CORROSION RESISTANCE OF COMMERCIAL ALUMINIUM IN SIMULATED CONCRETE PORE SOLUTION IN PRESENCE OF CURCUMIN EXTRACT

Susai Rajendran[a,d]*, K. Duraiselvi[b], P. Prabhakar[c], M. Pandiarajan[d] M. Tamilmalar[e] and R. Joseph Rathish[f]

Keywords: concrete corrosion, aluminium, simulated concrete pore solution, curcumin, green inhibitor.

The corrosion resistance of commercial aluminium (95% pure) in simulated concrete pore solution (SCPS) prepared in natural sea water has been evaluated in the absenceand presence of curcumin extract and Zn^{2+}.It is observed that Aluminium is more corrosion resistance in SCPS than in sea water. When curcumin extract is added to SCPS, the corrosion resistance of Al increases. However, in the presence of curcumin –Zn^{2+} system, the corrosion resistance of Al in SCPS decreases.

Corresponding Authors
[a] Department of Chemistry, Corrosion Research centre, RVS School of Engineering and Technology, Dindigul 624005, India. E.mail: srmjoany@sify.com
[b] Department of Chemistry, Karpagam University, Coimbatore, E.mail: Duraiselvik@gmail.com
[c] Department of Chemistry, APA College of Arts and Culture, E.mail: nivedhaprabhakar@rediff.mail.com
[d] Corrosion Research Centre, PG and Research, Department of Chemistry, GTN Arts College, Dindigul- 624005, India. E.mail: pandiarajan777@gmail.com,
[e] Department of Chemistry ,B.S Abdur Rahman Univeristy,Vandalur, Chennai, Tamil Nadu, India. E-mail: manomalar_84@yahoo.co.in
[f] PSNA College of Engineering and Technology , Dindigul, India , Email: rathishjoseph@gmail.com

Introduction

Corrosion of reinforcing steel bars (rebars) in concrete is a serious and significant problem from both the economics and structural integrity standpoints. Many are the approaches that can be used to mitigate corrosion of reinforcing steel, among which, protective coatings and sealers, cathodic protection, concrete realkalinization and corrosion inhibitors are commonly employed. The use of corrosion inhibitors is probably more attractive from the point of view of economics and ease of application .[1] The application of corrosion inhibitors in reinforced concrete is possible by adding it to the mixing water during the concrete preparation or by applying it to the external surface of hardened concrete. In this last case, the inhibiting compound should diffuse through the concrete cover and reach the rebar in a sufficiently high concentration to protect steel against corrosion. Reviews of the most commonly used corrosion inhibitor types in concrete repair systems[2] and the various possible mechanisms of inhibition have been recently published.[3] Over the last years, the use of organic inhibitors, as an alternative to the more commonly employed calcium nitrite-based inhibitors, has been increasing. Organic inhibitors offer protection by adsorbing and forming a protective film on the steel surface. Usually, there is a polar group in the organic molecule that adsorbs on the metal and a nonpolar hydrophobic chain oriented perpendicular to this surface. These chains act, on the one hand, by repelling aggressive contaminants dissolved in the pore solution, and on the other, by forming a tight film (barrier) on the metallic surface. Duprat and Dabosi [4] examine the effect of various aminoalcohols as corrosion inhibitors of carbon steel in 3% NaCl solutions. The efficiency of the inhibitor increases when only one of the hydrogen atoms of the amino group is substituted, as the remaining one induces hydrogen bonds formation between surface-chelated molecules. In the case of 2-ethylamino-ethanol,[5] the inhibitive action in 3% NaCl solutions was interpreted both by its stabilisation effect on the prepassive ferrous hydroxide films and by its adsorption through surface chelate formation onto bare metal sites. The effect of pH on the inhibitive efficiency was also investigated.

Contradictory results have been recently reported when testing corrosion inhibitors in simulated pore solutions and in mortars.[6–8] Elsener et al.[6] studied the efficiency of an inhibitor based on alkylamines on steel corrosion in mortars and in calcium hidroxide solutions. In mortars, there is no apparent inhibition of pitting or a decrease in corrosion rate (*CR*), but the initiation of the corrosion process appears to be delayed. The beneficial effect decreases on carbonated mortars. In a recent publication of these same authors,[7] the discrepancy between the observed high diffusion rate of the migrating corrosion inhibitor (MCI) in mortar and the lack of corrosion inhibition was rationalised by the fact that only the diffusion of the volatile phase was measured. Migration of the nonvolatile component (carbonic acids) through concrete was not proved and assumed to be slow. Thus, the inefficiency detected in concrete, as compared to solutions, should be related to the inability of the nonvolatile components to reach the steel bars. In turn, Mammoliti et al.[8] assumed that the difference in the inhibitors efficiency tested in concrete or in synthetic pore solutions is the result of the dependence of the inhibition mechanism on chemical reactions within the cement phase.

The present work is undertaken to evaluate the corrosion resistance of commercial aluminium (95 % pure) in natural sea water (Table 1) and to evaluate the corrosion resistance of aluminium in simulated concrete pore solution (SCPS) prepared in natural sea water in the absence and presence curcumin extract and Zn^{2+}. The outcome of the present study will be useful to the concrete corrosion technologists.

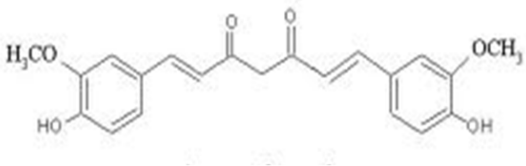
Materials and Methods

Metal specimens

Aluminium: commercial aluminium (95 % pure) was used in the present study.

Preparation of curcumin extract

10 g of turmeric powder was boiled with 50 ml of distilled water. The suspended impurities were removed by filtration .The filtrate was made up to 100 ml .It was used as inhibitor in the presence of Zn^{2+}. The structure of curcumin is shown in Scheme 1.



Scheme 1. Structure of curcumin

Simulated concrete pore solution (SCPS)

A saturated solution of $Ca(OH)_2$ is considered as simulated concrete pore solution.[9] SCPS was prepared in natural sea water.

Table 1. Physicochemical parameters of sea water

Parameters	Value
pH	7.66
Conductivity	44200 μohm^{-1} cm^{-1}
Chloride	6050 ppm
Sulphate	2616 ppm
TDS	30940 ppm
Total Hardness	2800 ppm
Calcium	120ppm
Sodium	6300 ppm
Magnesium	600 ppm
Potassium	400 ppm

Weight Loss Method

Aluminium specimens were immersed in 100 ml of the medium containing various concentrations of the inhibitor in the absence and presence of Zn^{2+} for 1 day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62.The corrosion products were cleaned with Clarke's solution[10]. The inhibition efficiency (*IE*, in %) was then calculated using the equation:

where

W_1 = corrosion rate in the absence of the inhibitor.

W_2 = corrosion rate in the presence of the inhibitor.

$$IE = 100\left[1 - \frac{W_2}{W_1}\right] \quad (1)$$

Potentiodynamicpolarization

Polarization studies were carried out in a CHI–Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The working electrode was aluminium (exposed area is 1 cm^2). A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafelslopes (anodic = b_a and cathodic = b_c) and linear polarization resistance (*LPR*) were calculated.

Results and Discussion

Analysis of Weight loss method

Corrosion rate of aluminium immersed in simulated concrete pore solution (SCPS) prepared in natural seawater, in the absence and presence of curcumin extract and Zn^{2+} are given in Table **2**. The inhibition efficiencies are also given in this Table.

Table 2. Inhibition efficiencies of inhibitors in controlling corrosion of aluminium in SCPS prepared in sea water. Immersion period: 1day

System	*CR* (mdd)	*IE* %
Sea water	32	----
SCPS prepared in sea water	6.4	80
SCPS +Curcumin 6 ml	0.64	98
SCPS + Curcumin 6 ml +Zn^{2+} 50 ppm	2.56	92

When aluminium is immersed in sea water, the corrosion rate is 32 mdd. When Aluminium is immersed in SCPS prepared in sea water the inhibition efficiency is 97 %. When 6 ml of curcumin extract is added the inhibition efficiency increases to 99 %. When 50 ppm of Zn^{2+} is added to the curcumin system, the inhibition efficiency decreases to 92 %. However, this corrosion rate is lower than that observed in presence of sea water.

Corrosion resistance of commercial aluminium in simulated concrete pore solution (SCPS) prepared in natural sea water(Table 1), in the absenceand presence of an aqueous extract of turmeric powder (curcumin) and Zn^{2+} has been evaluated by polarization study.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}) decreases.[11-20].The polarization curves of aluminium immersed in various environments are shown in Figs. 1 to 4.

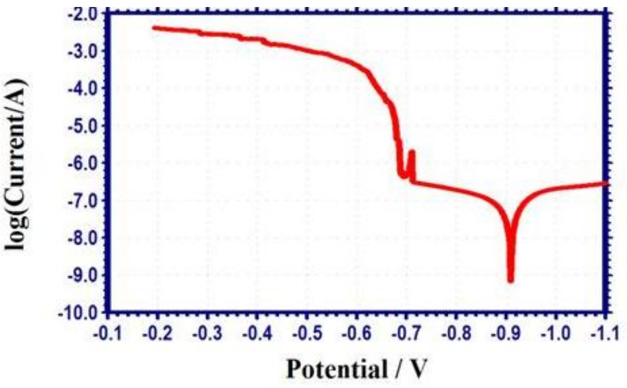


Figure 1. Polarization curve of aluminium immersed in natural sea water

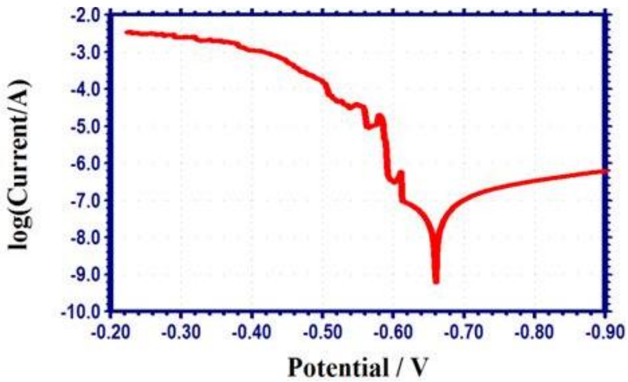


Figure 2. Polarization curve of aluminium immersed in simulated concrete pore solution(SCPS) prepared in sea water

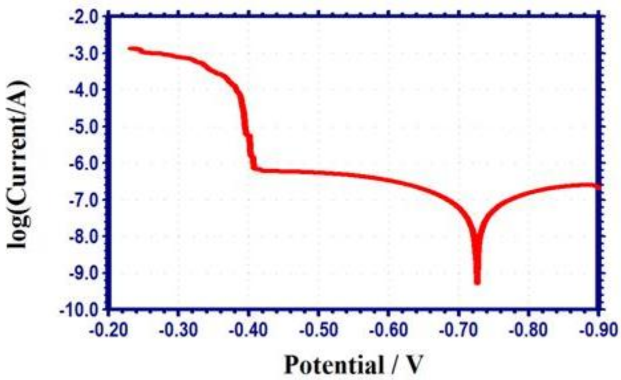


Figure 3. Polarization curve of aluminium immersed in SCPS and curcumin extract 6 ml

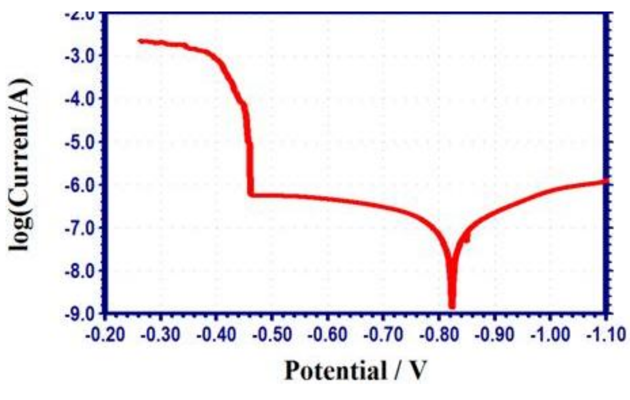


Figure 4. Polarization curve of aluminium immersedin SCPS + Curcumin extract 6 ml + Zn^{2+}50 ppm.

Analysis of Polarization Study

The corrosion parameters, namely corrosion potential (E_{corr}), Tafel slopes (b_c=cathodic ; b_a=anodic),Linear polarization resistance (*LPR*) and corrosion current (I_{corr}) values are given in Table **3**.

Aluminium in sea water

The polarization curves of aluminium in natural sea water in shown in Fig 1. The corrosion parameters are given in Table 2. It is seen that the corrosion potential is -909 mV vs SCE in the potential range of -0.7 volts to -1.1 V the two arms of the polarization curve are very similar. However breakdown potential is observed at -699 mV vs SCE. The passive film, is broken and corrosion current increases suddenly. Then, at -697 mV vs SCE, passive film is reformed. Hence corrosion current decreases. However, at -622 mV vs SCE, the passive film is broken and the corrosion current increases sharply. The passive film formed is oxides of aluminium. The breakage of passive film is due to the presence of aggressive ions such as chloride, present in sea water. When aluminium is immersed in natural sea water, the *LPR* value is 338005 Ω cm^2 and the corrosion current is 2.424x10^{-7} A cm^{-2}.

Aluminium in simulated concrete pore solution prepared is natural sea water

When aluminium is immersed in SCPS prepared in sea water, the corrosion potential is shifted to the anodic side, from -909 to -660 mV vs SCE (Fig 2). This is due to formation of a passive film formed on the metal surface .The film probably consists of aluminium oxide .The anodic Tafel slope is smaller than the cathodic Tafel slope.

That is the rate of change of current with potential is less during the anodic sweep than during the cathodic sweep. However, the passive film is broken at -607 mV vs SCE .As the potential is shifted to the anodic side, passive film is formed again at potential -605 mV vs SCE .Then again break down potential appears at -543 mV vs SCE .This trend is repeated as the potential is shifted to the anodic side. This indicates that the passive film produced on aluminium is disturbed when the potential is shifted to more anodic side. However the passive film is quite stable in the potential range of -606 to -641 mV SCE. It is observed from Table 2, that in presence of SCPS, aluminium is more corrosion resistant than in sea water. This is supported by the fact, that when aluminium is immersed in SCPS, the *LPR* value increases from 338005 to 418966 Ω cm^2 and the corrosion current decreases from 2.424x10^{-7} to 2.938x10^{-8}A cm^{-2}.

Influence of Curcumin on the resistance of aluminium in SCPS

Various inhibitors such as calcium nitrite,[21] molybdate,[22] sodium nitrite,[23] have been added to improve the corrosion resistance of metals in SCPS .The influence of a natural product, which is less toxic, namely, an aqueous extract of curcumin (extract from turmeric powder) on the corrosion resistance of aluminium in SCPS has been evaluated by polarization study(Fig. 3).

Table 3. Corrosion Parameters of aluminum immersed in simulated concrete pore solution (SCPS) prepared in sea water, in presence and absence of curcumin and Zn^{2+}, obtained from polarization study.

System	E_{corr}, mV*	b_a, mV**	b_c, mV**	*LPR*, ohm cm^2	I_{corr}, A cm^{-2}
Sea water	-909	474	313	338005	$2.424x10^{-7}$
SCPS	-660	219	33	418966	$2.938x10^{-8}$
SCPS +A	-726	234	183	451237	$9.894x10^{-8}$
SCPS+B	-823	175	255	340564	$1.324x10^{-7}$

A=Curcumin 6 ml, B=Curcumin 6 ml+ Zn^{2+} 50 ppm,*mV vs SCE; **mV in one decade

It is observed that when curcumin is added to SCPS, the corrosion potential is shifted to the cathodic side. However it is in the anodic region when compared with the corrosion potential in sea water alone .The LPR Value increases from 418966 to 451237 Ω cm^2 indicating that aluminium in SCPS is more corrosion resistant in presence of curcumin than in its absence, due to the formation of Al^{3+}-curcumin complex apart from the formation of aluminium oxide film formed on the metal surface. However, the increase in the value of corrosion current warns that the protective film is porous and flow of electron can take place from the metal to the environment. In the anodic region it is observed that the breakdown potential appears from -380 to -403 mV vs SCE. Interestingly, it is observed that the passive film is stable in a wide range of potential, namely, from – 400 to -600 mV vs SCE.

Influence of Curcumin –Zn^{2+} system on the corrosion resistance of aluminium in SCPS

In the corrosion inhibition study, it has been observed that the corrosion inhibition efficiency increases in the presence of inhibitor –Zn^{2+} system.[24-30] This concept has been tried in the case of corrosion resistance of aluminium in concrete solution. The corrosion resistance has been evaluated by polarization study (Fig 4.). It is observed that in presence of curcumin –Zn^{2+} system, the corrosion potential shifts to the cathodic side (-823 mV vs SCE). However this is anodic side, when compared with corrosion potential of aluminium in sea water, LPR value decreases from 451237 to 340564 Ω cm^2 and the corrosion current increases from 9.894x10-8 to 1.324x10-7 A cm^{-2}. This indicates that the corrosion resistance of Al in SCPS decreases in presence of curcumin –Zn^{2+} system. However this is more corrosion resistant, when compared with sea water alone. Hence it in conclude that addition of Zn^{2+} must be avoided when curcumin is added as an inhibitor in concrete environment. This is due to the fact that Zn^{2+}, when added to SCPS (which is an alkaline solution, pH=13.2) it is precipitated as $Zn(OH)_2$ in the bulk of the solution .Usually Zn^{2+} forms a weak complex with the inhibitors and transports the inhibitor towards the metal surface from the bulk of the solution. However under the present experimentalcondition, such a transport of inhibitor from the bulk of the solution towards the metal surface is prevented. Hence the corrosion resistance of aluminium in SCPS decreases, in presence of curcumin-Zn^{2+}system. However it is observed from Fig 4, that the film formed on the metal surface in stable in thepotential range of -459 to -700 mV vs SCE. The break down potential is in the range of -395 to -458 mV vs SCE .

Conclusion

The corrosion resistance of commercial aluminium (95% pure) in simulated concrete pore solution (SCPS) prepared in natural sea water has been evaluated in the absence and presence of curcumin extract and Zn^{2+}. It is observed that Aluminium is more corrosion resistant in SCPS than in sea water. When curcumin extract is added to SCPS, the corrosion resistance of Al increases. However, in the presence of curcumin –Zn^{2+} system, the corrosion resistance of Al in SCPS decreases.

Scope for the further study:

A systematic study in various concentrations of curcumin extract and Zn^{2+}. The corrosion resistance of aluminium in SCPS prepared in sea water has been evaluated in presence of one concentration of curcumin extract (6 ml) and also one concentration of Zn^{2+} (50 ppm) will lead to very intensity results . The conclusion of the future study will be very useful to the concrete corrosion technologists

Acknowledgement

The authors are thankful to their Managements and St,Joseph's Research and Community Development Trust, Dindigul, India for their help and encouragement.

References

[1]Sastri,V. S., *Corrosion Inhibitors. Principles and Applications,* Wiley,England, **1998**.

[2]Page, C. L., Ngala, V. T., Page, M. M., *Mag. Concr. Res*, **2000**, *52*, 25.

[3]Hansson,C. M., Mammoliti, L., Hope, B. B., *Cem. Concr. Res.* **1998**, *28*, 1775.

[4]Duprat, M., Dabosi, F., *Corros.*, **1981**, *37*, 89.

[5]Duprat, M., Bui, N., Dabosi, F., *Corros.*, **1979**, *35*, 392– 397.

[6]Elsener, B., Buchler, M., Stalder, F., Bohni, H., *Corros.*, **1999**, *55*, 1155.

[7]Elsener, B., Buchler, M., Stalder, F., Bohni, H., *Corros.*, **2000**, *56*, 727.

[8]Mammoliti, L., Hansson, C. M., Hope,B. B., *Cem. Concr. Res.* **1999**, *29*, 1583.

[9]Pandiarajan, M., Prabhakar ,P., Rajendran, S., *Eur. Chem.Bull.*, **2012**, *1(7)*, 238.

[10]Wranglen, G., *Introduction to Corrosion and Protection of Metals*.: Chapman & Hall, London., **1985**, 236.

[11]Angelin Thangakani, J., Rajendran, S., Sathiyabama, J., Lydia Christy, J., Surya Prabha, A., Pandiarajan, M., *Eur. Chem. Bull.,* **2013**, *1(5)*, 265-275.

[12]Vijaya, N., Peter Pasgal Regis, A., Rajendran, S., Pandiarajan, M., Nagalakshmi, R., *Eur. Chem.Bull.*, **2013,** *2(5)*, 275-278.

[13]Agila Devi, S., Susai Rajendran, Jeyasundari, J., Pandiarajan, M., *Eur. Chem. Bull.*, **2013**, *2(2)*, 84.

[14]Rajendran, S., Anuradha, K., Kavipriya, K., Krishnaveni, A., and Angelin Thangakani, J., *Eur. Chem. Bull.*, **2012**, *1(12)*, 503.

[15]Nagalakshmi, R., Rajendran. S., Sathiyabama, J., Pandiarajan, M., Lydia Christry, J., Eur. Chem. Bull., **2012**, 1(17), 238.

[13]Sahayam Raja, A., Nagalakshmi, R., Rajendran. S., Angelin Thangakani, J., Pandiarajan, M., *Eur. Chem. Bull*., **2013**, 2(3)., 130-136

[14]Shyamala Devi, B., Rajendran. S., *Eur. Chem. Bull*., **2012**, *1(5)*, 150-157.

[15]Gowri, S., Sathiyabama, J., Rajendran, S., and Angelin Thangakani, J., *Eur. Chem. Bull.*, **2013**, *2(4)*, 214-219.

[16]Manimaran, N., Rajendran, S., Manivannan, M., John Mary, S., *Res. J. Chem. Sci.,* **2012**, *2(3)*, 52.

[17]Arockia Selvi, J., Rajendran, S., John Amalraj, A., Narayanasamy, B., *Port. Electrochim. Acta.*, **2009**, *27(1)*, 1.

[18]Ostoner, T. A., Justness, H., *Adv. Appl. Ceram*, **2011**, *110*, 131.

[19]Zhou, X., Yang, H.-Y., Wang, F- H., *Corros. Sci. Protect. Technol.* **2010**, *22*, 343.

[20]Zhu, Y., Lin, C., *Metallurg. Sinica*, **2010,** *46(2),* 245.

[21]Johnsirani, V., Sathiya bama, J., Rajendran, S., Suriya Prabha, A., *ISRN Corros*., **2012**, *2012*, 1.

[22]Gowri,S., Sathiyabama, J., Prabhakar, P., Rajendran, S., I*nt. J. Res. Chem. Environ.*, **2013**, *3(1),*156.

[23]Manivannan, M., Rajendran, S., *Res. J. Chem. Sci,* **2011**, *1(8),* 42.

[24]Wilson Sahayaraj, J., John Amalraj, A., Rajendran, S., Vijaya, N., *J. Chem.,* **2012**, *9(4)*, 1746.

[25]Kavipriya, K., Sathiyabama, J., Rajendran, S., Krishnaveni, A., *Int. J. Adv. Engg. Sci. Technol.*, (IJAEST), **2012**, *2(2)*, 106.

[26]Manivannan, M., Rajendran, S., *Asian J., Chem.*, **2012**, *24(10),* 4713.

[27]Muthumani, N., Rajendran, S., Pandiarajan, M., Lydia Christy, J., Nagalakshmi, R., *Port. Electrochim. Acta*, **2012**, *30(5)*, 307-315.

Received: 18.04.2013.

Accepted: 21.06.2013.