INFLUENCE OF Na_2WO_4 AND SUCCINIC ACID ON THE CORROSION RESISTANCE OF GALVANIZED STEEL IN SIMULATED CONCRETE PORE SOLUTION PREPARED IN SEA WATER.

S. Rajendran,[a],[b]* C. Nathiya,[c] P. Prabhakar,[c] P. Shanthy,[d] S. Umadevi, [e] and M. Pandiarajan[a]

Keywords: simulated concrete pore solution; galvanised steel; sodium tungstate; succinic acid.

Corrosion resistance of galvanized steel (GS) in Simulated concrete pore solution (SCPS) prepared in sea water, in the presence of sodium tungstate and succinic acid has been investigated by polarization study. Inclusion of sodium tungstate and also succinic acid in SCPS reduces the corrosion resistance of GS, Hence it is concluded use of sodium tungstate or succinic acid shall be avoided while GS rebar are used in construction of buildings, bridges especially in marine environment.

* Corresponding Authors
E-Mail: pandiarajan777@gmail.com
[a] Corrosion Research Centre, PG and Research, Department of Chemistry, GTN Arts College, Dindigul- 624005, Tamil Nadu, India
[b] Corrosion Research Centre, Department of Chemistry, RVS School of Engineering and Technology, Dindigul- 624005, Tamil Nadu, India
[c] Research Department of Chemistry, APA College of Arts and Culture, Palani, Dindigul, India
[d] Kunthavai Naachiaar Government Arts College, Thanjavur-613007, India
[e] Sri GVG Vishalakshi College for Women, Udumalpet-642124, India

Introduction

Several methods have been used in order to reduce the concrete reinforcement corrosion.They include cathodic protection,coatings, addition of inhibitors to concrete and a combination of these mrthods.[1] Corrosion inhibitors have been successfully used in steel pipelines, tanks etc, for many decades.[1,2] Their use in concrete field is more recent, but is of an increasing interest[3-7] since it can be considered as a promising technique offereing an easy practice with reduced costs. For this reason, a large range of inhibitors is, nowadays, available for the customer. However, there is still a controversy regarding the inhibitors protection efficiency.[8] Some authors reports that inhibitors are effective in reducing corrosion rate in concrete contaminated with chlorides.[8] The most frequently used technique is adding the inhibitors to the mixing water of concrete as admixtures for new structures. Calcium nitrite was the most extensively tested corrosion inhibitor.[9] Nitrite acts by stabilizing the passive film and its effectiveness had interestingly been proved however environmental limitations have highly reduced its use.[10] Laboratory studies of the preventive inhibitive action carried out on monofluorophospahte (MFP) showed that a critical concentration ratio MFP/chlorides greater than 1 had to be achieved; otherwise the reduction in corrosion rate was not significant.[11] Furthermore, in solutions based on $Ca(OH)_2$ MFP is reported to react with th calcium ion and as a result, its active substance disappear from solution due to precipitation.

The amino-alcohols are common inhibitors based on mixtures of alkanolamines and amines or alternatively on organic acids.[4] They were widely applied and rapidly established in the market since they are non toxic and cost attractive. Furthermore, amino-alcohols can be applied for different purposes. In fact, Wombacher et al.[12] reported that amino-alcohols based mixed inhibitors can be used either as concrete admixtures or in repair products for existing structures.[12] They transport mechanism through the concrete cover had been studied by Tritthart[13] who demonstrated that the amino-alcohol compound is not bound by cement but remains largely dissolved in the pore liquid which provides optimal conditions for high mobility. However, according to another study carried out by Tritthart[14] on cement paste samples, he found that in the case of surfaces application only a very small amount of amino-alcohol penetrated from mixed inhibitors which suggested that the penetration is inhibited by some mechanisms such as the clogging of the pores by solidification of other compounds of the mixed inhibitor.

Experimental

Preparation of Simulated Concrete pore solution (SCPS)

Simulated concrete pore solution is mainly consisted of saturated calcium hydroxide ($Ca(OH)_2$, sodium hydroxide (NaOH) and potassium hydroxide (KOH) with the pH ~ 13.5.[15] However in numerous studies of rebar corrosion, saturated $Ca(OH)_2$ has been used as a substitute for pore solution.[16] A saturated calcium hydroxide solution is used in present study, as SCP solution with the pH ~ 12.5.

Metal specimen

Galvanized Steel (18% Cr, 12% Ni, 2.5% Mo < 0.03 C) and balance iron wires of 1mm diameter are used in the present study.

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The parameter of sea water used in the present study is given in Table 1.

Table 1. Parameters of sea water

Parameter	Results
pH	7.06
Total dissolved solids	30539 ppm
Electrical conductivity	44910 $\mu\Omega^{-1}cm^{-1}$
Total Hardness as $CaCO_3$	100ppm
Calcium as Ca	19ppm
Magnesium as Mg	12ppm
Chloride as Cl	11400ppm
Fluoride as F	0
Sulphate as SO_4	6708ppm

Result and Discussion

Analysis of Polarization curves

Corrosion resistance of galvanized steel (GS) in simulated concrete pore solution (SCPS) prepared in natural sea water, in presence of sodium tungstate and succinic acid has been evaluated by polarization method. Polarization study has been used to evaluate the corrosion resistance of metals. If corrosion resistance increases, linear polarization resistance (LPR) value increases and corrosion current (I_{corr}) value decreases.[17-30]

Table 2. Corrosion paramaters of galvanised steel (GS) in simulated concrete pore solution (SCPS) prepared in natural sea water, in presence and absence of inhibitors, obtained from polarization study.

System	E_{corr}, mV vs.SCE	b_c	b_a	LPR ohm cm^2	I_{corr} Acm^{-2}
		mV $decade^{-1}$			
SCPS	-843	150	267	18561	$2.249x10^{-6}$
SCPS+A	-887	148	301	11985	$3.603x10^{-6}$
SCPS+B	-874	146	246	4975	$8.020x10^{-6}$

A=sodium tungstate 50 ppm, B=succinic acid 50 ppm

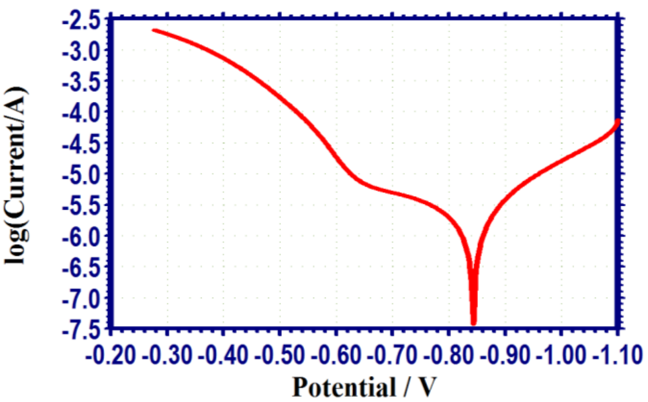

Figure 1. Polarisation curve of galvanized steel immersed in SCPS

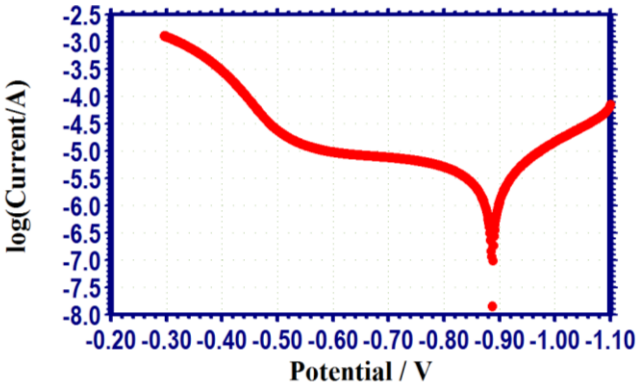

Figure 2. Polarization curve of galvanized steel in immersed in SCPS+ sodium tungstate 50 ppm

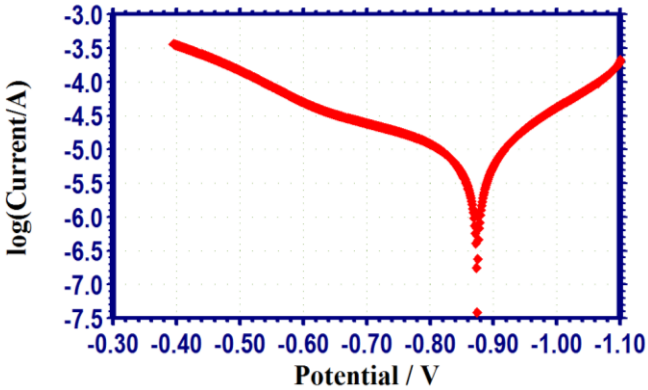

Figure 3. Polarization curve of galvanized steel in immersed in SCPS+ succinic acid 50 ppm

The polarization curves of GS, immersed in SCPS in the absence and presence of inhibitors, namely sodium tungstate and succinic acid are shown in Figure 1 to 3. The corrosion parameters, namely corrosion potential (E_{corr}), Tafel slope (b_c=cathodic;b_a=anodic) linear polarization resistance (*LPR*) and corrosion current(I_{corr}) values are given in Table 2.

When GS is immersed in SCPS prepared in sea water, the corrosion potential is -843 mV vs SCE. The LPR value is 18561 $ohmcm^2$ and the corrosion current is 2.249x10-6 Acm^{-2}.

Influence of sodium tungstate on corrosion resistance of GS

When 50 ppm of sodium tungstate is added to the SCPS, the corrosion resistance of GS decreases. This is revealed by the fact that LPR value decreases from 18561 to 11985 $ohmcm^2$. Further, the corrosion current value increases from $2.249x10^{-6}$ to $3.603x10^{-6}$ A cm^{-2}. This may be artibuted to the fact that when sodium tungstate is added SCPS which is a saturated solution of $Ca(OH)_2$,(pH=13.9), calcium is precipited as calcium tungstate. Hence calcium is not available for the formation$CaCO_3$ and CaO on the metal surface, which is the usual case in the absence of any foreign inhibitors. This accounts for the weakening of the protective layer, decrease in LPR value and increase in corrosion current value. Another factor to be considered is that the protective film formed on the metal surface is porous and amorphous.

Through the pores of the film the corrosive ions, such as chloride ion, present in sea water diffuse towards the metal surface and enhance the corrosion of the metal. Hence decreases in LPR value and increase in corrosion current value.

Another aspect to be considered is that the experimental condition, dezincification may take place from galvanized steel, which may be enhanced due to the formation of zinc tungstate.

Influence of succinic acid on the corrosion resistance of GS

When succinic acid is added to SCPS, the corrosion resistance further decreases to a great extent and the corrosion current increases from $2.249x10^{-6}$ to $8.020x10^{-6}$ A cm^{-2}. This is artibuted to the fact that, succinic acid, being a dicarboxylic acid, consists of succinate anions in the basic medium(pH=13.9).Moreover it forms insoluble salt of calcium succinate in the bulk of the solution. Hence calcium is not available to be transported towards the metal surface, to form $Ca(OH)_2$, CaO and $CaCO_3$. Other Factors include porous and amorphous nature of the protective film and dezincification process of galvanized steel which is enhanced by the formation of Zinc succinate is the bulk of the solution.

Analysis of the corrosion potential values indicate that in the presence of sodium tungstate and also at succinic acid, the corrosion potential is shifted to the cathodic side. This is due to the release of Zn^{2+} ion from galvanized steel because of dezincification process. The cathodic Tafel slopes and not affected very much. That is reduction of oxygen molecules into hydroxide ion is not altered very much during polarization process. However, the anodic slopes are very much. This is due to the dissolution of protective films formed on the anodic sites of the metal surface by addition of sodium tungstate and also succinic acid. The ion tungstate and ion succinate formed as protective film formed on the anodic sites go in to the solution. Hence the anodic slopes are changed when sodium tungstate and succinic acid are added to SCPS which galvanized steel is used as rebar.

Conclusion

Corrosion resistance of galvanized Steel (GS) in simulated concrete pore solution (SCPS) prepared in sea water, in the presence of sodium tungstate and succinic acid has been investigates by polarization study. Inclusion of sodium tungstate and also succinic acid in SCPS, reduces the corrosion resistance of GS, Hence it is concluded that use of sodium tungstate or succinic acid shall be avoided while GS rebar are used in construction of buildings, bridges especially in marine environment.

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