Mater. Environ. Sci. 5 (S1) (2014) 2250-2256
ISSN: 2028-2508
CODEN: JMESCN
MPE14

Electrochemical behavior of stainless steel UR45N and carbon steel in solutions simulating the concrete interstitial electrolyte

M. Mekkaoui Alaoui[1], B. Ouaki[2], N. Labjar[1], M. Serghini-Idrissi[1], S. El Hajjaji[1*]
[1] LS3ME, University Mohamed V, Faculty of Sciences, Av. Ibn Batouta, BP 1014 Rabat, Morocco
[2] Laboratoire de génie des Matériaux, ENIM, Rabat, Maroc

Received 7 Dec 2013, Revised 16 July 2014, Accepted 17 July 2014

***Corresponding authors: E-mail: hajjaji@fsr.ac.ma Tel: (+212) 6 61 30 31 02

Abstract:

Electrochemical studies and surface analysis were performed in order to compare the electrochemical behavior of reinforced stainless steel (UR45) and carbon steel. The investigations were done in presence of chloride ions and using solutions simulating the concrete interstitial electrolyte. The evolution of open circuit potential of steel samples shows that potential decreases with time of immersion. Currents are more important in seawater for carbon steel than stainless steel UR45N. Stainless steel UR45N resist better than the carbon steel in concrete solution.

Key Words: reinforced concrete; corrosion; electrochemical behavior; stainless steel; carbon steel

1. Introduction

Reinforcement corrosion is the most common degradation in concrete structures [1]. The presence of aggressive species, such as chlorides and carbon dioxide can diffuse through concrete and causes localized breakdown of the passive film inducing degradation of the metal [2-7]. To minimize the corrosion processes, many procedures can be used based on metallurgical properties of the steel, the composition of the concrete pore solution, and the interface conditions of steel / concrete [8-10]. Generally, the almost metal used is carbon steel. But actually, stainless steel reinforcement [11-13] can be also, for some applications, considered as a solution to minimize the reinforcement corrosion in concrete structure. Its excellent corrosion resistance can increase the durability of structures exposed to aggressive environment [14-15]. Despite the advantages of stainless steel in construction, this type of reinforcement is still limited compared to carbon steel [16].

The aim of this work is to study the electrochemical behavior of stainless steel UR45N and carbon steel in solution simulating the concrete interstitial electrolyte in presence of different concentration of chlorides ions. The study was performed through the use of electrochemical techniques, surface analysis and standard pitting test.

2. Experimental section

2.1. Concrete simulating solutions

An extract solution was obtained from a cement mix having a water/cement ratio of 0.5. The cement mix was continuously stirred, before obtaining the extract. Since the reactions of cement hydration are exothermic the temperature of the mix increases with time. However, the remaining aqueous electrolyte was recovered and filtered only after temperature stabilisation. The pH of the extract solution was between 12.5 and 13. The chemical composition of the extract solution was presented in Table 1. To study the effect of chlorides ions, different concentrations of chlorides ions were added to the extract solutions.

Table 1: Composition of the extract solution (ppm)

CaO	Al_2O_3	SO^{2-}_4	P_2O_5	K_2O	Fe_2O_3	Na_2O	Cl^-
233.34	560	6752	4.53	12275	2568.6	1242.7	314

The second simulating solution used was prepared with 4.66 $g.L^{-1}$ of KOH and 1$g.L^{-1}$ of NaOH. The pH of the solution was about 13.07.

The working electrodes were commercial steel (stainless steel and carbon steel). There compositions were given in Table 2.

Table 2: Chemical composition of stainless steel and carbon steel

Chemical composition in wt%	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Fe
Carbon steel	0.38	0.36	1.20	0.016	0.011	0.0324	0.077	0.032	0.096	97.7
Stainless steel UR45	0.017	0.34	1.46	0.024	0.002	5.31	22.06	2.96	0.23	67.1

2.2. Electrochemical investigation

Electrochemical experiments were performed of aerated concrete simulating solutions by means of potentiostatic techniques. The cell contained a platinum disc as counter electrode, a saturated calomel electrode as reference and the working electrode (UR45N, carbon steel).

Before every run, the surface of the electrode was abraded using emergy paper of 1200 grades. The potential scanning rate was 50mv/min. The cathodic and anodic curves were recorded separately from the free corrosion potential after a 20min preliminary hold time.

The polarization curves were performed on different solution of cement extract without and with addition of chloride ions. In order to get more information about the redox processes and to determine the changes of pitting potential values due to the presence of NaCl, the potential range was adjusted for different % NaCl to avoid excess reduction or oxidation reactions on the electrode surface.

2.3. *Pitting standardized test*

Standardized test of pitting corrosion was performed using the two studied materials at different temperatures in solution containing Ferric chloride. Performs the test was standardized corrosion bite for different materials studied.

2.4. Preparation of specimen

To study the behavior of steels into mortar, immersion tests were done in seawater on steel UR45 and carbon steel embedded in mortar. The mortar composition was given in Table 3. The water/cement ratio was 0.5. The amount of sand was two times that of cement. The mortar disks were then cured for 28 days in a high humidity environment (100% relative humidity) at room temperature.

Table 3: Composition of mortar

Aggregates	content (Kg/m^3)
Gravel [15/25 mm]	570
Gravel [5/15 mm]	470
Rice grain [2/8 mm]	200
Sand [0/1.25 mm]	640
Cement CPJ 45	350
water	175

3. Results and discussion

3.1. Pitting test result

To evaluate the material´s resistance to pitting corrosion, critical pitting temperature (CPT) according to the ASTM standard G48-03 was determinate (standard test methods for pitting and crevice corrosion of stainless steel and alloys by use of $FeCl_3$). The critical pitting temperature (CPT) is the minimum temperature to produce pitting corrosion. The Pitting standard test was performed at different temperatures in ferric chloride solution. The immersion time was about three days at selected temperature. The obtained results are presented in figure 1 and 2.

As shown in figure 1, the sensitivity of stainless steel to pitting corrosion increases with the temperature. At 40 ° C, it is clear that there is deep pitting on stainless steel. For the temperature 30° C the surface is attacked but less than 40 ° C. At 25°C, no damage on the surface state is observed.

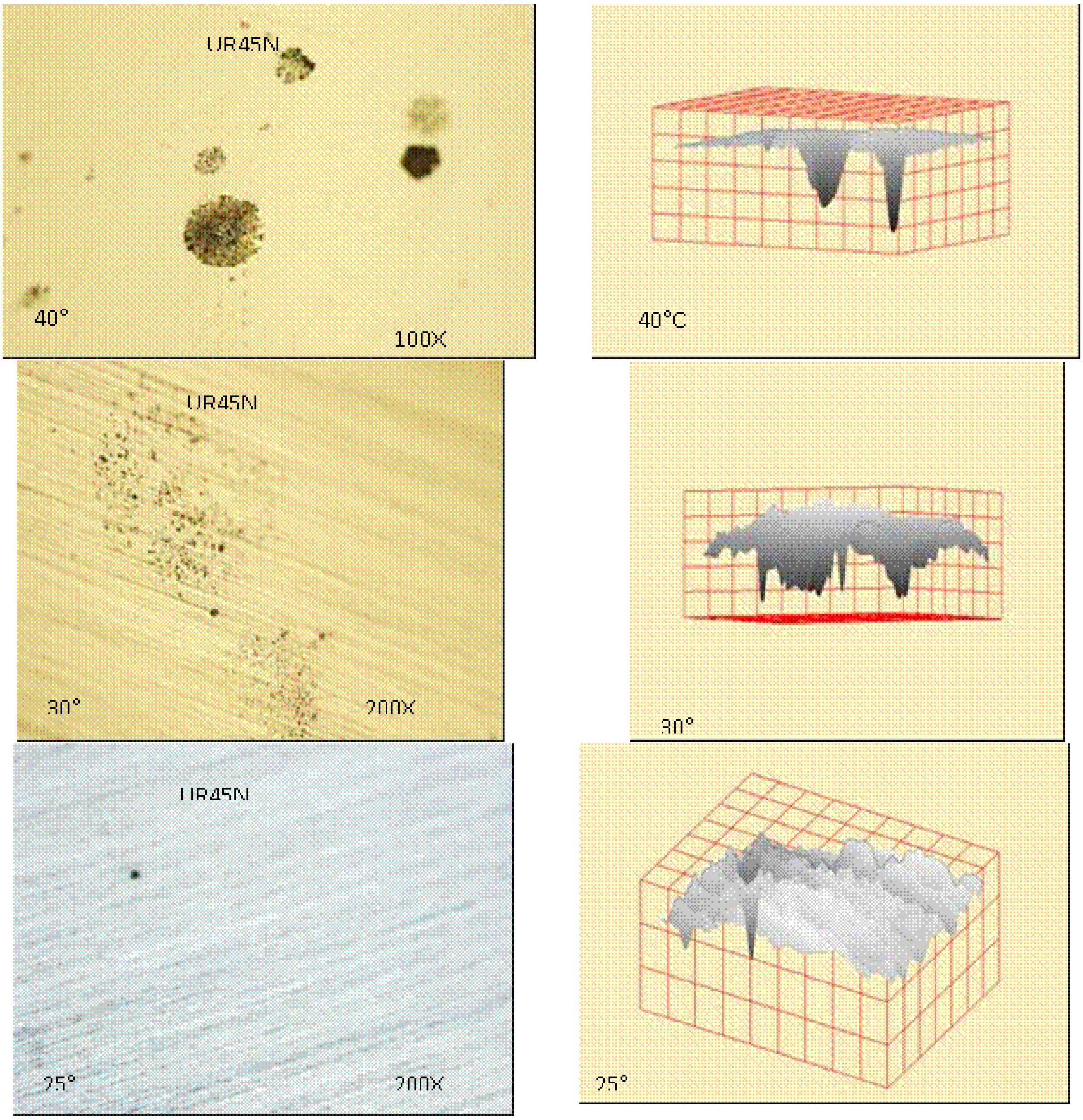

Figure 1: Surface analysis of stainless steel UR45N after 3 days of immersion in solution containing $FeCl_3$ at different temperature.

The obtained results for carbon steel are presented in Figure 2. At 25 °C, the surface is greatly attacked by $FeCl_3$. So, the CPT for carbon steel is 25 ° C.

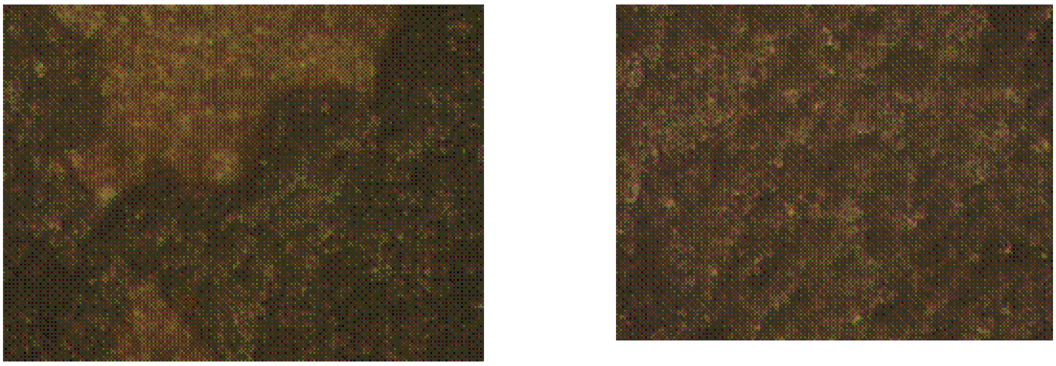

Figure 2: Surface analysis of carbon steel after 3 days of immersion in solution containing $FeCl_3$ at 25°C.

3.2. Open circuit potential

Figure 3 shows the evolution of open circuit potential of steel samples in cement extract solution and simulating solution. The potential values of the carbon steel decreases with time. For stainless steel, a continuous shift of the potential towards positive vales is observed corresponding a hindering the corrosion reactions.

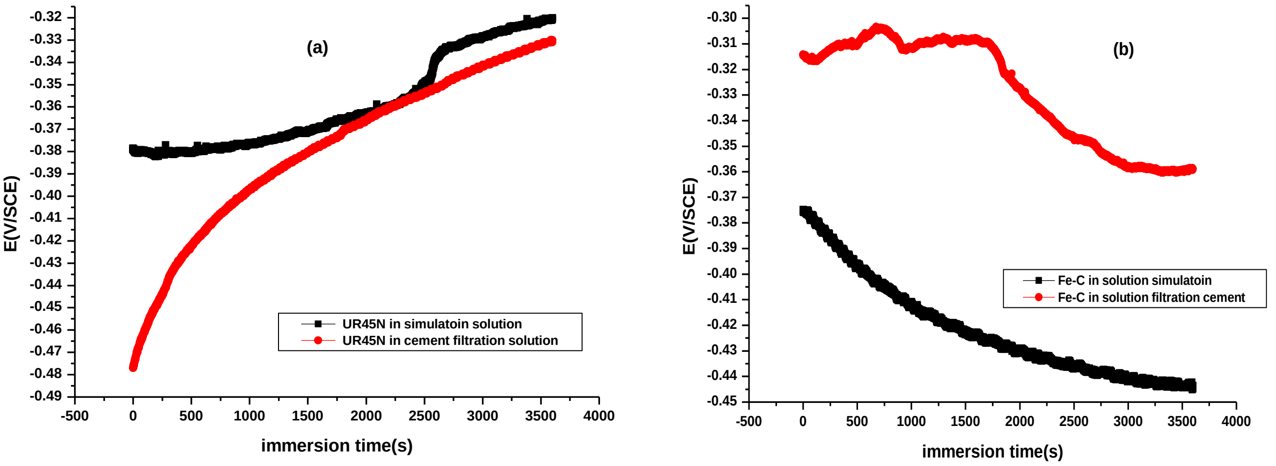

Figure 3: Open circuit potential evolution for two steels immersed in the stimulating solution and cement extract solution (a) UR45N, (b) Fe-C.

Figure 4 depicts the evolution of open circuit potential of steel samples in cement extract solution containing different concentration of chloride ions (NaCl).

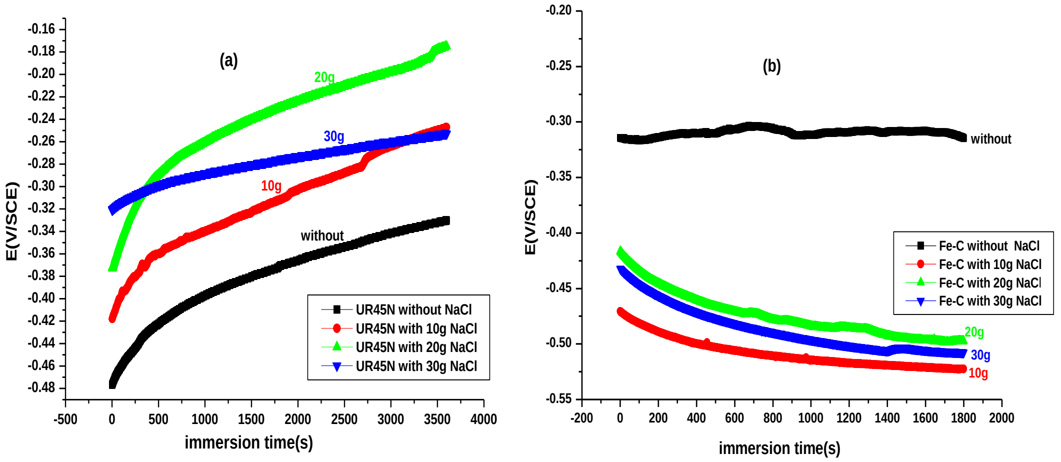

Figure 4: Open circuit potential evolution for two steels immersed in the cement extract solution (a) UR45N, (b) Fe-C.

Monitoring the open circuit potential as a function of immersion time of the two steels shows that the addition of chloride does not change the overall behavior of steel in the filtrate. For UR45N, the potential increases until to reach stationary state while in the case of carbon steel, there is a displacement of the potential to more negative values. However, increasing the amount of chloride in the middle has little effect on the values of the potential and the general shape of the curves.

3.3. Electrochemical study

- behaviours of UR45N and Fe-C steels in simulating solution and cement extract

The polarization curves of steels electrode immersed in the stimulating solution and cement extract solution are presented in figure 5. Electrochemical parameters like corrosion potential (E_{corr}) and corrosion current density

(I_{corr}) were determined (Table 4). As presented in figure 5 and table 4, the cathodic currents for UR45N are significantly decreased in the simulating solution. The contrary behavior is observed for Fe-C steel. The data show that rate of corrosion of stainless steel UR45N is less than Fe-C steel in all studied medium.

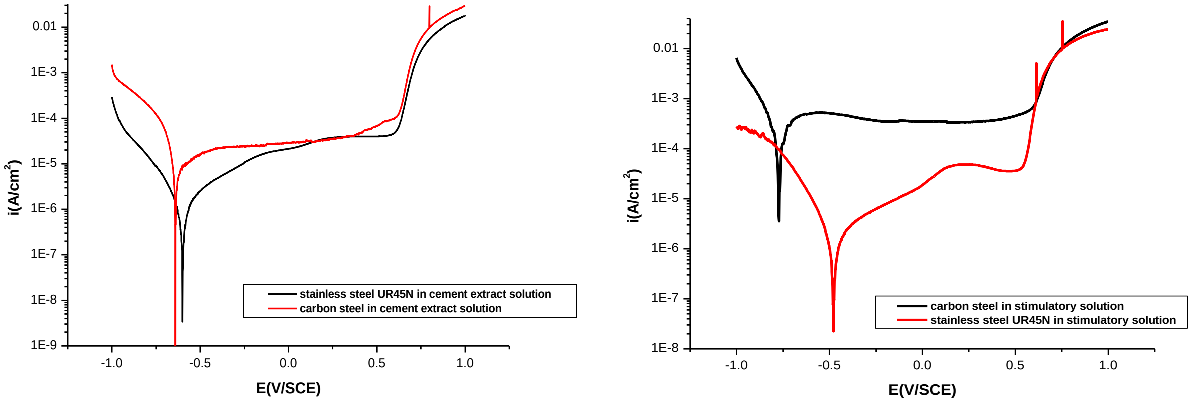

Figure 5: polarisation curves of UR45N and Fe-C immersed in the stimulating solution and cement extract solution

Table 4: electrochemical parameters

Solutions ***steel***	***Cement extract solution***			***Stimulating Solution***		
	E_{corr} mV/SCE	I_{corr} mA.cm^{-2}	V_{corr} mm/year	E_{corr} mV/SCE	I_{corr} mA.cm^{-2}	V_{corr} mm/year
Stainless steel UR45N	-597	$1.927\ 10^{-6}$	$1.491\ 10^{-5}$	-479	$7.322\ 10^{-6}$	$5.642\ 10^{-5}$
Carbon steel	-635	$4.335\ 10^{-5}$	3.20710^{-4}	-773	$4.289\ 10^{-4}$	$3.268\ 10^{-3}$

- *Effect of chlorides ions*

In order to study the effect of chloride ions on the electrochemical behavior of studied steels in cement extract, different mass of NaCl is added to the medium. The obtained curves are presented in figure 6. Addition of Cl- induce different behavior depending on the nature of steel. For Fe-C steel, an increase of the corrosion current density (Icorr) with the increase of chlorides concentration for Fe-C steel. The presence of chlorides resulted in a shift of the corrosion potential (Ecorr) toward more negative values in comparison to the result obtained in the absence of chlorides. For UR45N, the increase of chlorides concentration in cement extract induce a decrease of anodic current and shift the corrosion potential to more positive value.

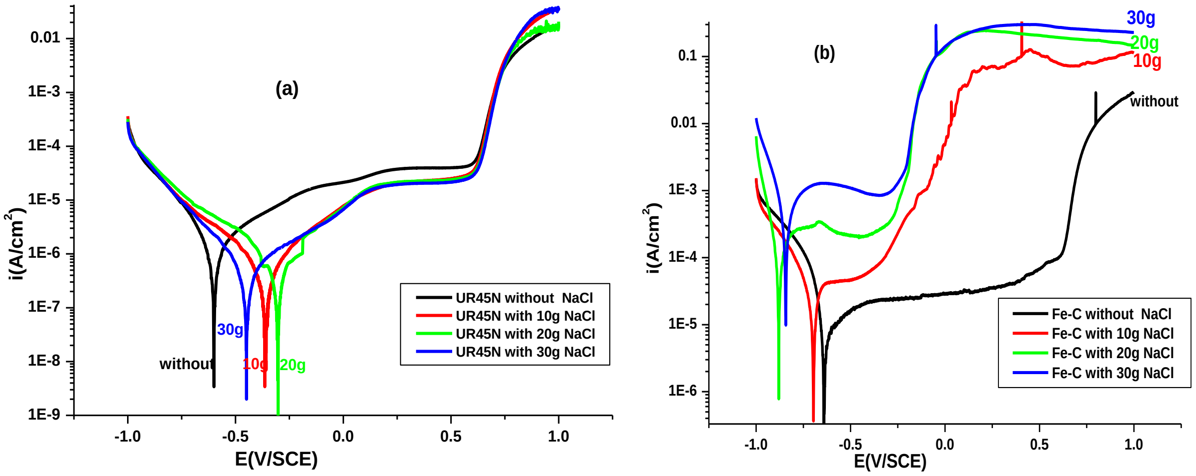

Figure 6: polarization curves for (a) UR45N, (b) Fe-C immersed in cement extract solution without and with different concentration of chlorides.

The electrochemical parameters for the different chloride concentrations are given in Table 5.

Table 5: Electrochemical parameters for UR45N and Fe-C immersed in cement extract solution without and with different concentration of chlorides.

	Parameters	**Without NaCl**	**With 10g**	**With 20g**	**With 30g**
Stainless steel UR45N	**E_{cor} (mV)**	-599	-370	-304	-453
	I_{cor} (A/cm^2)	9.86110^{-7}	3.2410^{-7}	3.09610^{-7}	$3.704\ 10^{-7}$
	V_{cor} (mm/year)	$7.599\ 10^{-6}$	$2.496\ 10^{-6}$	$2.385\ 10^{-6}$	$2.854\ 10^{-6}$
Carbon steel	**E_{cor} (mV)**	-637	-694	-890	-838
	I_{cor} (A/cm^2)	2.7110^{-5}	$2.92\ 10^{-5}$	$1.41\ 10^{-4}$	$2.74\ 10^{-4}$
	V_{cor} (mm/year)	$2.005\ 10^{-4}$	$2.160\ 10^{-4}$	$1.043\ 10^{-3}$	$2.027\ 10^{-3}$

- *Studies of specimens (in the mortar)*

Concrete acts as a barrier and blocks aggressive species, such as chlorides and carbon dioxide which can diffuse through and causes localized breakdown of the passive film inducing degradation of the metal. For structure immersed continually in seawater and the porosity of concrete can facilitate the diffusion of chlorides ions. When the concentration of chlorides ions is up to the critical value ([Cl$^-$]/ [OH-] > (0.6)), the corrosion begin and its rate increase with the concentration of chlorides.

The aim of this part of work is to study the behavior of UR45N and Fe-C steels embedded in concrete in seawater for different time of immersion. The obtained curves are presented in figure 7. For Fe-C steel, there is no modification on the behavior according to the immersion time and anodic current is high. When immersion time increases, the anodic current for UR45N decreases due to the passivation behavior of stainless steel. It is well known that stainless steel has a great corrosion resistance in the oxidizing corrosive environment because of the passive film which forms on the steel surface to protect the material from destroyed in the atmosphere.

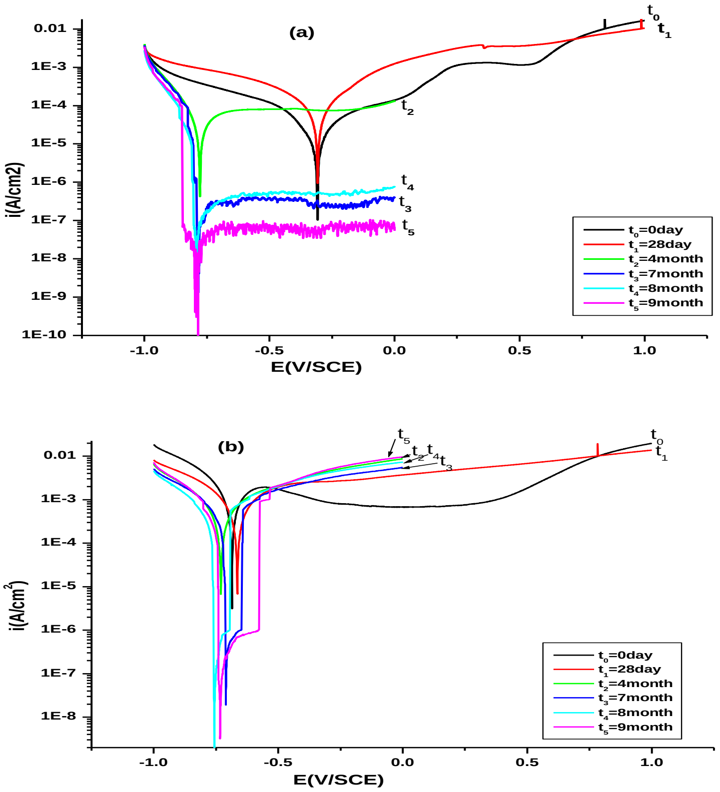

Figure 7: Polarisation curves of UR45N (a) and Fe-C (b) embedded in concrete for different time of immersion in seawater.

Conclusion

Failure of concrete structures due to corrosion of embedded steel is a major problem causing significant loss of money and time. Hence, there is a need to fully understand the root causes of failure before the repairing for effective remediation. The measure corrosion is a fundamental requirement for planning maintenance, repairing, and removal for reinforced concrete structures. The objective of this work is to study the corrosion of UR45N and Fe-C steels in different media (cement extract, simulating solution and embedded in concrete in seawater). Electrochemical studies combined with pitting tests show that the use of UR45N results in a reduction of the corrosion rate of reinforced stainless steel. A good agreement is observed between the pitting test results and those from electrochemical measurements. The investigations were done in presence of chloride ions and using solutions simulating the concrete interstitial electrolyte. Currents are more important in seawater for carbon steel than stainless steel UR45N. Stainless steel UR45N resist better than the carbon steel in concrete solution.

References:

1. BCA – Development of an holistic approach to ensure the durability of new concrete construction. Research report for the Department of the Environment, Project 38/13/21 (cc 1031), October 1997.
2. Tutti K. “Corrosion of Steel in Concrete”, Swedish Cement and Concrete Research Institute, Rapport 1982.
3. Tuuti, K., American Concrete Institute, Detroit, Michigan, SP-65 (1980). 223.
4. Browne, R.D., Proceedings, 7th European Ready Mixed Concrete Congress, Institute of Concrete Technology, London, England, 1983.
5. Ming-Te L., Ji-Jie L., *Cement and concrete Research*, 35 (2005) 540.
6. Quang Thanh N., Caré S., Berthaud Y., Millard A., *Fissuration du béton soumis à la corrosion*, 8 (2005) 1.
7. Fajardo G., Escadeillas G., Arliguie G., *Corros. Sci*. 48 (2006) 110.
8. Abdelkader N. thèse « La corrosion des aciers dans le béton à l’état passif et par carbonatation: Prise en compte des courants galvaniques et des défauts d’interface acier– béton », Université Toulouse III, Paul Sabatier (2010).
9. Elsener B., Bu¨ chler M., Stalder F., Bo¨hni H., *Corrosion* 56 (2000) 727.
10. Cigna R., Familiari G., Gianetti F., Proverbio E., Sheffield, Sheffield Academic Press, (1994) 878.
11. Velasco F., Blanco G., Bautista A., Martínez M.A., *Construction and Building Materials*; 23 (2009) 1883.
12. Bouchaïr A., Averseng J., Abidelah A., *Journal of Constructional Steel Research*; 7(9) (2008) 1.
13. Anis, M. A., Farid, B.J., Al-Janabi, A. I. M., JKAU: *Eng. Sci*., 2 (1990) l83.
14. Bautista A., Blanco G., Velasco F., Martınez M.A., *Construction and Building Materials*; 21 (2007) 1267.
15. Malumbela G., Alexander M., Moyo P., *Construction and Building Materials*, 24 (2010) 1051.
16. Ellobod E., *Thin-Walled Structures*, 45 (2007) 259.