

# Evaluation of organic based corrosion inhibiting admixtures for reinforced concrete

M. Vishnudevan and K. Thangavel

Central Electrochemical Research Institute, Karaikudi, India

## Abstract

**Purpose** – Admixtures are materials that are added to concrete at some stage in its production to give concrete new properties whether in fluid or plastic conditions. The admixtures used in the construction industry are broadly classified into Mineral and Chemical admixtures. In recent years, the use of mineral and chemical admixtures in producing high performance concrete has increased significantly. The chemical reaction of cement with admixtures differs from material to material. Calcium nitrite based corrosion inhibiting admixtures have gained popularity for protection of reinforced and pre-stressed concrete structures but calcium nitrite is not commercialized indigenously in India due to manufacturing difficulties. Hence, the objective of the present investigation was to study a novel corrosion inhibiting admixture system and to compare its effectiveness with sodium nitrite.

**Design/methodology/approach** – Di-sodium phthalate, sodium orthophosphate and sodium nitrite-based corrosion inhibiting admixtures were selected for the present investigation. The critical quantities of corrosion inhibiting additives were determined by accelerated laboratory tests. The following types of tests were conducted to evaluate the efficiency of the corrosion inhibiting admixtures: compressive strength of  $100 \times 100 \times 100$  mm concrete cubes after 3,7,14 and 28 days of curing, linear polarization resistance measurements, electrochemical impedance spectroscopy measurements, an accelerated 12 V controlled potential test.

**Findings** – From the above tests, the inhibitor admixed concrete not only improved in compressive strength but also increased its corrosion resistance properties. Of the inhibitors studied, di-sodium phthalate showed superior corrosion resistance properties, compared to sodium nitrite.

**Originality/value** – Di-sodium phthalate may be considered a better substitute for calcium nitrite-based corrosion inhibiting admixtures for durable concrete structures. This fulfils the objective of the investigation.

**Keywords** Corrosion, Concretes, Inhibitors, Compressive strength

**Paper type** Research paper

## Introduction

Corrosion is a spontaneous phenomenon. It can affect the integrity of the structures such as buildings, bridges, dams, etc. Every year millions of dollars are lost due to corrosion and its consequent damage continue all over the world. Many researches have been carried out on corrosion of reinforced concrete structures. In recent years, the use of chemical and mineral admixtures in producing high performance concrete has increased significantly (Aitcin, 2003; Mohammed and Hamada, 2003; Surlaker, 2002). Corrosion inhibiting admixtures (Berke, 1989; El Jazairi and Berke, 1999) are mainly used in concrete exposed to sea water. The use of different classes of corrosion inhibiting admixtures in concrete have been reviewed by various authors (Gu *et al.* (1997), Nmai *et al.* (1992), Berke and Rosenberg (1989), Griffin (1975), Berke (1991)). Nurnberger and Beul (1991), Colleparidi (1990) and Cigna *et al.* (1994) cautioned about the possibility of accelerated pitting of steel reinforcement in the presence of chloride when insufficient nitrite dosage is present in concrete. Monticelli *et al.* (2000) studied more than 30 compounds as corrosion inhibitors for concrete application.

Hansson *et al.* (1998) also studied the principles of corrosion inhibitors in concrete. Sagoe-Crentsil *et al.* (1993) found water soluble carboxylic acid was an effective inhibitor in the presence of 2.5 percent chloride contamination. Andrade *et al.* (1992) studied the inhibition performance of 0.5 M  $\text{Na}_2\text{PO}_3\text{F}$  in saturated  $\text{Ca}(\text{OH})_2 + 0.5 \text{ M NaCl}$  solution by anodic polarization tests and found that the inhibitor increased the pitting potential (+600 mV), and noted also that the inhibition effect was enhanced when this inhibitor penetrated through the hardened concrete.

The main aim of this corrosion protection system is to prevent aggressive agents, particularly chloride ions, from attacking the surface of the reinforcing steel. During the past 15 years, corrosion-inhibiting admixtures (mainly calcium nitrite) have been used increasingly. They have wide popularity for protection of reinforced and pre-stressed concrete components of highway bridges and other structures but calcium nitrite is not commercialized indigenously in India. Hence, the objective of the present investigation was to study a novel corrosion inhibiting admixture system and compare its effectiveness with the already existing inhibitive system.

## Experimental procedure

### Materials used

Ordinary Portland cement: conforming to IS (456-2000)



Coarse aggregate: locally available aggregate conforming to graded aggregates of normal size greater than 4.75 mm and less than 10 mm of IS: 383-1970

Fine aggregate: local clean river sand (fineness modulus equal to 2.6) conforming to grading zone III of IS: 383-1970.

Chemicals used:

- AR grade sodium chloride
- AR grade sodium phthalate
- AR grade sodium nitrite
- AR grade tri sodium orthophosphate

System studied (Table I).

Mix design (1:1.53:1.93, W/C = 0.53) used (Table II).

### Preparation of concrete specimens for compressive strength test

About 100 × 100 × 100 mm concrete cubes were prepared using 1:1.53:1.93 mix designed with a W/C ratio of 0.53. Inhibitor admixtures, namely 4 percent di-sodium phthalate, 4 percent tri sodium orthophosphate and 3.5 percent sodium nitrite, were added on the basis of weight of cement. The concrete cubes were demoulded after 24 h of casting and subjected to water curing. The specimens were removed after 3, 7, 14 and 28 days of curing and subjected to compressive strength testing (as per Indian Standard IS:10261-1982) using an AIMIL compression testing machine of 2000 KN capacity. Triplicate specimens were tested and average values were reported.

### Preparation of cylindrical reinforced concrete specimens for electrochemical tests

Cylindrical concrete specimens of size 50 mm in diameter and 80 mm in height were cast using 1:1.53:1.93 mix design of W/C ratio 0.53. The embedded area of reinforced cylindrical steel was 7 cm<sup>2</sup>. About 3 percent sodium chloride (as control), 4 percent di-sodium phthalate, 4 percent tri sodium orthophosphate and 3.5 percent sodium nitrite were added as inhibitor systems to the base mixture on the basis of weight of cement. After 24 h of casting, the specimens were demoulded and subjected to moist curing at 28°C for 28 days. After 28 days of moist curing, the cylindrical reinforced concrete specimens were subjected to linear polarization resistance (LPR) measurements and electrochemical impedance spectroscopy (EIS) studies. Measurements were carried out after 28 days of

Table I

System	Designation
Control concrete [OPC + 3 percent NaCl]	CON
Control concrete + 4 percent di-sodium phthalate	PH
Control concrete + 3.5 percent sodium nitrite	NI
Control concrete + 4 percent tri sodium orthophosphate	PO

Table II

Constituents	Materials for a single specimen (gm)	
	For cylinders (50 mm dia. × 80 mm length)	For 100 mm × 100 mm × 100 m cubes
Cement	83.00	538.0
Fine aggregate	127.0	823.0
Coarse aggregate	161.0	1,038
Water/cement ratio	0.53	0.53

moist curing at 28°C. The specimens were continuously partially immersed (accelerated laboratory condition) in potable water up to 90 days of exposure.

### Linear polarization resistance tests

The cylindrical reinforced concrete specimen immersed in potable water was used as the working electrode in a three-electrode cell system. A cylindrical stainless steel electrode was used as counter electrode and a saturated calomel electrode was used as reference electrode. Polarization measurements were carried out ±20 mV from the open circuit potential with a scan rate of 0.1 mV/s. From the linear plot,  $R_p$  values were obtained and then converted into corrosion rate for control concrete and inhibitor admixed concrete.

### Electrochemical impedance tests

After 28 days of curing, the cylindrical reinforced concrete specimens were immersed in potable water and used as the working electrode in a three-electrode cell system. A cylindrical stainless steel electrode was used as counter electrode and saturated calomel electrode was used as the reference electrode (Figure 1).

The measurements were made at open circuit potential using Electrochemical Impedance Analyzer (Model 6310 EG & G, UK) as per ASTM standard G106-89. The frequency range used was from 10 mHz to 100 kHz. An AC signal of 15 mV amplitude was applied to the system and the resultant current and phase angles were measured at various frequencies. The impedance data were displayed in the form of Nyquist plots (Figure 2).

The equivalent electrical circuit of a corroding rebar embedded in concrete adopted in the present study is as in Figure 3.

Measurements were carried out after 28 days of moist curing at 28°C. The specimens were continuously partially immersed (accelerated laboratory condition) up to 90 days of exposure for control concrete and inhibitor admixed concrete. The polarization resistance ( $R_p$ ) values obtained from Nyquist plot were converted into corrosion rate using stern-Geary equation:

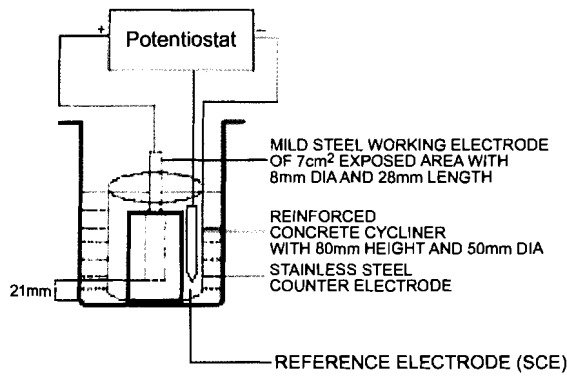
$$I_{\text{corr}} = \frac{B}{R_p}$$

where  $B$  is a function of the anodic and cathodic Tafel slopes,  $b_a$  and  $b_c$

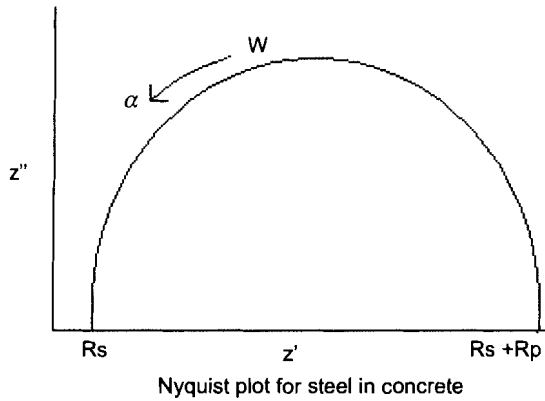
$$B = \frac{b_a \times b_c}{2.303(b_a + b_c)}$$

For the rebar corrosion, a  $B$  value of 26 or 52 mV has been used in the calculation for the bare steel in the active and passive stages, respectively, (Andrade and Gonzales, 1978).

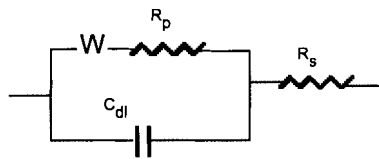
**Figure 1**



**Figure 2** Nyquist plot for steel in concrete



**Figure 3** Equivalent circuit of a corroding rebar in concrete



- W = warburg impedance (a diffusion term)
- Rp = Polarisation resistance (inversely proportional to corrosion current)
- Rs = Solution resistance (concrete resistance)
- Cdl = Double layer capacitance

Equivalent circuit of a corroding rebar in concrete

In the present investigation *B* value of 26 mV/decade only used as all the system was premixed with sodium chloride.

The corrosion rate (mmpy) of the exposed rebar is measured by using the following formula:

$$\text{Corrosion rate (mmpy)} = \frac{3.2}{(\text{mA/cm}^2)} \times I_{\text{corr}} \times \frac{\text{Equivalent weight}}{\text{Density}}$$

the double layer capacitance is calculated from *R<sub>p</sub>* values using the formula:

$$C_{dl} = \frac{1}{2\pi \times F_{\text{max}} \times R_p}$$

where *F<sub>max</sub>* = frequency maximum, *R<sub>p</sub>* = polarization resistance.

**Accelerated 12 V impressed voltage test**

In this technique, the cylindrical reinforced steel in the concrete sample is made anodic with respect to an external stainless steel electrode serving as cathode by applying a constant positive potential of 12 V to the system from a DC source. The variation of current is recorded with time. A sharp rise in current indicates the onset of corrosion and cracking of the concrete. The time taken for the initial crack to appear was noted from the current vs time graph. After the appearance of initial crack in the concrete (indicated by high magnitude of current flow) the experiment was terminated. The specimen was removed from the test apparatus and the embedded steel was taken out and subjected to weight loss measurement. From the weight loss, the corrosion rate of embedded steel was calculated using the formula:

$$\begin{aligned} \text{Corrosion rate (mmpy)} \\ = \frac{87.6 \times \text{Loss in weight (mg)}}{\text{Density (g/cc)} \times \text{Area (cm}^2) \times \text{Time (h)}} \end{aligned}$$

Finally, core samples were collected from the cylindrical concrete specimens and were crushed mechanically to get the concrete in powder form. Then 100 g of powdered concrete was shaken with 200 ml of distilled water in a conical flask using a microid flask shaker for 1 h. The extract was then filtered through a Whatman filter paper No. 42. Extract prepared from the powdered samples was then analyzed for alkalinity and free chloride contents. About 20 cc of filtered solution was taken and the free chloride was estimated by standard silver nitrate titration using potassium chromate as indicator. The free chloride contents were expressed in terms of parts per million.

**Results**

**Compressive strength of concrete**

The compressive strength of control and inhibitor admixed concrete cubes tested after 3, 7, 14 and 28 days of exposure to moisture at 28°C are reported in Table III.

**Linear polarization resistance technique and electrochemical impedance spectroscopic studies**

The polarization resistance (*R<sub>p</sub>*) and corrosion rate (mmpy) calculated from the LPR technique for control and inhibitor admixed concrete are reported in Table IV.

The double layer capacitance (*C<sub>dl</sub>*), polarization resistance (*R<sub>p</sub>*), corrosion rate (mmpy) calculated from EIS studies for control concrete (chloride added concrete) and inhibitors admixed concrete were reported in Table IV and shown in Figure 4.

**Accelerated 12 V impressed voltage test**

The time taken for initial crack (h), the magnitude of current flow (mA) and the corrosion rate (mmpy) calculated for control concrete and inhibitor admixed concrete were reported in Table V and shown in Figures 5-9.

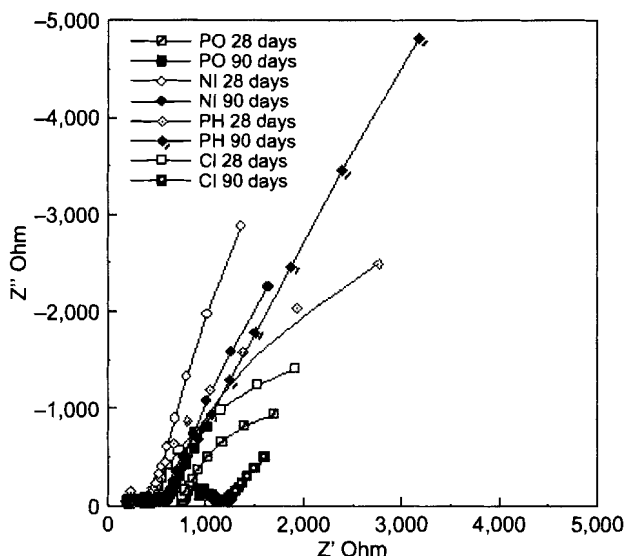
**Table III** Compressive strength test (MPa)

System	3 days	7 days	14 days	28 days
CON	16	20	26	30
PH	22	25	30	32
NI	25	24	30	33
PO	16	18	23	27

**Table IV** Measurement of corrosion rate by impedance and LPR techniques

System studied	Period of exposure	LPR			EIS			
		$R_p$ (K $\Omega$ )	$i_{corr}$ ( $\mu$ A/cm <sup>2</sup> )	C.R. ( $\times 10^{-3}$ ) (mmpy)	$C_{dl}$ (mF)	$R_p$ (K $\Omega$ )	$i_{corr}$ ( $\mu$ A/cm <sup>2</sup> )	C.R. ( $\times 10^{-3}$ ) (mmpy)
CON	After 28 days	1.562	2.378	28.30	0.998	2.450	1.516	18.04
	After 90 days	1.421	2.614	31.11	0.590	0.212	17.52	208.5
PH	After 28 days	4.199	0.885	10.53	0.620	9.373	0.396	4.716
	After 90 days	10.12	0.367	4.367	0.057	126.2	0.029	0.349
NI	After 28 days	16.02	0.232	2.761	0.108	56.70	0.066	0.779
	After 90 days	2.234	1.663	19.79	1.488	2.561	1.450	17.26
PO	After 28 days	0.894	4.154	49.44	3.413	4.363	0.851	10.13
	After 90 days	1.826	2.034	24.20	0.925	8.924	0.416	4.953

**Figure 4** Nyquist plot for control concrete and inhibitor admixed concrete



**Table V** 12-Volt impressed potential accelerated test

System studied	Applied voltage (V vs SCE)	Current (mA)	Time taken for initial crack (h)	Free chloride content (ppm)	Corrosion rate (mmpy)
CON	12	17	24	4,800	28.900
PH	12	4	218	1,500	0.7480
NI	12	8	84	2,400	3.8857
PO	12	15	66	2,400	9.2727

**Discussion**

**Compressive strength of concrete**

The results of the compressive strength test indicated that the addition of phthalate and nitrite inhibitors increased the compressive strength of concrete when compared to the control concrete. On the other hand, the addition of phosphate inhibitor lowered slightly the compressive strength. Moreover, the accelerating type of admixtures like phthalate and nitrite increased the strength, even with 3 days of moist curing at 28°C.

**Linear polarization resistance measurements**

The results of the LPR tests indicated that the  $R_p$  values were much lower for inhibitor admixed concrete after 28 days of curing as compared to the control concrete. On the other hand, the  $R_p$  values increased after 90 days of exposure for inhibitor admixed concrete, compared to readings obtained after 28 days of curing. The corrosion rate also reduced considerably after 90 days of exposure for inhibitor admixed concrete. For example, for phthalate and nitrite admixed concrete, the corrosion rates were reduced by seven and two times, respectively. On the other hand, the phosphate admixed concrete showed only a one times decrease in corrosion rate.

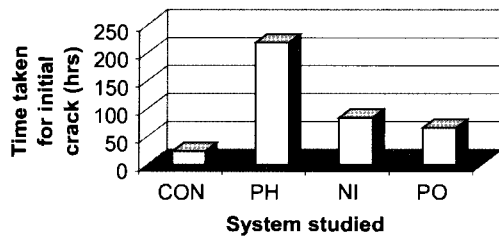
**Electrochemical impedance spectroscopic study**

The results of the EIS study confirmed the LPR data in that all the inhibitor admixed concretes showed higher  $R_p$  values after 90 days of exposure, as compared to 28 days of curing. In correlation with higher  $R_p$  values the double layer capacitance  $C_{dl}$  also reduced considerably after 90 days of exposure. The corrosion rate doubled for control concrete from 28 days curing to 90 days of exposure in potable water. These data indicate that the steel surface was depassivated by aggressive chloride ions. On the other hand, the corrosion rate was reduced considerably for the inhibitor admixed concrete. For example, phthalate system showed 597 times reduction in corrosion rate.

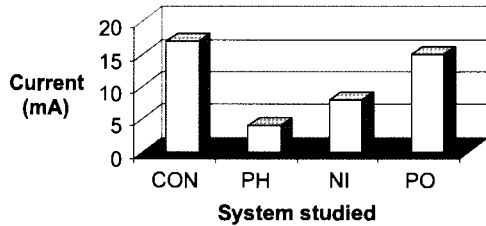
**Accelerated 12 V impressed voltage test**

The results of the impressed voltage test indicated that the time taken for initial crack for control concrete was 24 h. Hence, the systems which showed > 24 h may be regarded as more corrosion resistant than control concrete. The data indicated that the time taken for initial crack measured for all the inhibitors mixed systems showed > 24 h. Among the inhibitors studied, the time taken for initial crack for sodium phthalate admixed concrete was found to be 218 h (nine times higher) when compared to control concrete. These data proved that in OPC concrete, permeation of chloride accelerated the corrosion of embedded steel and the volume of corrosion products increased within a short time (i.e. 24 h). On the other hand, in phthalate inhibitor mixed system, the calcium-phthalate complex formation filled the micropores and reduced the permeability of chloride. In consequence, the time taken for initial crack to form was increased. Nitrite and phosphate inhibitors also exhibited 84 and 66 h, respectively, as the times taken for initial cracking. These data also show

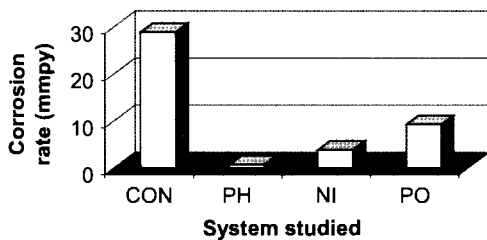
**Figure 5** Evaluation of inhibitors by 12-volt impressed potential test



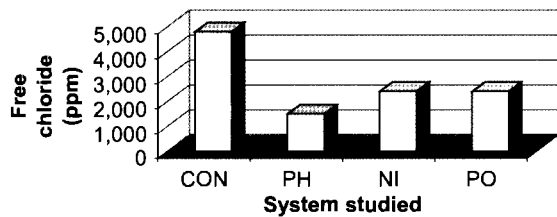
**Figure 6** Evaluation of inhibitors by 12-volt impressed potential test



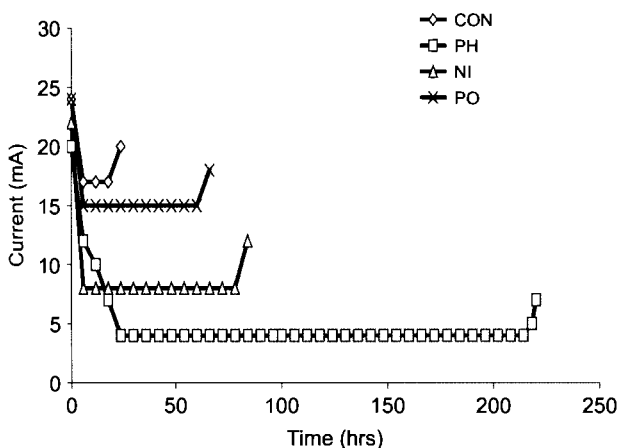
**Figure 7** Evaluation of inhibitor by 12-volt impressed potential test



**Figure 8** Evaluation of inhibitor by 12-volt impressed potential test



**Figure 9** Evaluation of inhibitors by 12-volt impressed potential test



that calcium nitrite and calcium phosphate formation enhanced the time taken for the initial crack to occur. The magnitude of current flow was 17 mA for control concrete (Figure 6). On the other hand, the current flow was considerably lower in the case of inhibited systems. For example, the phthalate system showed a four times decrease in current flow and the nitrite system showed a two times decrease in current flow. The corrosion rate calculated for control concrete was 28.9 mmpy. The inhibited system thus was effective in reducing the corrosion rate. For example, the phthalate system showed a 38 times decrease in the corrosion rate of steel embedded in the concrete under the accelerated test condition. Nitrite and phosphate systems showed eight times and three times decreased in corrosion rate, respectively.

The decrease in corrosion rate values observed were due to the formation of corresponding calcium salts. In the case of phthalate system, the Ca-phthalate complex filled completely the micro pores in concrete and reduced the permeability of chloride. Also, iron(III)-phthalate complex formation on the metal surface further reduced the corrosion rate. Hence, the corrosion rate was reduced considerably.

## Conclusions

The compressive strength data collected indicate that, compared to the control concrete, the addition of phthalate and nitrite inhibitors increased the compressive strength of the concrete, compared to the control concrete. On the other hand, the addition of the phosphate inhibitor lowered the compressive strength slightly.

LPR measurements showed that phthalate and nitrite admixed concretes reduced the corrosion rate of steel by seven and two times, respectively. On the other hand, the phosphate admixed concrete showed only a one times decrease in corrosion rate of steel.

Impedance measurements revealed that the corrosion rate doubled for control concrete from 28 days to 90 days of exposure. However, the phthalate system showed a 597 times reduction in corrosion rate but of the inhibitors studied, phthalate showed the least value of double layer capacitance reading in correlation with higher polarization resistance.

The accelerated 12-volt impressed potential test showed that of the inhibited concretes studied, sodium phthalate showed a nine times increase in time taken for initial crack formation, a four times decrease in the magnitude of current flow and a 38 times decrease in corrosion rate of steel embedded in concrete, compared to the control concrete. In the sodium phthalate system, the formation of Ca-phthalate complex compounds completely filled the micro-pores in concrete and reduced the permeability of chloride and hence the corrosion rate is considerably reduced.

As a consequence of the multi-beneficial action of sodium phthalate, this compound may be considered as a better substitute for calcium nitrite-based corrosion inhibiting admixtures for use in durable concrete structures.

## References

- Aitcin, P.C. (2003), "The durability characteristics of high performance concrete: a review", *Cement and Con Comp*, Vol. 5 Nos 4/5, p. 409.

- Andrade, C. and Gonzales, J.A. (1978), "Quantitative measurements of corrosion rate of reinforcing steels embedded in concrete using polarization resistance measurements", *Werkstoffe und Korrosion*, Vol. 29, pp. 515-9.
- Andrade, C., Alonso, C., Acha, M. and Malric, B. (1992), "Preliminary testing of  $\text{Na}_2\text{PO}_3\text{F}$  as a curative corrosion inhibitor for steel reinforcements in concrete", *Cement and Concrete Research*, Vol. 22, pp. 869-81.
- Berke, N.S. (1989), "Corrosion inhibitors in concrete", paper presented at Corrosion '89, Symposium on Corrosion of Metals in Concrete, NACE, Houston.
- Berke, N.S. (1991), "Corrosion inhibitors in concrete", *Concrete International*, Vol. 13 No. 7, p. 24.
- Berke, N.S. and Rosenberg, A. (1989), "Technical review of calcium nitrite corrosion inhibitor in concrete", *Concrete Bridge Design and Maintenance: Steel Corrosion in Concrete*, Transportation Research Record 1211, Transportation Research Board, National Research Council, Washington, DC, p. 18.
- Cigna Familiari, F.R., Giancetti, F. and Proverbio, E. (1994), "Influence of calcium nitrite on the reinforcement corrosion in concrete mixtures containing different cements", in Swamy, R.N. (Ed.), *Proc. Int. Conf. held at the Univ. of Sheffield, UK, No. 24-28*, pp. 878-92.
- Collepari, M. (1990), "Admixtures for concrete", *RILEM Proc. 1*, p. 287.
- El Jazairi, B. and Berke, N.S. (1999), "The use of calcium nitrite as a corrosion inhibiting admixture to steel reinforcement in concrete", in Page, C.L., Treadaway, K.W.J. and Bamforth, P.M. (Eds), *Corrosion of Reinforcement in Concrete*, Elsevier Applied Science, New York, NY, pp. 571-85.
- Griffin, D.F. (1975), "Corrosion inhibitors for reinforced concrete: corrosion of metals in concrete", *Am. Concrete Inst.*, SP 49, American Concrete Institute, Detroit, MI, p. 95.
- Hansson, C.M., Mammoliti, L. and Hope, B.B. (1998), "Corrosion inhibitors in concrete. Part I. The principles", *Cement and Concrete Research*, Vol. 28, pp. 1775-82.
- Mohammed, T.U. and Hamada, H. (2003), "Durability of concrete made with different water-reducing chemical admixtures in tidal environment", *ACI Materials Journal*, Vol. 100 No. 3, p. 194.
- Monticelli, C., Frignani, A. and Trabaneli, G. (2000), "A study on corrosion inhibitors for concrete application", *Cement and Concrete Research*, Vol. 30, pp. 635-42.
- Nmai, C.K., Farrington, S.A. and Bobrowski, G.S. (1992), "Organic based corrosion inhibiting admixtures for reinforced concrete", *Concrete International*, Vol. 14 No. 4, pp. 45-51.
- Nurnberger, U. and Beul, W. (1991), "Einfluss einer Feuerverzinkung und PVC-Beschichtung von Bewehrungsstählen und von Irbitoren auf die Korrosion von Stahl in gerissenem Beton", *Werkstoffe und Korrosion*, Vol. 42, p. 537.
- Sagoe-Crentsil, K.K., Yilmaz, V.T. and Glasser, F.P. (1993), "Corrosion inhibition of steel in concrete by carboxylic acids", *Cement and Concrete Research*, Vol. 23, pp. 1380-8.
- Surlaker, S. (2002), "New generation superplasticiser for high performance concrete", *The Indian Concrete Journal*, p. 574.

### Further reading

- Indian Standard (2000), IS-456.
- Ping, G., Elliott, S., Hristova, R., Beaudoin, J.J., Brousseau, R. and Baldock, B. (1997), "A study of corrosion inhibitor performance in chloride contaminated concrete by electrochemical impedance spectroscopy", *ACI Materials Journal*, Vol. 94 No. 5, pp. 385-95.