concrete. The amount

of current being received at the reinforcing steel was controlled through the adjustment of the power supply. Current density was calculated by dividing the current by the exposed area of rebar after subtracting the surface area at both ends coated with the epoxy.

Two different current densities, low (20mA/m^2) and high (7370mA/m^2), were applied for different period of time. Figure 8.1 presents the general set up used for both these experiments. Even though the set up as well as the method for application of current in both the experiments were similar, the duration of application of current, the period of depolarisation and the method of monitoring depolarisation were different.

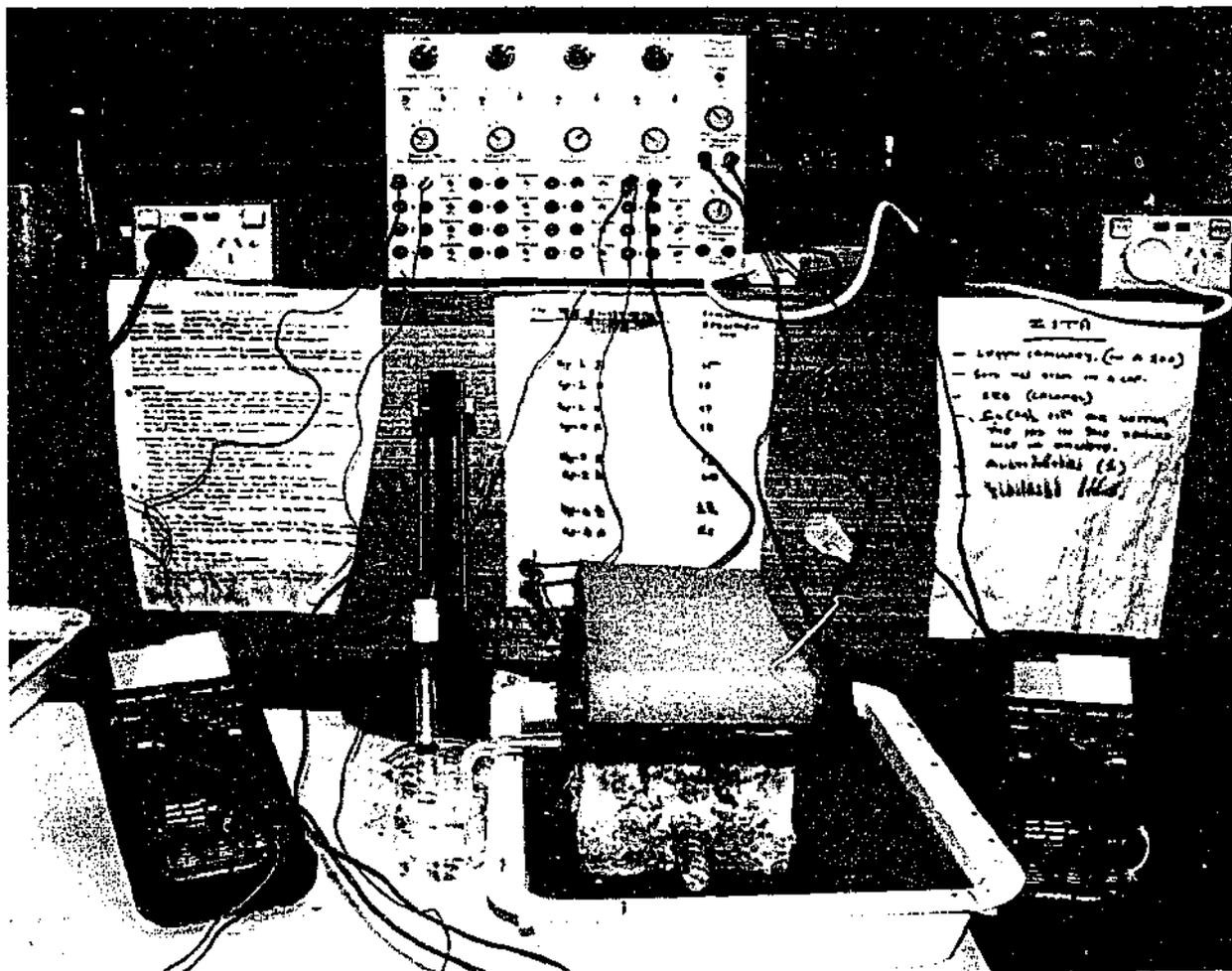


Figure 8.1 – The set up used for the application of electric field to the reinforced concrete specimens

8.2.1 - Application of Low Magnitude Electric Field (Cathodic Protection Tests)

All the experiments were performed in duplicate (2x4) using reinforced concrete specimens with admixed chloride to simulate the deteriorating conditions in concrete.

Three inhibitors, DICHAN, DMEA and MCI were selected for surface application. A fourth pair of specimens without any surface applied inhibitor was used to evaluate the effect of cathodic polarisation alone on the chloride-contaminated reinforced concrete. These specimens were termed "control_{CP}" and were used for evaluating the corrosion behaviour of the reinforcement protected with the combined "cathodic protection-inhibitor" system. It should be noted that "control_{CP}" is different from the "control" sample used in chapter 7 as the "control" sample represents the specimen without any applied (inhibitor or cathodic polarisation) protection.

The specimens were cathodically protected for more than seven months in six weekly periods using a constant current density of 20mA/m². After each protection period of six weeks the specimens were allowed to depolarise for 72 hours. These long-term tests were interspersed with the depolarisation procedure to monitor the effect of cathodic polarisation on the corrosion behaviour of steel. At the end of the 72 hours period, the corrosion behaviour of rebar was assessed using the linear polarisation resistance technique and corrosion potential measurements.

Depolarisation tests

The cathodic protection current was switched off at the end of each six week protection period and the concrete specimens were allowed to depolarise for at least 72 hours during which the following measurements were carried out. The potential of the rebar was recorded every minute during the first five minutes after the current was switched off. After five minutes the potentials were recorded every hour during the first four hours and at 24, 48 and 72 hours thereafter using a high input impedance digital multimeter. The purpose of this measurement was to examine the long-term depolarisation characteristics of the cathodically protected specimens (control_{CP}) and compare it with those for the specimens subjected to a combined protection system. The influence of inhibitors on parameters such as rest potential and current rest potential was also investigated.

- a. *Determination of the "instantaneous off" potential:* When the polarised potential is measured during the passage of current the value measured may include an ohmic potential drop and the measured value may be different from the true polarised potential. The current interruption technique can be used to remove the ohmic component of the polarised potential and the true polarised potential is determined

as the potential measured immediately after current interruption. In the present work "the instantaneous off potential" was determined by measuring the potential immediately after switching off the current. The results showed a difference of maximum 14 mV_{SCE} between the potential measured before the current was switched off, and that measured immediately after the current was switched off. This was probably due to the resistance offered by a thin layer of concrete existing between the rebar and the tip of the luggin probe.

- b. *Determination of the "current rest" potential (CE_{rest}):* The term "current rest potential" represents the full depolarised potential obtained after each protection period. It was generally observed that on switching off the current the rebar potential continuously moved to more positive values for a certain period, after which it slowly started to move to more negative values. The reversal was considered to indicate that the potential had approached as close as it was going to, to the full depolarisation potential and that the process was being reversed. The potential after which the depolarisation trend is reversed is termed as the "current rest potential". It was observed that the reverse in the depolarisation process occurred in some specimens after only 24 hours depolarisation, whereas in others it did not occur even after 72 hours depolarisation. In the cases where reversal did not occur, it was considered that the system was not yet fully depolarised and the potential was still moving in the positive direction. Hence in such a case the current rest potential was determined as the maximum (positive) potential obtained at the end of the 72 hours depolarisation period.
- c. *Determination of the "Rest" Potential (E_{rest}):* Rest potential E_{rest} is again a non-polarised potential, which was measured immediately before each protection period. E_{rest} before each protection period is considered to be the potential measured at the end of depolarisation (72 hours) in the previous protection period. E_{rest} for a given protection period may coincide with the CE_{rest} of the previous protection period if the system is not fully depolarised at the end of 72 hours.

All the above potentials in the case of specimens treated with inhibitor-cathodic protection system were compared with those of the cathodically protected specimens (control_{CP}). The potentials were measured with respect to a saturated calomel electrode (SCE).

The LPR and corrosion potential measurements

After depolarising the system for 72 hours, the polarisation resistance of all the concrete specimens was measured using the linear polarisation resistance technique. The % inhibition offered by CP, inhibitor or the combined "CP-inhibitor" system was calculated by substituting the respective polarisation resistance values in the Equation 2.4. In the present case $R_{p_{control}}$ refers to the polarisation resistance of the control sample without any applied protection, whereas $R_{p_{sample}}$ can describe the polarisation resistance of the concrete specimens with the combined protection, or with cathodic protection ($control_{CP}$) or inhibitor treatment alone. Theoretical considerations regarding the LPR measurements and the procedure involved have already been discussed in section 2.4.4.

The corrosion potentials were measured with respect to a saturated calomel electrode using a high input impedance PAN 2710 digital multimeter.

8.2.2 - Application of High Magnitude Electric Field

The experiments were performed with duplicate (2x3) reinforced concrete specimens with the admixed chloride to simulate a corroding situation. Two inhibitors, DICHAN and MCI were selected for surface application on the concrete specimens. Specimens with the applied electric field but without application of inhibitors were used as "control_{EM}" samples to evaluate the effect of high current density alone on the chloride-contaminated specimens. A constant current density of 7370mA/m^2 (7.37A/m^2) was applied for a period of two weeks. The current was switched off after two weeks and the system was allowed to depolarise. Linear polarisation resistance and corrosion potential measurements were carried out periodically on these specimens over a period of 300 days to investigate the effect of time lag on inhibition of reinforcement which was exposed to the combined effect of high current density and inhibitors. Figure 8.2 shows the flow chart for the control and inhibited specimens with and without application of electric field.

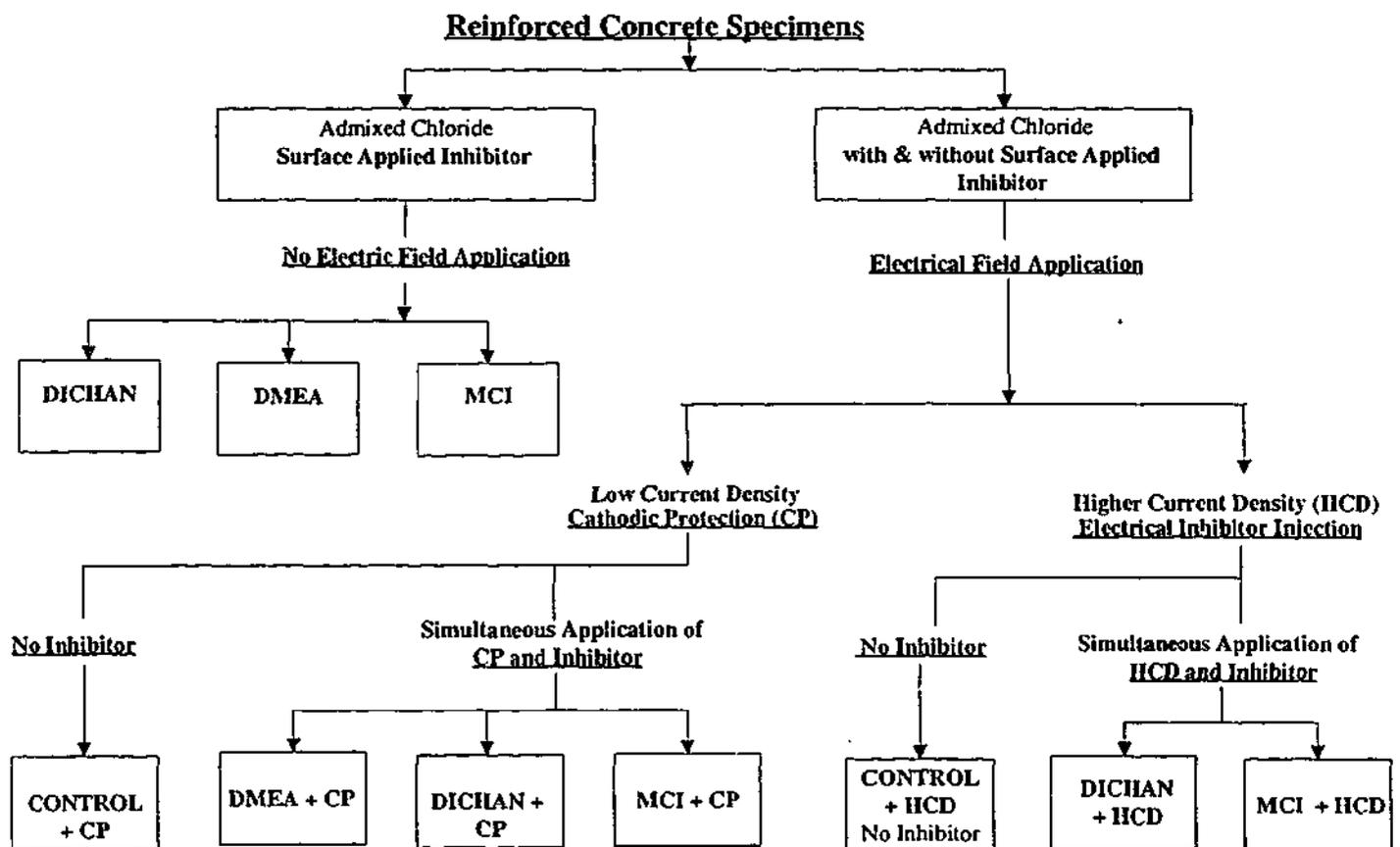


Figure 8.2 – The flow chart for reinforced concrete specimens with and without application of an electric field

8.3 – EVALUATION OF THE COMBINED PERFORMANCE OF INHIBITORS AND ELECTRIC FIELD IN REINFORCED CONCRETE SPECIMENS

In the present work the effect of a combined protection is studied by examining the corrosion behaviour of the steel embedded in concrete subjected to a combined treatment of inhibitor and electric field and comparing the results with those obtained with either inhibitors or electric field alone. It may be stated here that the results, obtained in terms of polarisation resistance $R_p/\%$ protection and corrosion potential in the following sections, will be discussed only in terms of the repair and consequent stabilisation of the passive film, although other possibilities such as the change in the concrete resistivity etc. caused by the transport of inhibitor in concrete may contribute to the changes in some of the above parameters.

8.3.1 - Application of a Low Current Density/Cathodic Protection

Before investigating the effect of cathodic protection on the mechanism of inhibition it would be important to know how to estimate whether the corrosion rate has been reduced to an appropriate level. Several criteria such as the absolute potential criterion, the 100 mV potential decay, the potential shift and the E-log I curve have been adopted in practice which to a greater or lesser degree correlate with the reduction of the corrosion rate to an acceptable level. The most accepted criteria to assess the effectiveness of cathodic protection are criteria based on the absolute value of the "instantaneous off" potential, the depolarisation (decay) and the polarisation (shift) values. In this part of the work the criteria used are the depolarisation values (100 mV decay in 4 hours), examination of the current rest potentials and the rest potentials. Table 8.1 presents a comparison of the depolarisation values obtained at 4, 24, 48 and 72 hours, the current rest potentials and the rest potentials of a cathodically protected system and a combined "inhibitor-cathodic protection" system.

The rest potential

The rest potentials of all the specimens before the first protection period (ranging from $-435 \text{ mV}_{\text{SCE}}$ to $-461 \text{ mV}_{\text{SCE}}$) indicate a high probability of corrosion, before application of cathodic protection and/or inhibitors in all the specimens. The rest potentials in the case of both the control_{CP} and inhibited specimens moved to less negative values with successive polarisation periods. Values ranging from $-285 \text{ mV}_{\text{SCE}}$ to $-345 \text{ mV}_{\text{SCE}}$ were obtained for the specimens exposed to inhibitor and cathodic current, which may indicate that the passive film was gradually restored during each protection period. In the case of control_{CP}, this was considered to be clearly the effect of application of cathodic protection current. It has been suggested (Lourenco, 1998) that the shift in potential to less negative values could possibly be due to:

- the establishment of passivity (or a gradual restoration of the passive film)
- increase in the pH of the pore water solution with cathodic protection
- the removal of the chloride ion from the steel/concrete interface.

However, in the inhibited specimens, restoration of passivity could be due to some combination of the two protection systems or each acting alone. The magnitude of shift in the rest potential and the absolute value of the rest potential after each of the five protection periods in the case of control_{CP} and in the combined inhibitor-CP systems

were not found to be significantly different (Table 8.1). This clearly suggests that the extent of passivity developed in the cathodically polarised specimens with or without application of inhibitors is similar. It may be postulated that the passive film formed due to application of cathodic protection may hinder the possibility of inhibitor film formation at the rebar or alternatively the extra presence of inhibitor may not offer any additional protection.

Depolarisation

The potential continuously moved to more positive values for the first 24 or 48 hours and then slowly started to move to more negative values thereafter in a few cases. A positive shift in the potential during the process of depolarisation possibly indicates the stabilisation of passive film formed during cathodic polarisation. The reversal of the depolarisation process indicates the probability of the breakdown of this film. The depolarisation value at 4 hours decay in the first protection period for control_{CP} was 106 mV_{SCE} whereas those for the inhibited specimens were lower than 100 mV; however, in the subsequent protection periods they ranged from 61 to 189 mV with 88% of the results higher than 100 mV. Similarly, most of the results (more than 95%) at 24, 48 and 72 hours after the first protection period were higher than 100 mV. The actual depolarisation values in these specimens after the first protection period ranged from 72 to 270 mV at 24 hours, from 80 to 301 mV at 48 hours and from 86 to 304 mV at 72 hours. This suggests the formation/stabilisation of passive film in all the specimens with successive protection periods. It was found that the reverse in the depolarisation process occurred in some specimens after only 24 hours depolarisation, whereas in some cases it did not occur even after 72 hours. The non reversal of the potential until 72 hours may be due to the fact that the potential of the system after switching off the current had not probably reached the fully depolarised potential and the system was still depolarising. On comparing the depolarisation behaviour of control_{CP} with the specimens treated additionally with inhibitors, again no significant difference was observed within the measurement period. This suggests that the extent of passivation or the resistivity of the passive film in the case of both systems may be similar.

Specimen	Period Days	E_{rest} (mV _{SCE}) (before each protection period)	E_{off} (mV _{SCE}) (Instant Off Potential)	Depolarisation (mV)												CE_{rest} (mV _{SCE}) (Current Rest Potential)	Total Depol (mV)
				Potential 4h	Depoln 4h	% Depoln 4h	Potential 24h	Depoln 24h	% Depoln 24h	Potential 48h	Depoln 48h	% Depoln 48h	Potential 72h	Depoln 72h	% Depoln 72h		
Control + CP	45	-457	-521	-415	106	89	-404	117	98	-405	116	97	-402	119	100	-402	119
	90	-402	-531	-402	129	54	-346	185	78	-335	196	83	-294	237	100	-294	237
	135	-294	-472	-325	147	81	-290	182	100	-328	144	79	-359	113	62	-290	182
	180	-359	-492	-303	189	73	-255	237	92	-233	259	100	-316	176	68	-233	259
	225	-316	-500	-327	173	59	-240	260	88	-214	286	97	-206	294	100	-206	294
DMEA _{Rest} + CP	45	-461	-551	-474	77	75	-452	99	97	-449	102	100	-450	101	99	-449	102
	90	-450	-503	-442	61	71	-431	72	84	-423	80	93	-417	86	100	-417	86
	135	-417	-531	-422	109	54	-390	141	70	-377	154	77	-330	201	100	-330	201
	180	-330	-545	-411	134	56	-365	180	75	-327	218	90	-303.8	241	100	-304	241
	225	-304	-558	-413	145	56	-330	228	88	-300	258	100	-342	216	84	-300	258
DICHAN _{Rest} + CP	45	-435	-587	-498	89	68	-469	118	90	-460	127	97	-456	131	100	-456	131
	90	-456	-583	-473	110	78	-448	135	96	-446	137	97	-442	141	100	-442	141
	135	-442	-546	-417	129	66	-385	161	82	-362	184	94	-350	196	100	-350	196
	180	-350	-590	-450	140	57	-373	217	89	-374	216	88	-345	245	100	-345	245
	225	-345	-551	-402	149	49	-300	251	82	-260	291	96	-246.6	304	100	-247	304
MCI _{Rest} + CP	45	-439	-504	-431	73	76	-420	84	88	-412	92	96	-408	96	100	-408	96
	90	-408	-516	-418	98	78	-401	115	92	-391	125	100	-392	124	99	-391	125
	135	-392	-473	-372	101	62	-340	133	81	-309	164	100	-325	148	90	-309	164
	180	-325	-476	-350	126	66	-307	169	89	-293	183	96	-285.2	191	100	-285	191
	225	-285	-472	-346	126	58	-291	181	83	-265	207	95	-254.5	218	100	-255	218

Table 8.1 – A comparison of the depolarisation kinetics of various inhibitor/CP systems with that of a CP system alone

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Figure 8.3 illustrates the plots of current rest potentials (CE_{Rest}) vs time for the representative specimens of the control_{CP} and with the combined protection system. No obvious trend has been found between the behaviour of the current rest potentials vs time for the cathodically polarised systems with and without application of inhibitors. The shifts in CE_{Rest} on successive polarisation periods as well as the actual values of current rest potentials in the case of control_{CP} and for those with the combined treatment were not significantly different. This supports our earlier postulation that the resistance offered by the protective film to chloride attack in both the uninhibited and inhibited specimens subjected to cathodic polarisation is equivalent. Normally, the strengthening of any passivating film is expected to delay the reversal of the depolarisation process and is also expected to shift the current rest potential in a positive direction. However no evidence of such an effect is observed in the relevant plots. On the contrary except for the first and the third protection periods, the current rest potential values for control_{CP} are found to be more positive than those observed in the inhibited specimens. These observations suggest that the passive film formed due to cathodic protection itself under these experimental conditions is possibly more protective than that formed due to the additional inhibitor treatment.

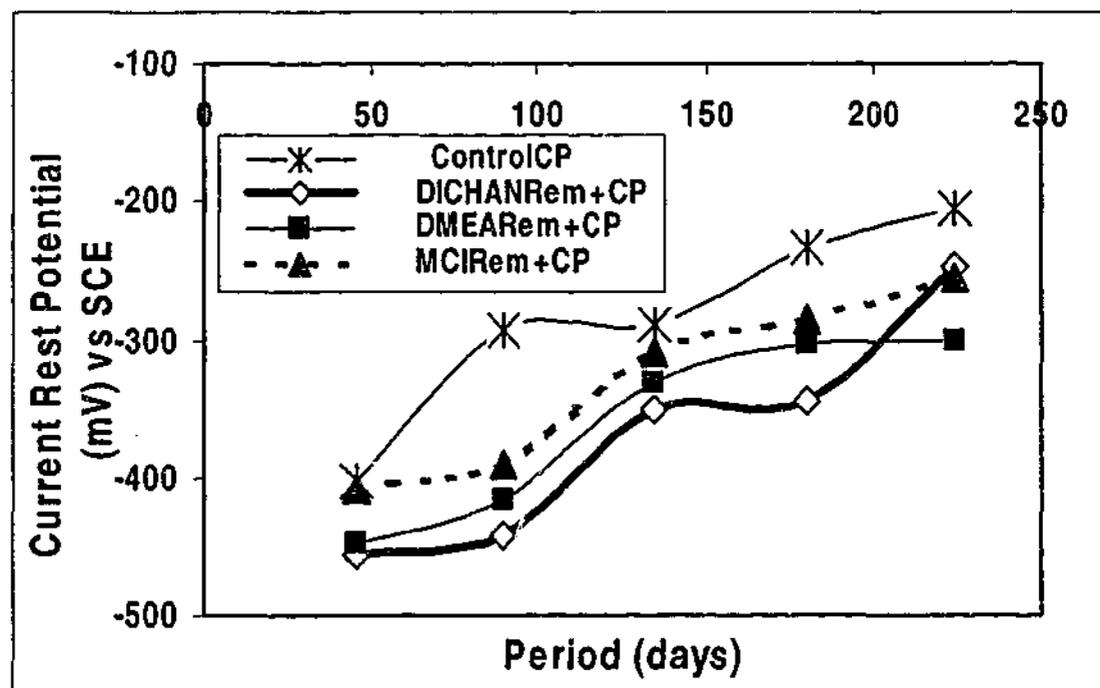


Figure 8.3 – Comparative study of the current rest potentials vs time for concrete specimens with application of CP and CP plus inhibitor

Comparative study of % inhibition based on R_p

Figures 8.4a, b and c show plots of % inhibition for specimens treated with cathodic protection system, inhibitors (DMEA, DICCHAN, and MCI) and a combined (CP+inhibitors) system. Figure 8.5 presents a comparison of inhibition levels offered by different inhibitors in the presence of cathodic protection and control_{CP} (no inhibitor). The measurement performed on the zeroth day does not show any effect of inhibitor, CP or (CP+inhibitors). This measurement corresponds to the first measurement after the 28 days fog room period and the corrosion behaviour of the specimens at this time is considered to be equivalent to that of the control sample as described in section 7.2.4. The second measurement, after 45 days, is the reading taken after the first protection period. The results obtained in the case of "surface application of inhibitors" (section 7.3.1) have been used here for representing the concrete specimens with surface applied inhibitor in the absence of electric field, where inhibitor transport through concrete is controlled by a natural diffusion process.

All the specimens subjected to a combined treatment showed a rapid initial increase in the protection to 40-50% within 90 days followed by a further gradual increase. The percentage inhibition at the end of test period of 225 days, showed a plateau effect indicating stabilisation of the passivating film. The inhibition levels obtained at different times for various specimens subjected to the above treatments are summarised in Table 8.2. On application of electric field to the concrete specimens treated with DICCHAN, an increase of maximum inhibition from 14 to 41% was observed around 90 days, which increased further to reach 60% towards the end of the test period. This was distinctly different from the decrease in inhibition to the corrosion acceleration level, suggesting the rupture of inhibitor film, observed in the absence of electric field. Similarly in the case of DMEA after 90 days the protection level increased from 17 to 42% on application of cathodic protection current, and was sustained. This was again different from the decrease in inhibition observed for surface inhibitor application without any application of current. The specimens treated with the MCI, showed a less obvious increase from 41% (without CP) to 52% (with CP) after 90 days application of constant current. However, the difference later increased from 38% (without CP) to 64% (with CP) towards the conclusion of the test period. The likely reason behind this increase in the protection could be the strengthening of the passive film due to continuous application of cathodic protection current.

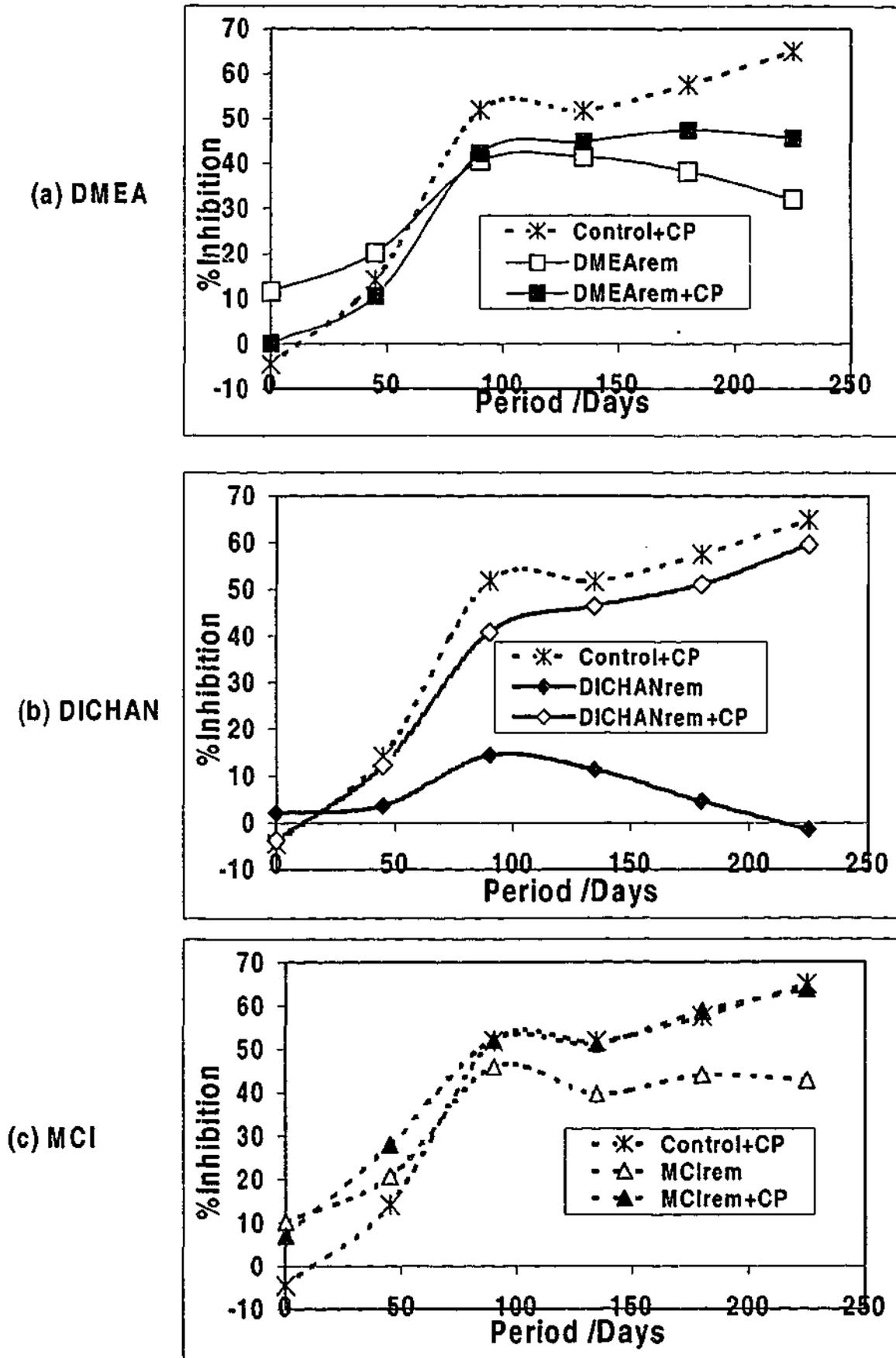


Figure 8.4 – Comparative study of % inhibition for concrete specimens with application of CP, inhibitors and CP plus inhibitors

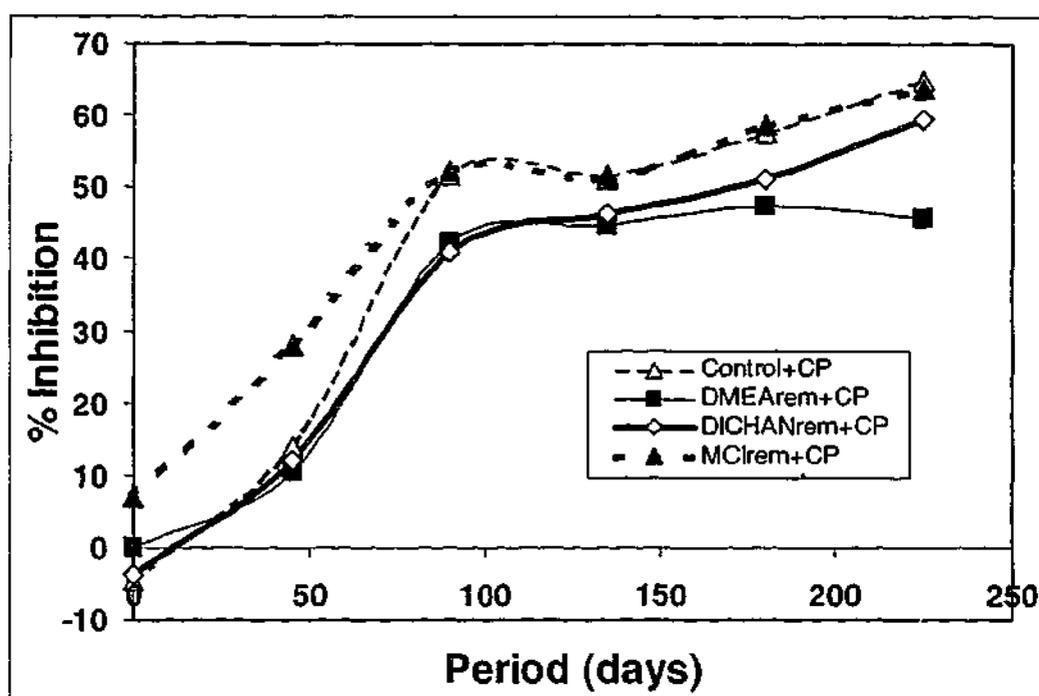


Figure 8.5 – Comparative study of % inhibition for concrete specimens with application of CP and different inhibitors

It is evident that increase in the protection occurred on applying a current density typical of that used in a CP system. However, it is not very clear whether this increase is due to electric field (cathodic protection) alone or it is because of the synergistic effect of inhibitor action and cathodic protection. The inhibition levels exhibited by control_{CP} at any given time are slightly higher than those for the combined treatment (Figures 8.4a, b, c and 8.5. This observation indicates that the enhancement of protection was likely to be due to the application of cathodic protection alone, at least under the set of experimental conditions prevailing in this work.

Prot Period Days	% Inhibition						
	Control+CP	DMEA _{rem}	DMEA+CP	DICHAN _{rem}	DICHAN+CP	MCI _{rem}	MCI+CP
0	-5	12	0.1	2	-4	10	7
45	14	20	11	4	12	21	28
90	52	41	42	14	41	46	52
135	52	41	45	11	46	40	51
180	58	38	47	5	51	44	59
225	65	32	46	-2	60	43	64

Table 8.2 –Comparative study of % inhibition for concrete specimens with application of CP, inhibitors and CP plus inhibitors

Figures 8.6a, b, c and Table 8.3 compare corrosion potentials over a test period of 225 days for the specimens subjected to a combined protection and individual treatment of cathodic polarisation and inhibitor. All the specimens with the combined protection and control_{CP} showed a consistent positive shift in the corrosion potentials as a function of time. e.g. the cathodically polarised reinforced concrete specimen with the surface applied DICHAN, displayed a significant anodic shift (Figure 8.6b and Table 8.3). This behaviour was in contrast with that exhibited by the concrete specimens with surface applied DICHAN in the absence of electric field (section 7.3.2) where a cathodic shift in the potentials was observed suggesting active corrosion. In the case of DMEA, the corrosion potential was found to move anodically by 155 mV, and the magnitude of the positive shift obtained for MCI was 176 mV. This is again contrary to the cathodic shift observed in the case of the organic amine-based inhibitors DMEA and MCI (section 7.3.2), suggesting cathodic inhibition. In a later experiment, when comparing the corrosion potential shifts for the combined protection system with that obtained in the case of control_{CP}, it was observed that a higher shift in the corrosion potential (i.e. 242 mV) was exhibited. This observation combined with the trend observed in the polarisation resistance R_p suggest that equivalent or slightly higher passivation occurred in the control_{CP} as compared with that observed in the presence of inhibitors. Thus the positive effect obtained due to simultaneous application of inhibitors and cathodic protection seems to be the result of the application of cathodic protection to the specimens. This is consistent with the trends observed with the % inhibition (the polarisation resistance), the rest potentials and the depolarisation behaviour of the concrete specimens.

Prot Period Days	E _{corr} mV _{SCE}						
	Control+CP	DMEA _{rem}	DMEA+CP	DICHAN _{rem}	DICHAN+CP	MCI _{rem}	MCI+CP
0	-457	-443	-479	-443	-441	-452	-447
45	-412	-469	-460	-463	-464	-452	-411
90	-375	-473	-423	-465	-451	-477	-401
135	-371	-469	-342	-471	-368	-480	-342
180	-359	-467	-321	-464	-367	-484	-301
225	-215	-460	-324	-465	-261	-478	-271

Table 8.3 – Comparative study of corrosion potentials (E_{corr}) for concrete specimens with application of CP, inhibitors and CP plus inhibitors

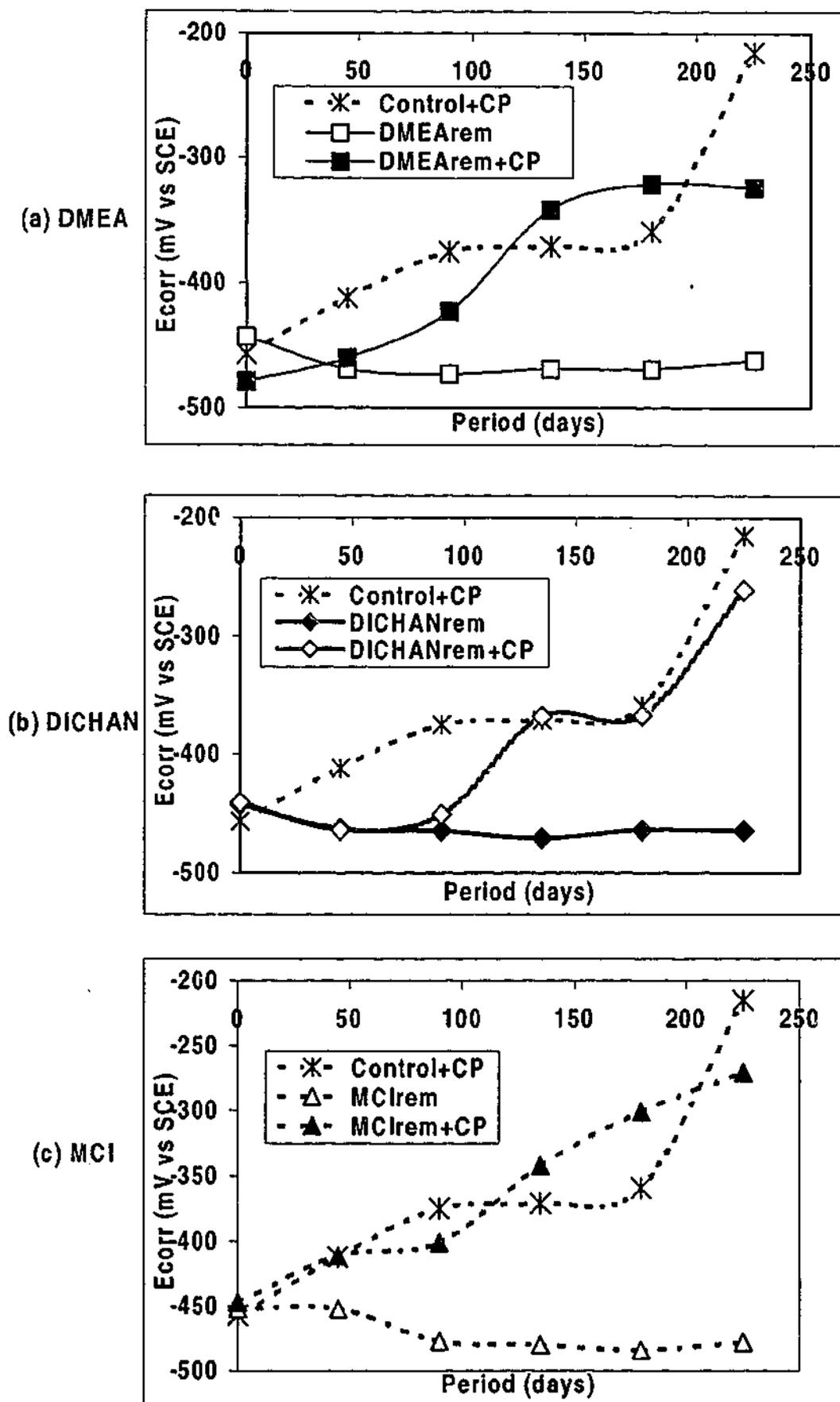


Figure 8.6 –Comparative study of corrosion potentials (E_{corr}) for concrete specimens with application of CP, inhibitors and CP plus inhibitors

The results obtained by combined application of CP and inhibitors are found to be in contrast with those obtained by Rosenfel'd (Rosenfel'd, 1953), who observed increase in the protective action of certain corrosion inhibitors (chromates, zinc and calcium salts) on application of cathodic polarisation technique to the steel in soft water. However, it should be recognised that those experiments were carried out in the solution medium, where the metal surface was in direct contact with the electrolyte. Hence the main function of the applied electric field was to aid in the formation a protective film. In the case of reinforced concrete, inhibitor is applied at the surface of the concrete and needs to be transported through the concrete to reach the rebar. Hence the function of the current density in this case is two fold; it is not only supposed to enhance the adsorbability of inhibitor molecules to form a more protective film at the steel surface, but more importantly it is expected to accelerate their diffusion kinetics or the physical transport through the concrete. Further, in Rosenfel'd's work the mechanism of action of inhibitors at the steel surface under the influence of the applied current was primarily by favouring the deposition of sparingly soluble salt due to alkalisiation of the near electrode layer to form a protective film at the rebar. The mechanism of inhibition (the combined protection) in the current work may be slightly different. The adsorbability of the species on a metal in this case is considered to be dependent primarily on the change in its potential (E) in relation to the potential of zero charge of the metal ($E_{q=0}$); the difference between the two being represented by $\phi = E - (E_{q=0})$. The ϕ value may become negative as a result of a metals cathodic polarisation. This results in the increase in the adsorption of a cation active inhibitor under the action of electrostatic forces. The amount of adsorption may depend upon the magnitude of the change in the potential i.e. potential of a metal and $E_{q=0}$.

In order to investigate the mechanism of combined protection, it is important to examine the mechanism of cathodic protection and inhibitor action in concrete separately. The mechanism of cathodic protection has been discussed earlier in section 2.7.2. One of the effects of the application of cathodic polarisation is to generate the alkalinity or hydroxyl ions due to reduction of oxygen. The production of hydroxyl ions and increase in the pH help in the formation of the passive film on the reinforcement. Another likely effect of cathodic polarisation is the transport of negatively charged chloride ions away from the steel concrete interface and therefore it is expected that the chloride ion activity would decrease with cathodic polarisation. This may help in further reinforcing the passive film. The mechanism of inhibitor action is postulated to

be by chemisorption of inhibitor molecules at the steel surface and this has been previously discussed in detail in section 4.3.5.

The above observations suggest that simultaneous application of cathodic protection and inhibitor may facilitate three competing effects at the steel/concrete interface; namely build up of hydroxyl/high pH condition which generates a passive film, formation of inhibitor assisted passive film, and removal of chloride ions further helping to strengthen the passive film. All three can occur separately or simultaneously. Synergy may be observed, if one effect can occur conjointly with the other e.g. reinforcement of the high pH condition passive film by an inhibitor-induced film or increase in the protective properties of the inhibitor film due to the presence of hydroxyl ions.

While modeling the behaviour of inhibitors in concrete it was postulated that the inhibition process in concrete is governed by both the transport kinetics of inhibitor molecules in concrete and the ability of these molecules to protect steel. It is believed the transport kinetics plays a major role as this may decide the inhibitor concentration at the steel surface (section 7.3.2). It seems from the results that the magnitude of the applied current density may not be large enough to enhance the rate of inhibitor transport in concrete. Hence inhibitor build up obtained at the interface may not be sufficient to facilitate the process of the formation of an inhibitor film in competition with a much more active process of reconstruction of the passive hydroxy film around the reinforcement. Slightly lower inhibition level obtained in the case of combined protection suggest that if inhibitor molecules are not sufficiently present in the vicinity of the steel reinforcement, it may adversely affect the hydroxyl-induced passive film formation. Hence it is postulated that with the conjoint action of inhibitor and cathodic protection, the kinetics of reactions at the steel concrete interface is likely to be determined by the relative concentrations of hydroxyl ions and inhibitor molecules. If the concentration of inhibitor molecules is lower than the threshold concentration, the kinetics of film formation at the steel-concrete interface may be governed by the hydroxyl ions. In such a case the presence of insufficient inhibitor molecules may not be able to improve the protective properties of the passive film. It should be stated that there may be a possibility of observing a synergistic effect under simultaneous application of inhibitor-current density at longer time i.e. more than the 72 hours depolarisation period after the switching off of the current, as the system was not fully depolarised even after 72 hours of depolarisation. Hence it is considered that if the

corrosion behaviour of the reinforcement is monitored for a longer period after switching off the current, the high pH generated passive film may lose its protective properties faster compared to those of the inhibitor reinforced film, especially in the presence of chloride ions.

It would be interesting to find out what happens when the inhibitor molecule concentration increases considerably compared with the hydroxyl ion concentration at the steel/concrete interface. Would this lead to a scenario where protective inhibitor film formation will dominate the formation of passive oxide film? The next objective of this work is to increase the current density and to investigate its long-term effect on the corrosion behaviour of the reinforcement.

8.3.2 - Application of a High Current Density or Electrical Injection (EM) of Inhibitors

The present section is devoted to evaluation of the effect of increase in the current density on the performance of inhibitors. Figures 8.7a and b and Figure 8.8 present the protection levels observed in the reinforced concrete specimens under the influence of high current density with and without application of inhibitors (DICHAN and MCI) and also for the specimens with the applied inhibitors in the absence of current. The measurements taken before the zeroth day represent the corrosion behaviour of the specimens 20 days before the application of electric field or the combined protection. A high current density was applied on the zeroth day (on the graph) for a period of two weeks. The first measurement on the 15th day indicates the protection level observed fifteen days after the current was switched off. It was difficult to determine the polarisation resistance of the rebar earlier than fifteen days, as rebar was highly polarised due to application of high current density and exhibited high cathodic potentials.

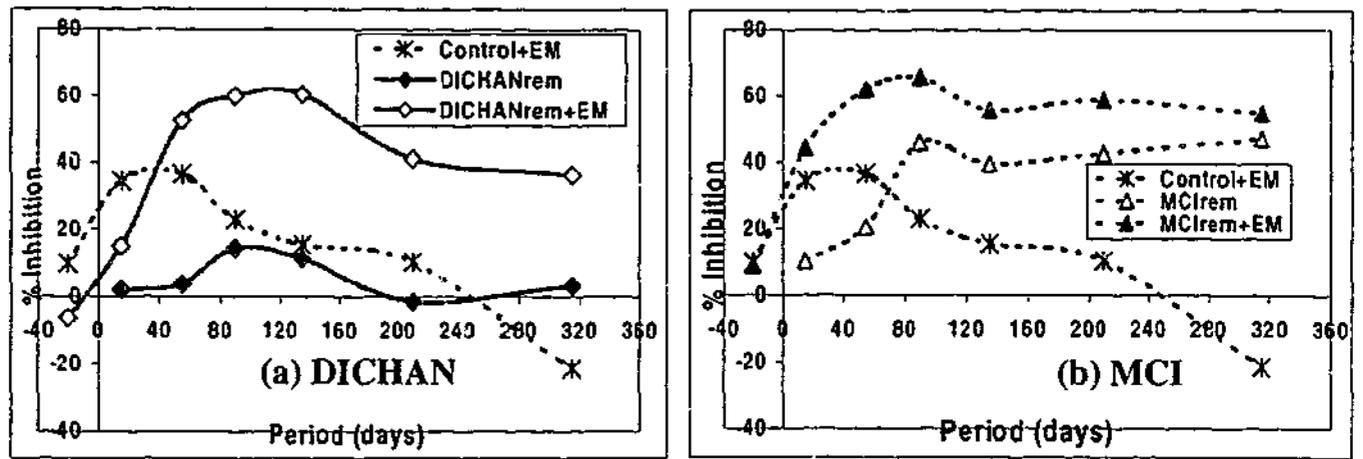


Figure 8.7 – Comparative study of % inhibition for concrete specimens with application of high current density (EM), inhibitors and EM plus inhibitor

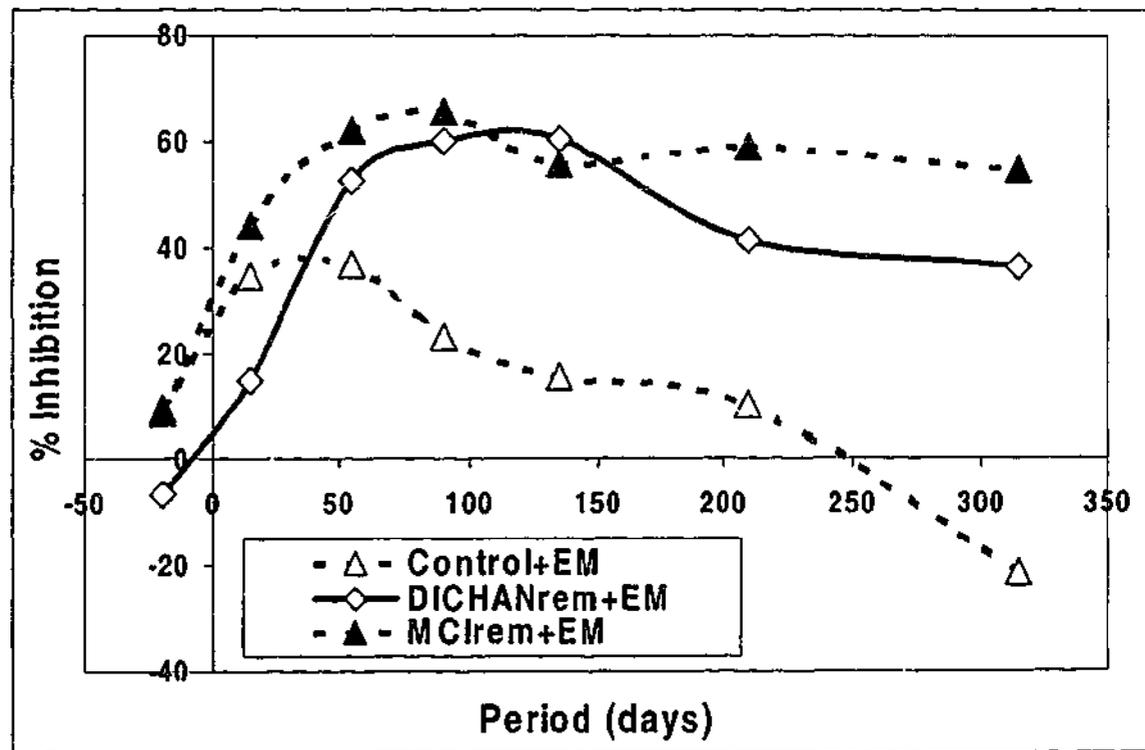


Figure 8.8 – Comparative study of % inhibition for concrete specimens with application of high current density (EM), and EM plus inhibitors

The specimens with the applied current density including control_{EM} showed a rapid increase in protection with time after switching off the current. The protection reached a maximum value and then decreased towards the end in some cases depending upon the type of treatment. The drop in the protection is indicative of breakdown of the passive film and the onset of corrosion. In the case of DICHAN the level of protection increased from the accelerated corrosion level to an inhibition plateau of 60% after 90

days, the inhibition was sustained at this level for approximately 6 weeks and then gradually dropped to 40% towards the completion of the experiment. Control_{EM} exhibited a similar behaviour, however, the plateau was obtained at much lower inhibition within 15 days and finally the protection level dropped below the zero level around 250 days suggesting accelerated corrosion. Specimens treated with MCI exhibited similar trends, however the maximum level of protection obtained with MCI was higher suggesting a more protective film than that observed for DICHAN. Further, the high level of inhibition in this case was maintained until the end of the test period indicating a persistent film, compared with the decreasing trend observed for both DICHAN and control_{EM}. Inhibition levels exhibited by steel subjected to the simultaneous application of inhibitors and electric field were higher than those obtained without the applied electric field (Figure 8.7). The enhancement in the protective effect could be due to either the electric field alone or due to a conjoint action of inhibitors and an applied current density. However, the higher level of inhibition obtained for the combined system as compared with that observed for control_{EM} suggests that this significant increase is attributable to the enhancement of the protective action of inhibitors.

On comparing the trends for both inhibitors with and without application of electric field, it was observed that maximum inhibition for DICHAN increased significantly on application of electric field. The increase in the protection level observed in the case of DICHAN may be due to the restricted penetration of DICHAN under normal conditions (section 7.3.1). The surprisingly high degree of protection with the combined protection method may be assigned to the accelerated transport of charged quaternary ammonium ions (as discussed in sections 2.7.3, 4.3.5 and 7.3.1) under the influence of high current density. It may also be due to a decrease in the Cl/NO₂ ratio because of the removal of chloride ions from the vicinity of the rebar. The decrease in the inhibition level at longer time in the case of DICHAN could be accounted for by the predominant anodic nature of quaternary molecules (sections 4.3.4 and 7.3.1). In the case of MCI a comparatively high protection level was obtained because of the better diffusion characteristics in concrete even in the absence of any applied field. Maintaining a moderately high protection for MCI even at longer time, may be again consistent with the dominant cathodic inhibition provided by the amine based commercial inhibitor. As the performance of cathodic inhibitors is less concentration dependent, a decrease in the concentration (with time) in the case of these inhibitors is less likely to affect its

capacity to inhibit (Jones, 1996). Control_{EM} exhibited a decrease in inhibition to an accelerated corrosion level after a much shorter period of 55 days. This suggested a higher susceptibility of the film formed under passivating high pH conditions to chloride attack as compared to that of the film formed under the influence of both high pH and inhibitor. A comparison of inhibition levels in the case of concrete with and without application of inhibitors under the influence of high current density is presented in Table 8.4.

Period	% Inhibition					
	Days	Control+EM	DICHAN _{rem}	DICHAN+EM	MCI _{rem}	MCI+EM
	-20	10		-7		9
	15	34	2	15	10	44
	55	37	4	52	21	62
	90	23	14	60	46	65
	135	15	11	60	40	56
	210	10	-2	41	43	59
	315	-21	3	36	47	55

Table 8.4 – Comparative study of % inhibition for concrete specimens with application of high current density (EM), inhibitors and EM plus inhibitors

Corrosion potentials of control_{EM} and of the specimens with simultaneous application of inhibitors and electric field are presented in Figure 8.9. A comparison of specimens subjected to electric field or inhibitor treatment alone and with simultaneous application of inhibitor and electric field is presented in Figures 8.10a and b. The potential values corresponding to these graphs are summarised in Table 8.5. In the case of all specimens with the applied current density (control_{EM} and those treated additionally with inhibitors) the potentials exhibited a positive shift with time, reached a maximum and then decreased slightly towards the end of the test period. In the case of DICHAN, the potential of the steel exhibited a significant anodic shift after 90 days of depolarisation, and after maintaining this value for six weeks, the potential dropped off at the end (Table 8.5). Steel subjected to MCI displayed an anodic shift in the potential up to 90 days, the potential then moved cathodically and stabilised towards the end. The positive shift in the potentials observed in the case of DICHAN and MCI is completely different

from the negative shift to highly cathodic potentials displayed in the absence of electric field and may indicate a decrease in the anodic area due to formation of the protective film. In the control_{EM} this could be due to the formation of hydroxy film and the removal of chlorides. In the case of specimens with the combined protection, the potentials of the steel were more positive than those exhibited by steel in control_{EM}. This observation supports the postulation of obtaining additional protection due to inhibitor application. It also confirms an anodic mechanism of action of these inhibitors. Further, it was observed that the maximum corrosion potential obtained as well as the potential observed at the end of the test period in the case of DICHAN were slightly more positive than those observed with MCI (Table 8.5). This indicates the dominant anodic nature of $(C_6H_5)_2NH_2^+$ ions in DICHAN, which is consistent with the trend in the potential observed on addition of inhibitor to a pre-corroded steel coupon in the solution experiments (section 4.3.4).

Thus the higher current density appears to have facilitated electrical injection of inhibitor molecules in the vicinity of steel/concrete interface with the subsequent formation of a passive film under the combined action of high pH and inhibitor. The kinetics of passive film formation, which was governed by OH⁻ ion concentration earlier in cathodic protection, has shifted in favour of the concentration of inhibitor molecules. In order to model the mechanism of inhibition under the simultaneous influence of inhibitors and a high current density, it is important to understand the mechanism of protection under the influence of a high current density in the absence of inhibitors. This is similar to that observed in the case of electrochemical chloride extraction (ECE), and has been described in section 2.7.3.

The moderate level of protection and the decreasing trend in the protection with time in the case of concrete specimens subjected to high electric field alone (control_{EM}) indicate low persistency of the high pH induced passive film and high probability of its breakdown due to chloride attack. It is possible that the current density used in the present case is not large enough to remove sufficient chloride ions from the concrete. The current density recommended for the electrochemical chloride removal is 2-5 times higher than that required for inhibitor injection (Asaro et al., 1990). Further, there is a possibility of remigration of chloride ions towards the rebar after interruption of the current.

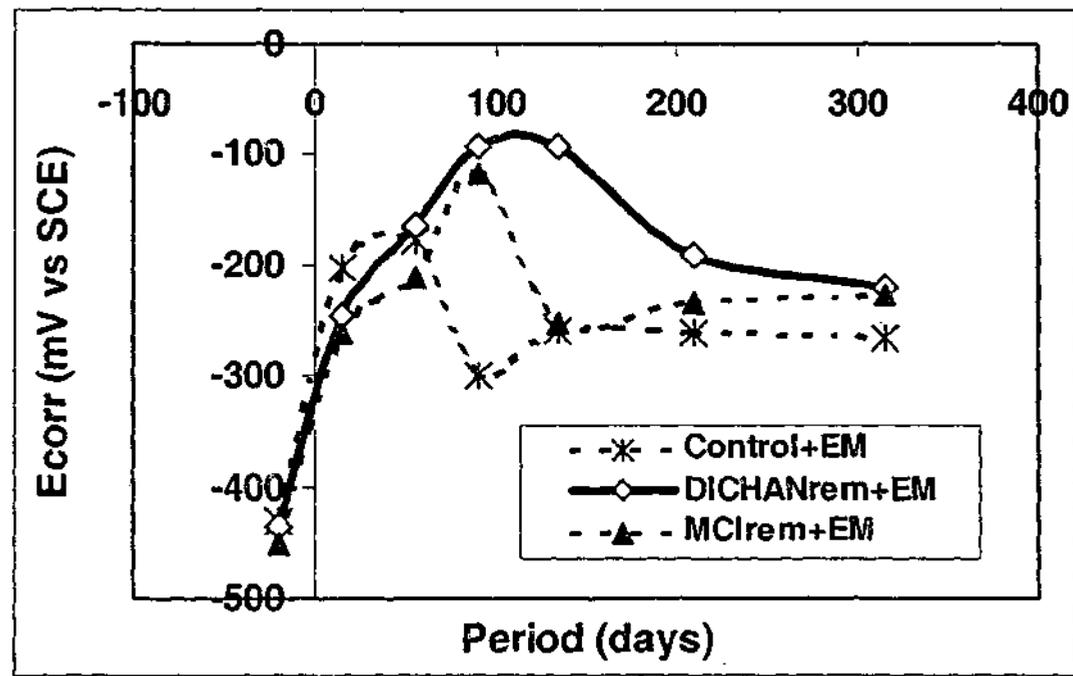
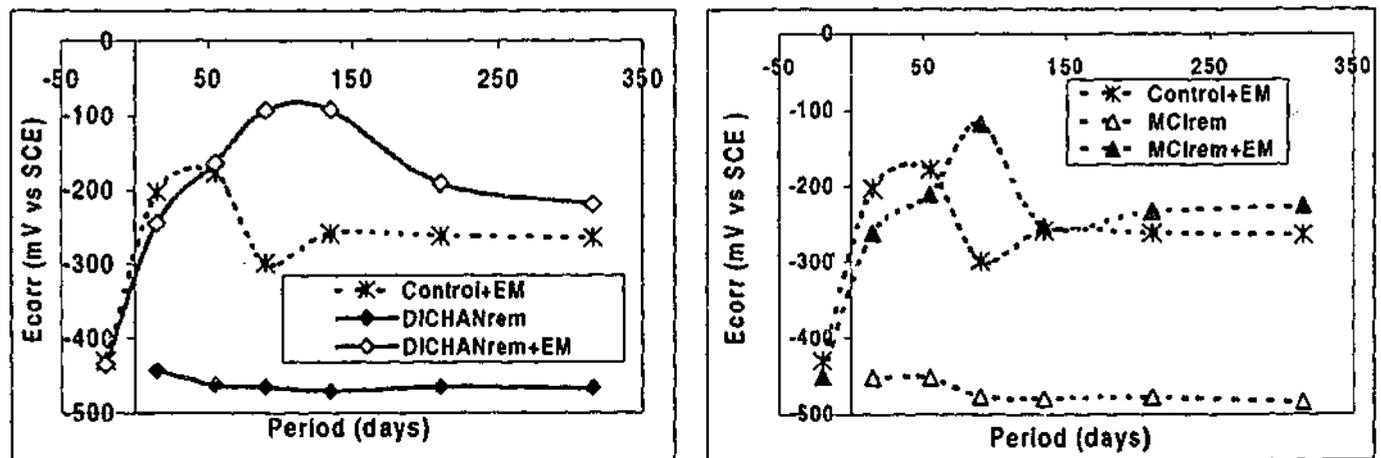


Figure 8.9– Comparative study of corrosion potentials (E_{corr}) for concrete specimens with application of high current density (EM) and EM plus inhibitors



(a) DICHAN

(b) MCI

Figure 8.10 – Comparative study of corrosion potentials (E_{corr}) for concrete specimens with application of high current density (EM), inhibitors and EM plus inhibitors

Period	E_{corr} (mV _{SCE})					
	Days	Control+EM	DICHAN _{rem}	DICHAN _{rem} +EM	MCI _{rem}	MCI _{rem} +EM
-20	-430			-434		-451
15	-203		-443	-245	-452	-262
55	-178		-463	-164	-452	-211
90	-299		-465	-93	-477	-118
135	-259		-471	-92	-480	-253
210	-262		-465	-191	-478	-234
315	-265		-467	-220	-485	-227

Table 8.5 – Comparative study of corrosion potentials (E_{corr}) for concrete specimens with application of high current density (EM), inhibitors and EM plus inhibitors

In the case of specimens treated with inhibitor and a high current density, a higher level of inhibition and a higher positive shift in the potentials is observed. This may be due to the molecules adsorbed on to the negatively charged rebar forming a barrier film through chemisorption. This results in the inhibition of steel corrosion, which is detected by an increased R_p or % inhibition. Further, the movement of E_{corr} in a positive direction indicates that the protection offered by this inhibitor is mainly at the anodic sites at least during the initial period. However, it is possible that the electromigrated DICHAN inhibitor content at the steel/concrete interface reaches a limiting value a few days after the electric field is cut off and gradually decreases in concentration as the further supply is restricted due to very slow ionic diffusion of this inhibitor. As the anodic component of the electromigrated DICHAN is consumed, inhibition tends to decrease slightly. However, some protection at the cathodic sites does persist due to cathodic component of the amine, which is partially reflected in the moderate level of % inhibition present at the end of the measurement period. The E_{corr} results at longer time show a cathodic shift thus supporting the above postulation.

In the case of MCI the maintenance of the high inhibition efficiency is consistent with the dominant cathodic inhibition. Even the corrosion potentials at longer time showed a negative shift confirming the cathodic nature of action, consistent with the above results. The corrosion potentials initially exhibited a positive shift, suggesting

protection at the anodic sites at least during the initial period. This suggests that MCI protects the steel by forming a chemisorbed film at both anodic and cathodic sites. During the initial period the inhibitor functions by acting anodically, whereas at longer time cathodic inhibition predominates. In the absence of the knowledge of the ingredients of MCI, accurate modeling of this effect may not be possible. However, it is likely that on application of a high current density the charged molecules which electromigrate towards the steel/concrete interface are anodic in nature and protect the active anodic sites resulting in passivation. The anodic inhibition in the case of MCI has also been observed in the cyclic voltammetry studies in the solution experiments in section 5.3.2.

8.3.3 - Inhibition Model under Simultaneous Application of Inhibitors and Current Density

It is hypothesised that simultaneous application of current and inhibitor facilitates three competing effects at the steel/concrete interface:

- build up of hydroxyl/high pH condition generated passive film,
- formation of inhibitor assisted passive film
- removal of chloride ions.

Synergy is possible, where one effect occurs conjointly with the other.

It is suggested that in the case of cathodic polarisation, the magnitude of the applied current density may not be large enough to enhance the rate of inhibitor transport towards the steel surface, resulting in insufficient build up of inhibitor at the interface. Hence, the protection is believed to be achieved due to a passive film generated under high pH condition.

An increase in the current density is likely to facilitate electrical injection of inhibitor molecules in the vicinity of steel/concrete interface. Hence the kinetics of passive film formation at the interface, which was assumed to be governed by hydroxyl ion concentration in cathodic protection, is possibly dominated by both hydroxyl ions (high pH) and inhibitor molecules. This results in the formation of inhibitor reinforced passive film. Removal of chloride ions from the vicinity of rebar may occur in both cases.

Finally, having studied the performance of inhibitors under different application conditions in concrete, it is important to compare the protection patterns under different situations. Figure 8.11a and b compare the trends in the protection (as a function of time), exhibited by DICHAN and MCI under different application conditions i.e. when added as admixtures to the concrete mix, applied at the surface of the contaminated concrete, and when combined with (high and low) current densities. The general features of the graphs suggest that except for the initial level (the first measurement), the levels maintained in the case of both DICHAN and MCI under admixed or surface applied conditions are not significantly different (as discussed in chapter 7). This may mean that the long-term concentration of inhibitor at the steel/concrete interface in the case of both protection methods is similar. Further, with the cathodic protection current there is a continuous increase in R_p , suggesting passivation of the rebar due to the generation of high pH conditions. The most interesting feature of these graphs, however, is the marked increase in the level of protection of steel due to electrical field assisted transport of inhibitor (DICHAN and MCI) molecules when subjected to the simultaneous application of inhibitor and a high current density. All these observations lead to the conclusion that the maximum concentration of inhibitor molecules attainable at the rebar level when a high current density is applied is significantly higher than that achieved by both ionic diffusion process as well as when physically added as an admixture in the prescribed quantity in the concrete mix. Further, the protection obtained in this case is even considerably higher than that achieved by application of cathodic protection alone.

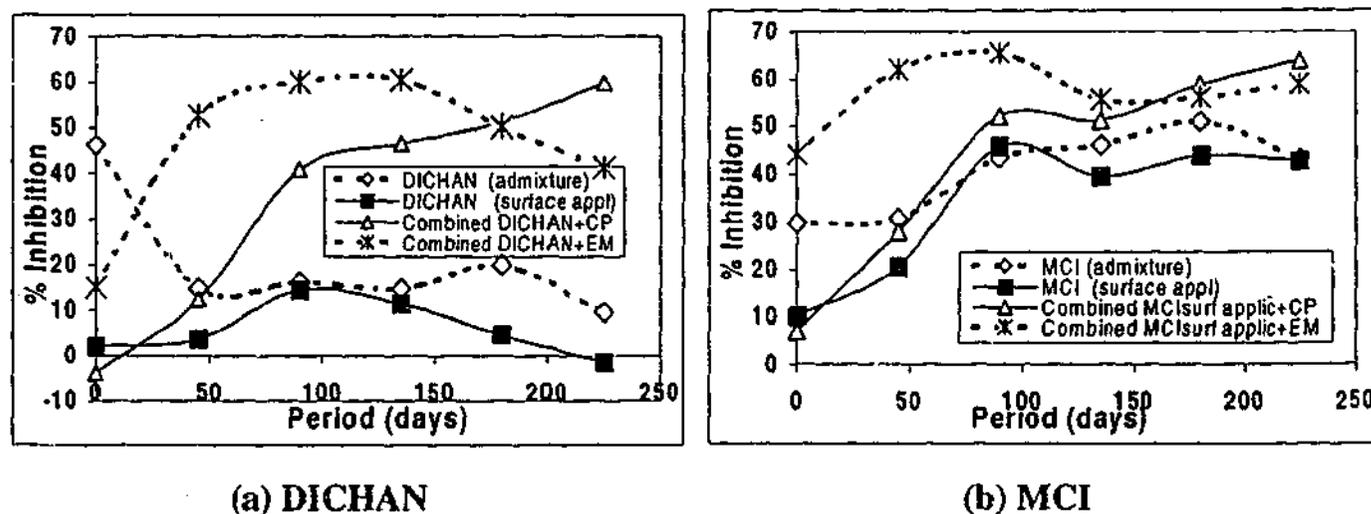


Figure 8.11 – Comparison of inhibition levels under different application conditions

It should be recognised that the situation in the case of electrical injection of inhibitor experiments possibly simulates the model of "chloride removal from the corrosive environment" discussed in section 4.3.7. It is evident that with the application of high current density, the low inhibition levels observed in inhibited concrete specimens due to poor penetration of inhibitors, are substantially improved. The efficiency of inhibitor in this case is defined by inhibition capacity alone, as was the case in chapter 4. Furthermore, the substantial removal of chloride ions from the concrete specimens would also simulate the experimental conditions under prepassivated conditions where the inhibitor is allowed to form and stabilise a film on the steel surface in the absence of chloride ions.

8.4 – CONCLUSIONS

The results obtained with two different experimental set ups i.e. low and high current density have shown that application of an electric field to reinforced concrete specimens in the presence of surface applied inhibitors can provide protection to reinforced concrete in a deteriorating situation. However, it is important to note that, the mechanism of protection observed in the two cases appears to be different. In the case of low current density, steel is protected primarily due to the cathodic polarisation, whereas with the higher current density the higher degree of protection is afforded principally by inhibitor injection. A comparison of the behaviour of the cathodically polarised (low current density) concrete specimens with those subjected to the simultaneous application of inhibitors and applied field suggest that no obvious synergy is obtained during the testing period. It is possible that if the system is allowed to depolarise for a time longer than the 72 hours (given under the present set of experiments), the additional protective effect offered by inhibitor film may become evident during the post-cathodic treatment periods. This is likely to be due to differences in the persistency of the cathodically formed passive film and the inhibitor assisted passive film.

The results on application of higher current density indicate that the rate of transport of inhibitor ions through concrete could be improved remarkably by simultaneous application of high current density with topical application of inhibitors. The inhibitor injection into concrete is feasible within a realistic time frame, and that adequate

protection of corroding steel can be achieved using this technique. Further, the mechanism involved here is mainly the "electrical field assisted" inhibitor ionic transport, which is possibly followed by the enhanced adsorption of the charged molecules on the steel surface to form a protective film. The additional factor in this process is the partial removal of chloride ions from the concrete.

The passive films formed under both high pH condition (low current density or cathodic protection) as well as electrical injection of inhibitors, are found to persist during the measurement period, after switching off the current. This is important specially considering the distinctly different polarisation and depolarisation periods used for these two processes. It will be interesting to measure the polarisation resistance of cathodically polarised concrete specimen, and that subjected to a combined treatment, several days after switching off the low density current. One could investigate the effect of the long-term depolarisation.

Thus the results obtained using both these techniques indicate that there is still much room for improvement in a number of parameters such as selection of inhibitors as well as the time of polarisation. Selection of inhibitors could be done with the emphasis on inhibitors, which can produce charged molecules to facilitate their electrically assisted injection in concrete. A combination of organic/inorganic inhibitor molecules which would be deposited at the steel/concrete interface (due to sparing solubility at the alkaline pH) could also be used. Besides the selection of inhibitors, the technique could also be improved by employing higher current densities for longer protection periods.

CHAPTER 9

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

This research has helped to improve an understanding of the mechanism of action of organic amine based migratory corrosion inhibitors, for corrosion mitigation of reinforced concrete structures. Based on the results of this work, it is concluded that these organic inhibitors can play a major role as admixtures in new concrete structures as well as in patch repairs or surface application of existing structures. The experimental findings of chapters 4 to 8 have been comprehensively analysed in terms of electrochemical and diffusion theories and are concluded at the end of each chapter. In this chapter all the conclusions are summarised and correlated and their scope and limitations are discussed. Further, based on the information gained as well as the inadequacies experienced in this research, suggestions have been made for the future work.

9.1 - THE MECHANISM OF CORROSION INHIBITION AT THE REBAR SURFACE

The results obtained from the experiments carried out in the saturated calcium hydroxide solution in chapters 4 and 5 have indicated that the amine based inhibitors DICHAN and MCI offer high level of inhibition as compared with purely nitrite-based inorganic inhibitor sodium nitrite or an organic amine DMEA. The inhibition capacities of these inhibitor systems estimated from these experiments can be arranged in the following order: MCI≅DICHAN>sodium nitrite>DMEA. The experimental evidences have also indicated that the mechanism of inhibition of organic amine-based inhibitors is predominantly through the build up of a protective barrier layer, which provides a resistive path to ions and electrons, thereby hindering both anodic and cathodic reactions. Whereas the nitrite-based inorganic inhibitors function by oxidising ferrous to ferric ions at the anodic sites thus preventing the anodic dissolution. While the nitrite-containing inhibitors reinforce the oxide film by accepting the electrons, the

amine-based organic inhibitors function through the electron donating $-NH_2$ group. The varied inhibition capacities of the amine-based inhibitors (MCI, DMEA and DICHAN), in the presence of chloride ions, have been attributed to the difference in the strengths of the chemisorptive bonds they form with the steel surface.

The electrochemical techniques (e.g. LPR, corrosion potential measurements, cyclic voltammetry and potentiostatic transients) used in chapters 4 and 5 have confirmed that the sodium nitrite and DICHAN (a mixed inhibitor) are predominantly anodic in their inhibition action. In contrast MCI and DMEA are predominantly cathodic inhibitors, at least in solution experiments. Cyclic voltammetry and the potentiostatic transients have additionally revealed the anodic characteristics of the amine-based inhibitors MCI and DMEA, which were not obvious in the LPR and corrosion potential experiments.

The studies in both a saturated calcium hydroxide solution as well as in concrete specimens, have successfully established a relationship between the corrosion state of the steel at the time of inhibitor addition and the subsequent level of protection. A noticeably higher level of inhibition has been observed for the prepassivated steel (simulating a rebar condition prevailing in a new structure), as compared with that observed in the corroding structure. This clearly suggests the need for admixing inhibitor at the outset in the new construction. At longer times, a decreased inhibition capacity has been observed in the presence of chloride ions. This waning of inhibition is clearly related to the type of inhibitor system used. Also the experiments involving the removal of aggressive ions from a calcium hydroxide solution containing a steel coupon have resulted in no loss of inhibition. This suggests that the removal of chloride-contaminated concrete above reinforcing steel and its subsequent replacement with the fresh inhibitor containing concrete, can achieve long term protection due to the unhindered inhibitor film formation process.

The kinetics of corrosion or inhibition reactions was found to be dependent on the relative concentrations of chloride and inhibitor species in the vicinity of the steel reinforcement embedded in concrete. In the case of nitrite containing inhibitors it is necessary to maintain the chloride: nitrite ratio below the threshold level. Hence an inhibitor, containing both an organic component and nitrite, such as DICHAN is considered more appropriate for offering long-term protection than purely nitrite based inorganic inhibitors.

Thus the results obtained using various electrochemical techniques, under simplified and controlled conditions in the solution medium have provided a sound basis for the evaluation of a more complex situation that may be prevailing in the reinforced concrete. It may, however, be mentioned that even though the technique such as cyclic voltammetry, involving potential sweeping at high scan rates, has been successfully used for comparing inhibition mechanisms of different inhibitor systems, it could not provide information regarding the pitting, protection potentials, or the passivity regions for the corroding steel exposed to both aggressive/inhibiting environments. Hence to obtain information on these aspects, use of additional polarisation technique such as steady state cyclic potentiodynamic polarisation (CPP) is recommended.

9.2 - DIFFUSION MECHANISM OF INHIBITORS IN CONCRETE

Based on the results obtained in chapter 6, a simplified model for the inhibitor transport in concrete has been presented. According to this model inhibitor transport in concrete is a time dependent phenomenon: with the initial phase being dominated by Fickian diffusion, and the latter phase controlled by a time-dependent diffusion anomaly showing a "diffusion plateau". Diffusion coefficients, calculated by applying steady state conditions to the initial data, have been found to show specific trends depending upon physico-chemical characteristics of the diffusant (inhibitor) and the properties of the host material (concrete) such as porosity and the cover-depth.

Attempts to fit Fick's second law of diffusion by iterative comparison of the measured and predicted data have shown a poor fit, especially at early times because of the initial absorption of inhibitor. This may be due to (a) capillary action because of partial saturation of fog room cured concrete and/or (b) gas permeation of inhibitor through partially empty/dried concrete pores because of its high vapour pressure.

An interesting outcome of the diffusion experiments is the observation of a diffusion plateau at longer time^s. This anomaly is thought to be a result of a sequence of reactions, such as interaction between inhibitor and reactive groups of concrete, formation of an immobile product, reduction of the pore size and finally decrease in the amount of diffusant. This phenomenon is intriguing and warrants further investigation using other methods such as examination of concrete pore structure using microscopy as well as the

actual analysis of expressed concrete pore solution for estimating the free inhibitor content and hence the extent of possible inhibitor binding.

The above considerations defining the shape of the diffusion curves have individual limitations. The first hypothesis needs accurate data on the downstream concentration, whereas the second approach requires a specific knowledge of the physico-chemical factors involved in the actual binding processes. Hence it may be suggested, that future work may concentrate on obtaining more early age data points in order to have an accurate fit and also to better estimate the induction time to penetrate through the thickness of the concrete membrane. The examination of the inhibitor concentration profiles in concrete, using some of the advanced techniques (e.g. radioactive isotope technique) is also suggested.

9.2.1 - Limitations

Some of these points have already been discussed earlier in relevant chapter but are reproduced here in the overall context. One of the limitation in application of the model developed in this work to real structures is that it is based on the assumption that inhibitor transportation takes place purely by the liquid phase (ionic) diffusion process only. This is possible only in the case of fully saturated conditions, which could be expected in submerged concrete structures. In actual structures the splash/spray zones, are likely to undergo periodic wetting and drying, in which case there is likely to be faster inhibitor transportation possibly because of capillary action and gaseous permeation. Hence the future modification to the currently developed model should also take into account these additional transport mechanisms.

Another limitation of the model is the assumption that concrete is a homogeneous material having a continuous pore structure. However, in real structures concrete generally has a certain intensity of defects such as microcracks, paste separation and voids as well as macrocracks, which are likely to increase the permeability of the concrete matrix. Hence further research could involve use of cracked reinforced concrete and monitoring the corrosion activity of the rebar using electrochemical measurements. This could alternatively be achieved by modifying the diffusion cell i.e. by using a concrete membrane containing cracks, by inserting a rebar in the downstream cell and subjecting it to corrosion by addition of a known concentration of sodium

chloride. Inhibitor diffusion through the concrete membrane, with the cracks, can then be followed by monitoring the electro-chemical activity of the rebar.

9.3 - MECHANISM OF INHIBITION PROCESS IN CONCRETE

The investigations in concrete specimens have demonstrated the ability of amine based migratory corrosion inhibitors to reduce corrosion by diffusing through concrete and forming a protective film at the steel surface regardless of the method of application/treatment. The difference in the inhibition levels of amine-based and nitrite-based inhibitors under short-term and long-term application studies can be attributed to different inhibition mechanisms (as described in section 9.1).

An important finding of chapter 7 is that the overall inhibition levels for all inhibitors in concrete are lower than those observed in the previously reported solution experiments (chapter 4). This has been mainly attributed to the physical differences between both concrete and solution media. Since the concentration and replenishment of inhibitor species at the steel/concrete interface is decided primarily by inhibitor diffusion characteristics, the results obtained have confirmed the hypothesis that "the performance of inhibitors in concrete is controlled by diffusion kinetics rather than the electrochemical kinetics".

Thus in conclusion these studies have shown that nitrite-based DAREX is an effective inhibitor when applied as concrete admixture in higher quantities or the quantities prescribed by the supplier. The effectiveness of DICHAN in the concrete specimens seems to be limited because of its poor solubility in water and poor diffusion properties through the concrete. Organic amine based DMEA and MCI can extend the life of a structure by protecting the steel surface not only when used as admixtures but also when applied to the surface as migrating inhibitors. Even though the level of protection offered by these organic inhibitors at shorter time period is slightly lower than the ones offered by the nitrite based inorganic inhibitors, at longer time they provide much better protection and their performance is not concentration dependent.

9.3.1 - Optimisation of Application Technique

Even though this part remains more of an area of commercial interest, the following recommendations can be made based on this study. In order to ensure better penetration of inhibitors, the capillary action as well as gas permeation transports should be enhanced. To achieve this, the concrete should be allowed to dry out between the various applications and then different methods such as ponding, gel application, injection or spray application of inhibitors could be used.

9.4 - PROTECTION OF REINFORCEMENT BY COMBINING INHIBITORS AND ELECTRIC FIELD

This section sets out to answer the final aim of section 1.4 "... to find ways of improving inhibitor performance and to determine the factors, which are likely to influence this enhancement effect". The results obtained with low and high current density set ups have shown that application of an electric field to reinforced concrete specimens in the presence of surface applied inhibitors can provide a reliable protection to reinforced concrete in a deteriorating situation. However, it is concluded that the mechanism of protection observed in the two cases is different. In the case of low current density, steel is protected primarily due to the cathodic protection, whereas with the higher current density, the mechanism involved is the "electrical field assisted" inhibitor ionic transport.

It has been concluded that simultaneous application of current and inhibitor facilitates three competing effects at the steel/concrete interface; namely build up of hydroxyl/high pH condition generated passive film, formation of inhibitor assisted passive film and removal of chloride ions further helping to strengthen the passive film. Synergy may be observed, when one effect occurs conjointly with the other.

It is suggested that in the case of cathodic polarisation, the magnitude of the applied current density is not large enough to enhance the rate of inhibitor transport towards the steel surface. This results in insufficient build up of inhibitor at the interface to facilitate the process of the formation of an inhibitor assisted passive film in competition with a much more active process of reconstruction of the passive hydroxy

film. Hence it is postulated that with the conjoint action of inhibitor and cathodic protection, the kinetics of reactions at the steel concrete interface is determined by the relative concentrations of hydroxyl ions and inhibitor molecules. If the concentration of inhibitor molecules is lower than the threshold concentration, the kinetics of film formation at the steel-concrete interface may be governed by the hydroxyl ion concentration.

An increase in the current density facilitates electrical injection of inhibitor molecules in the vicinity of steel/concrete interface. Hence the kinetics of passive film formation at the interface, which is governed by hydroxyl ion concentration alone in cathodic protection, is dominated by both hydroxyl ions (high pH) and inhibitor molecules. This results in the formation of an inhibitor reinforced passive film. Removal of chloride ions from the vicinity of rebar occurs in both cases.

The passive films formed under (i) high pH condition (low current density or cathodic protection) and (ii) electrical injection of inhibitors, are found to persist during the measurement period, after switching off the current. This observation warrants a further examination, especially in view of the distinctly different polarisation and depolarisation periods used for these two processes. It is believed that if the cathodically polarised concrete specimens are allowed to depolarise for a period longer than the 72h, the differences between the persistency of the cathodically formed passive film and the inhibitor assisted passive film may become evident. Similarly, it will be interesting to examine the effect of application of higher current density for longer duration, on the level and the persistency of the inhibitor induced passive film in the presence of chloride ions.

Besides the improvement in the technique, another parameter, which is worthy of attention, is selection of inhibitors for the combined application of inhibitor and current. Studies employing quaternary ammonium or phosphonium/sulphonium compounds, capable of producing charged molecules, whose transport through concrete can be enhanced under the influence of the current, are recommended. A combination of organic/inorganic inhibitor molecules, which would be deposited at the steel/concrete interface due to sparing solubility at the alkaline pH, could also be used.

Besides the above suggestions, based on the limited time and scope of this study, some additional recommendations can be made:

- Long-term monitoring of concrete specimens, especially after discontinuing the surface inhibitor application, should be done to understand the persistency of the inhibitor film and subsequently decide the frequency of inhibitor treatment.
- Further research should be conducted to understand the effect of inhibitors on the mechanical properties of concrete such as compressive strength, tensile strength, freeze and thaw resistance etc.
- A better device containing a guard ring electrode should be used to confine the area of the rebar while conducting LPR measurements for more quantitative corrosion rate evaluation.
- Considering the heterogeneity of concrete and the random nature of the corrosion process occurring at the steel surface, it is suggested that the future experiments in reinforced concrete specimens could be planned using more specimens to obtain a better statistical average.
- Also it would be more appropriate to accelerate the chloride induced corrosion through wet/dry cycling with salt water, which can not only simulate real world conditions better, but it can also help to maintain a uniformity in the concrete saturation levels.
- Finally, the various concepts developed in the laboratory should be applied to the actual structures exposed to the different corroding environments.

Thus, in summary, this work has evaluated the concept of inhibition in concrete and developed an understanding of the dominant mechanisms controlling the overall inhibition process. It has further indicated that the comparative evaluation, carried out in the laboratory, can be used to predict the levels of protection offered by different inhibitor systems to the concrete structure. This work should help engineers to design an appropriate inhibitor application system for the corroding or newly built reinforced concrete structure, thus providing a significantly longer service life.

CHAPTER 10

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