CORROSION INHIBITORS FOR CONCRETE CORROSION - AN OVERVIEW

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Reinforced concrete is widely used for building materials and plays a significant role in economic development. However, the premature degradation of reinforced concrete structures due to the reinforcing steel corrosion has become a serious problem in modern society, which results in a huge economic loss. Under normal conditions, reinforcing steel in concrete can be protected from corrosion by forming a compact passive film on its surface in concrete pore solution with high alkalinity (pH 12.5-13.5). However, the passive film can be locally damaged and the localized corrosion of reinforcing steel takes place when pH and/or the chloride concentration at the steel/concrete interface reach the critical values for corrosion. Corrosion behaviour of metals and alloys in concrete solution has been investigated in presence and absence of inorganic and organic inhibitors. Usually carbon steel and steel rebars have been used. Sometimes galvanized steel and SS316L have been used. Organic inhibitors, inorganic inhibitors, and natural products have been used as inhibitors along with concrete admixture. Corrosion resistance of metals has been evaluated by weight loss method, electrochemical studies such as polarization study and AC impedance spectra. Galvanostatic pulse technique has also been employed. The protective film formed on the metal surface have been analyzed by SEM, FTIR spectroscopy, XPS, AFM and EDAX. The protective film consists of metal-inhibitor complex, calcium carbonate and calcium hydroxide. Experiments have been carried out at room temperature. Corrosion inhibitors fill up the pores and prevent the penetration chloride ion towards the metal surface. Passive films formed on the metal surface also increase the life time of concrete rebars.

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Introduction

Corrosion behaviour of metals and alloys in concrete solution has been widely studied[1–65]. In the past, most of the design studies in the literature and research in reinforced concrete assumed that the durability of reinforced concrete structures could be taken for granted. However, many reinforced concrete structures are exposed during their lifetimes to environmental stress (for example, corrosion and expansive aggregate reactions) which attacks the concrete or steel reinforcement[66]. Researchers and engineers are continuously in search of cost-effective means to prevent the corrosion of reinforcing steel for the duration of a concrete structure's design life. The cement paste in concrete is alkaline with a pH typically between 12 and 14. This paste forms a passive film surrounding reinforcing steel in concrete which further thicken iron oxide layer on the steel surface. Many researchers believe this alkaline environment facilitates the protective passive film around the steel[67,68]. The passive film is not invulnerable, though it can be damaged both chemically and mechanically. Some examples of chemical damage are carbonation, chloride ingress (seawater, de-icing salt, unwashed sea sand, admixtures etc) and sulphate attack. Proper design and preparation of concrete in accordance with relevant standards and timely maintenance of the structures under those conditions would guarantee them a long and efficient life in aggressive media. However, these requirements are not always met and adhered to. Preventive measures being used in the construction industry to salvage the service life of steel reinforcement in concrete structures are cathodic protection, inhibitors, coatings, penetrating sealers and chloride removal[69]. One of the practiced methods popularly used for the control of steel corrosion in concrete is the corrosion inhibitors either preventive or curative.

In recent years, the use of these inhibitors in producing high performance concrete has increased significantly. Inhibitors are chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration without significantly changing the concentration of any other corrosion agent[70]. Many synthetic compounds (inhibitors) were developed to combats this endemic corrosion problem, but most of them are highly toxic to both human beings and environment[71]. Inhibitors toxicity according to ref. [72] is measured as lethal dose (LD) and lethal concentration (LC). LD_{50} is the lethal dose of a chemical at which 50% of a group of animals are killed for 24 h exposure time, whilst LC_{50} is lethal concentration in air or water which kills 50% of test population. Inhibitor biodegradation or biological oxygen demand (BOD) should at least be 60%. The BOD is a measure of how long the inhibitor will persist in the environment. Hence it becomes imperative to review the current inhibitors in order to find more appropriate, suitable and sustainable inhibitor.

Metals

Corrosion resistance of various metals in concrete solution has been investigated. Corrosion resistance of various metals such as Fe[3,4,5,6,7,8,10,11,12,13,17], carbon steel[9,54,62], mild steel[1,15,16,18,20,24,25,29,30,31], stainless steel[19,40,44,65] and galvanized steel[14,19,22,50,57] has been investigated.

Inhibitors

Among various inhibitors which have been used along with concrete admixtures, mention may be made of trisodium citrate[2], phosphate, nitrite[37], sodium gluganate[4], calcium nitrate, calcium nitrite[5], sodium molybdate[6], di-2 ethylhexyl sebacate[11], and uracil derivatives[13]. Organic inhibitors[2,4,8,9,11,12,13,48,61] have been used to control the corrosion of various metals and its alloy in various medium.

Medium

The inhibition efficiency of various inhibitor is controlling corrosion of metals and its alloys in SCPS medium [1,2,3,7,8,9,10,11,12,13,14], concrete medium[5,15,16,17,19,20,21,22,23,25] and alkaline medium[3,6,30,34,36,38] have been investigated.

Methods

Various methods have been used to evaluate the inhibition efficiency of corrosion inhibitors. Usually weight loss method[1,2,15,30,39,47,52,53,60], Electrochemical studies (polarization and AC impedance)[3,4,5,6,7,8,9,,12,13,14,15,18] and Galvanostatic pulse technique[34], and Gravimetric measurement[46] studies have been employed.

Surface analysis

The protective film formed on the metal surface, during the process of corrosion protection of various metals by inhibitors have been analyzed by various surface analysis technique such as SEM[3,10,14,62,64], FTIR[3,13,51], XPS[13,33], AFM[64], and EDAX[14,29]. In general it has been observed that the protective film consists of the metal-inhibitor complex along with $CaCO_3$ and $Ca(OH)_2$.

Temperature

The inhibition efficiency of various inhibitors has been evaluated at room temperature[29].

Mechanism of enhanced corrosion resistance

It is observed that when inhibitors are used along with simulated concrete pore solution, the corrosion resistances of metals increase. In general, it is due to adsorption of these inhibitors on the metal surface and forming metal-inhibitor complex. It is also due to strengthening of $CaCO_3$ and $Ca(OH)_2$ deposits on the metal surface. The inhibitors may fill up the pores in the concrete structures, which are formed in the absence of inhibitors[59]. The inhibitors may further prevent the penetration of corrosive ions such as chlorides and sulphate towards the metal surface[59]. Organic inhibitors are specially used for this purpose. The inhibitors may be hydrophobic in nature[57] and prevent the water molecules reaching the metal surface. However after long time exposure (two years) the chloride ions break the protective film formed on the metal surface, in presence of phosphate and nitrite[3]. When calcium nitrate is used 3% dosage is enough to protect the rebar against corrosion[5]. When sodium molybdate is used passive film is formed on steel rebar[5,6]. The aggressiveness of chloride ion in concrete structures has been minimized by addition of inhibitors such as sodium nitrite[7] and disodium mono fluorophosphate[12]. The improved corrosion resistance in presence of uracil derivative is due to Langmuir adsorption isotherm of inhibitor on the metal surface[13]. Apart from inhibitors addition of red mud along with concrete structures improve corrosion resistance of metals. This has been confirmed by electrochemical measurements and electrical resistivity[17].

Zinc coating[23], and Epoxy coating on the steel rebar have improved the bond strength. Fluoride ion even in very low concentration (< 25 ppm) is found to be more corrosive than chloride ion[30]. Hence care must be taken to avoid presence of fluoride ion in water used to prepare concrete admixture. Zinc phosphate coating considerably reduced the corrosion rate of mild steel even in chloride medium[36].This has been confirmed by electrochemical studies. When sodium nitrite is used as inhibitor, the stability of the protective film increases[37]. Among the oxyanions, the use of dichromate has been found to be very effective for mild steel[43]. Corrosion resistance of mild steel has been investigated in carbonated and non-carbonated concrete, in presence of sodium monosulphate[46]. Use of steel wire mesh reinforcement in ferrocement has been investigated. Addition of inhibitors such as calcium nitrite and tannic acid improved the corrosion resistance. Sodium nitrite has the ability to fill up the pits formed during corrosion process, by formation of passive films, in carbonated concrete pore solution. This has been confirmed by electrochemical noise measurement[54]. The use of inhibitors along with, concrete admixture improved the corrosion resistance of metals. Various inhibitors and various metals and alloys used in this line are summarized in Table 1.

Conclusion

Corrosion behaviour of metals and alloys in concrete solution has been investigated in presence and absence of inorganic and organic inhibitors. Usually carbon steel and steel rebars have been used. Sometimes galvanized steel and SS316L have been used. Organic inhibitors, inorganic inhibitors and natural products have been used as inhibitors along with concrete admixture.

Corrosion resistance of metals has been evaluated by weight loss method, electrochemical studies such as polarization study and AC impedance spectra. Galvanostatic pulse technique has also been employed. The protective film formed on the metal surface have been analyzed by SEM, FTIR spectroscopy, XPS, AFM, and EDAX. The protective film consists of metal-inhibitor complex, calcium carbonate and calcium hydroxide. Experiments can be carried out at room temperature. Corrosion inhibitors fill up the pores and present the penetration chloride ion towards the metal surface passive films formed on the metal surface also increase the life time concrete rebars.

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Table 1. Inhibitors used to improve the corrosion resistance of metals in concrete admixture

Sl. No	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
1.	Mild steel, Galvanized steel, SS316L	Simulated concrete pore solution	-	-	Weight loss, Polarization, AC Impedance	Corrosion resistance decrease in scp solution in the order of SS316L>GS>MS	1
2.	SS316L	Simulated concrete pore solution	Tri sodium Citrate	-	Weight loss, Polarization, AC Impedance	Corrosion resistance of SS316L decrease in presence of Tri sodium citrate	2
3.	Steel	Alkaline medium	Phosphate and Nitrite	-	EIS, PC, OCP, SEM, XRD, FTIR	The efficiency of the tested inhibitors decreases with time after two years of immersion in chloride solution.	3
4.	Steel	Simulated concrete pore solution	D-Sodium glucanate	-	EIS	Formation of an adsorptive film on the steel surface	4
5.	rebar	Concrete	Calcium Nitrate, Calcium Nitrire, Potassium Nitrate	-	Electro chemical measurements	Inhibitor dosage on 3-4% of cement weight seems sufficient to protect the rebar against corrosion	5
6	Steel	5% NaCl SCP	Sodium Molybdate	-	Polarization, AC Impedance, Mott- Schotty Analysis Technique	Passive film formed on steel rebar surface in the presence of sodium molybdate	6
7.	Steel	SCP	Sodium Nitrite	-	Linear Polarization resistance, electrochemical impedance spectroscopy	The corrosion rate of Reinforcing Steel decreased with NO_2^- increasing concentration in SCP with Cl^-	7
8.	Steel	SCP	N-Laruroyl Sarcosine Sodium	-	Polarization, AC Impedance	Best inhibition effect on reinforcing steel in SCP	8
9.	Carbon Steel	SCP	Benzotriazol	-	Polarization, AC Impedance	Benzotriazol is a potentially attractive alternative to nitrites for inhibiting corrosion of reinforced in concrete	9
10.	Steel	SCP	Sodium Nitrate and D-Sodium GluGanate	-	SEM	The inhibition efficiency of the inhibitor was 99%	10
11.	Steel	SCP	di-2 ethyl hexyl sebacate	-		Anodic reaction of steel electrode was suppressed	11
12.	Steel	SCP	Disodium Mono flouro Phosphate	-	Polarization, AC Impedance, EIS	The Electrochemical reaction can be suppressed by forming a disposition film in the steel concrete. interface which retards the attack by aggressive Cl^-	12
13.	Steel	SCP	Uracil derivative	-	Polarization, FITR, XPS	Langmuir adsorption isotherm	13
14.	Hot dip Galvanized coated rebar	SCP	Molybdenum-Phosphorus	-	EIS, Raman Spectroscopy, SEM, EDXA, XRD	These Studies are expected to provide a new area in development of lesser polluting protective passive layer on galvanized coatings	14
15.	Mils Steel	Concrete	Zinc oxide	-	Weight loss, Potential time behavior and anodic polarization technique	The passivity of steel maintained by the addition of zinc oxide	15
16.	Zinc, Galvanized Steel, Mild steel	Concrete	-	-	Microscopy and X-ray micro analysis	Corrosion behavior of Zinc, Galvanised steel, Mild steel in concrete studied	16
17.	Steel	Concrete	-	Red mud	Conductivity of the anolyte electro chemical measurements, Electrical resistivity	The addition of the red mud is beneficial to concrete	17
18.	Mild Steel	Ferro cement	-	Cement Slurry Coating	Impedance, Anodic polarization	Cement slurry coating give better protection efficiency	18
19.	Bare mild Galvanized Epoxy coated Stainless Steel	Concrete	-	-	Reinforcing material and chloride content Studied	Among corrosion resisting Steels, the best durability performance is exhibited by the Stainless-clad reinforcing bars	19

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Sl. No	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
20.	Mild steel	Concrete	-	5% NaCl	AC impedance, Linear polarization	Formation of Surface layer on the rods	20
21.	Steel	Concrete	-	-	Resistance measurement	Corrosion current, corrosion potential values measured	21
22.	Galvanized Steel	Concrete	-	-	X-ray diffraction	All Zn must corrode before any of the underlying steel. Corroded	22
23.	Steel	Concrete	Zinc coating	-	-	The coated reinforcement has also been found to result in about 50 percent greater bond Strength as compared to Similar but uncoated plain mild steel	23
24.	Mild Steel	Dilute Sodium Nitrate, Chloride Contaminated concrete	Cathodic current	-	-	Cathodic System is to induce passivation	24
25.	Mild Steel	Concrete	Epoxy Coating	-	-	The coated Steel rebar improved the bond Strength.	25
26.	Steel	Concrete	-	-	Linear Polarization Resistant, Zero resistant ammeter	Decreasing the frequency of cracking leads to a decrease in corrosion	26
27.	1. Polished Steel 2. Unpolished Steel	SCP	Calcium Nitrite	-	-	Evaluated for their apparent influence on passivity and corrosion rate.	27
28.	Steel	SCP	Hydroxy alkyl amine	-	-	The efficiency of migrating corrosion inhibitor in reducing corrosion of steel has been investigated.	28
29.	Mild steel	SCP	-	-	Polarization, Impedance. SEM, EDAX	Protective film formed on the reinforcing steel	29
30.	Mild Steel	0.01 N NaOH, Saturated lime water, Cement Slurry, and embedded mortars	-	-	Weight loss, Electrochemical DC cyclic polarization and polarization resistance, Surface topographic and X-ray diffraction	Accelerating effect of fluoride (<25 ppm) has almost double corrosive effect than noted for equal concentration of chloride ion	30
31.	Mild Steel	SCP	-	-	Polarization, AC impedance	R_{ct}, R_f ,ci values measured	31
32.	Mild steel, Low alloy Steel	Concrete	-	-	DC polarization, AC impedance, acoustics emission, and SEM	The rate of increase in corrosion rate with chloride content in mortars is considerably higher for MS than the LAS	32
33.	Mild Steel	SCP	-	-	Polarization, EDS, XRD, XPS	At the free corrosion potential in an aerated solution, a decrease of the carbonate content increases the corrosion rate	33
34.	Mild Steel	Alkali activated cement	-	NaCl	Galvanostatic pulse method	Oxidation of sulphide anions to sulphur prevents potential rising into the pitting regime and leads to inhibition of the oxygen cathode reaction	34
35.	Mild steel	concrete	Cement polymer composite, Interpenetrating polymer network coating and epoxy coating	-	Open circuit potential measurement	Corrosion performance measured	35
36.	Mild steel	Concrete	Zinc Phosphate	-	Potentio dynamic polarization, cronoamperometry and EIS, XRD, SEM	Corrosion rate is considerably lowered by this phosphate coating	36
37.	Mild Steel	SCP	Sodium nitrate	NaCl	Polarization and Zero Resistance ammetery	The Stability and Improvement of the passive film	37
38.	Mild Steel	Concrete	Extracts of Kola Plant and Tobacco	-	Potential Monitoring Technique	Protective film formed on the surface	38
39.	Steel	Concrete	Calcium Nitrite	-	Weight loss, electro chemical measurement	Calcium Nitrite based treatment applicable only to carbonated concrete without chloride.	39

Table 1. (cont.) Inhibitors used to improve the corrosion resistance of metals in concrete admixture

Sl. No	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
40.	Duplex Stainless Steels	SCP	-	-	Polarization, SEM	The lean duplex 2304 has clearly better corrosion behavior than the 304 grade in simulated concrete pore solution	40
41.	Mild steel	Cement Paste	Stannous tin Sn(II)	-	Linear polarization, Analytical electron Microscopy.	Corrosion performance of Stannous tin (Sn(II)) is measured.	41
42.	Steel	SCP	Sodium Nitrate	-	EIS	Sodium Nitrate Reduce the corrosion Level	42
43.	Mild Steel	Concrete	Potassium dichromate	-	Electrochemical Potential Monitoring Method	The potassium dichromate inhibitor was Most effective amongst other inhibitor concentration	43
44.	Low Nickel Stainless Steel, AISI 304 SS Carbon Steel	SCP	-	5%NaCl	Cyclic anodic Polarization curve and EIS	Nickel Stainless Steel High corrosion resistance then carbon Steel	44
45.	Steel	-	Calcium Nitrite, Calcium nitrate, Amino alcohol, DMEA, Cyclo hexyl ammonium benzoate, Di isopropyl ammonium benzoate	3% NaCl	-	The chemical reactions of the corrosion process in concrete and of the most commonly used as inhibitors and discussed	45
46.	Steel	Concrete	Sodium mono sulphate	-	Gravimetric Measurement	Sodium mono fluoro phosphate had very little on the corrosion rates of steel in both non carbonated and carbonated concrete under the conditions studied.	46
47.	Steel	Concrete M15,M20, M30,M35	-	5% NaCl	Weight loss, Linear polarization, Galvanostatic pulse technique	The Galvano static pulse technique is able to give reliable corrosion rate values of steel in concrete	47
48.	Steel	Concrete	Alkyl amino alcohol	-	Electro chemical measurement	The inhibitor is able to reduce the corrosion rate	48
49.	Steel	Concrete	Chromate	-		Repassivation as pH raised	49
50.	Galvanized steel	SCP	Zn	-	Potentio dynamic Polarization tests, Polarization resistance	Galvanized Steel is a very good alternative to avoid the early damage of the structure.	50
51.	Steel	Portland Pozzolona Slag cement	0.5%Sodium Citrate+0.5% Sodium Stannate Migrating inhibitor amino alcohol, Amines, Nitrides	-	FTIR	The better corrosion resistance of steel embedded in migrating corrosion inhibiting system	51
52.	Steel	concrete	Calcium Nitrite and tannic acid	-	Weight loss, potentiodynamic polarization	The dose of these inhibitors for the protection of steel wire mesh reinforce Ment in Ferro cement	52
53.	Rebar	Acidified concrete pore solution	Sodium molybdate, Sodium tungstate, Sodium Nitrite Sodium phytate	-	Weight loss, Anodic polarization measurements, EIS	The concentration is above 0.5% Sodium phytate shows inhibitive effect and passivation is promoted. Molybdate and tungstate are present on the steel surface.	53
54.	Carbon Steel	Carbonated concrete pore solution	Sodium nitrite	-	Electrochemical Noise Measurement	High concentration of nitrite can inhibit the nucleation of meta stable pits around the rust cover and accelerate the repassivation of stable pits	54
55.	Steel	SCP	Nitrite	-	Weight loss, Polarization, EIS	The dosage of high amounts of nitrites on concrete can be unfavorable.	55

Table 1. (cont.) Inhibitors used to improve the corrosion resistance of metals in concrete admixture

Sl. No	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
56.	Steel	Concrete	Calcium Nitrite	-	Polarization Resistance	The presence of nitrite ion efficient passivation of the rebar that maintain with time	56
57.	Galvanized Steel	Concrete	Surface and Bulk Hydrophobic	-	Water Absorption, electro chemical measurements, Chlorides penetration, Visual observation	Hydrophobic treatment is the most effective treatment to improve the corrosion resistance of Galvanized steel reinforcement in concrete	57
58.	Steel	Concrete	Sodium nitrite, Resorcinol, Phloroglucinol, Sodium Phosphate, Sodium gluconate, Calcium gluconate, zinc oxide, urotropin	-	Corrosion potential, polarization resistance	None of the alternative inhibitors studied was comparable to nitrite in terms of protective efficiency	58
59.	steel	Concrete	Sodium mono fluro phosphate, alkanolamines, amines, Zinc oxide molibdates, borates, Stannates	-	Potentio dynamic, potentiostatic measurement	The organic commercial inhibitors reduce the ingress of chlorides by filling concrete pores and blocking the porosity of concrete by the formation complex compound	59
60.	Steel	Concrete	-	-	Weight loss, linear polarization resistance	The technique can be used as qualitative measure of the corrosion rate of reinforcing steel in concrete	60
61.	Steel	Concrete	Alkyl amino alcohol	-	EIS	The inhibitor was able to reduce the corrosion rate only when the iniated chloride was below 0.16 wt %	61
62.	Carbon steel	Concrete	-	-	EIS,SEM	compressive stress produces more severe degradation of the passive film than does the tensile stress.	62
63.	Steel	Concrete	-	-	Embedded capacitor sensor (ECS)	Embedded sensor is robust and suitable for installation in reinforced concrete, hence capable of detecting changes in the immediate vicinity of the steel for a longer period.	63
64.	Steel	Concrete	-	-	SEM, AFM, EIS	AFM images revealed detail of the localized corrosion behavior	64
65.	Stainless steel	SCP	-	-	Potentio dynamic polarization, alternating current impedance	The Cl^{-} concentration had little effect on Stainless Steel.	65

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