

LABORATORY STUDY OF REINFORCEMENT PROTECTION WITH CORROSION INHIBITORS

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ABSTRACT

Concrete is a durable material and its performance as part of the containment function in NPPs has been good.

However, experience shows that degradation of the reinforced concrete structures caused by the corrosion of the reinforcing steel represents more than 80% of all damages in the world.

Much effort has been made to develop a corrosion inhibition process to prolong the life of existing structures and minimize corrosion damages in new structures.

Migrating Corrosion Inhibitor technology was developed to protect the embedded steel rebar/concrete structure. These inhibitors can be incorporated as an admixture or can be surface impregnated on existing concrete structures.

The effectiveness of two inhibitors (ethanolamine and diethanolamine) mixed in the reinforced concrete was evaluated by gravimetric measurements. The corrosion behavior of the steel rebar and the inhibiting effects of the amino alcohol chemistry in an aggressive environment were monitored using electrochemical measurements and SEM investigations.

Key words: (Concrete, Steel, amino alcohol-based inhibitors, Inhibition efficiency)

Introduction

Corrosion is one the main cause in the durability of material and structures. Much effort has been made to develop a corrosion inhibition process to prolong the life of existing structures and minimize new structures corrosion damage. Carbon steel is mostly used engineering materials despite its relatively limited corrosion resistance. Reinforcing steel embedded in concrete shows a high amount of resistance to corrosion. The cement paste in the concrete provides the alkaline environment that protects the steel from corrosion by forming a protective oxide film. The corrosive species like carbonation and chloride ions, can penetrate through the concrete pores to the rebar oxide layer and this passive layer can be deteriorate, thereby requiring additional help to prevent corrosion damage.

Corrosion protection can be achieved by isolating the reinforcement bars of the corrosive environment by using the "corrosion inhibitors," which forms a chemical barrier at the interface steel/concrete. Migrating corrosion inhibitors (MCI) have often been used to protect the embedded steel rebar/concrete structures.

MCI influences to both cathodic and anodic process by a protective layer at the surface of steel. The influence of MCIs on the steel rebar corrosion in concrete is indicated significantly to retard corrosion process and especially to act important role in delay of reinforcement steel corrosion in concrete.

MCI are mixed (anodic or cathodic), amine-based inhibitors and can be incorporated either in the initial concrete mixture or can be applied to existing concrete surface. These inhibitors can also be used as additives in concrete repair or can be injected into the cracks.

Experimental procedure

The objective of this study was to investigate the corrosion resistance of mild steel rods embedded in concrete, by addition of organic inhibitor containing amine (e.g. ethanolamine and diethanolamine) in fresh concrete. The concentration of the inhibitors was 22.3 l/m³.

Generally, organic inhibitors use compounds that work by forming a monomolecular film between the metal and the water. In the case of film forming amines, one end of the molecule is hydrophilic and the other hydrophobic. These molecules will arrange themselves parallel to one another and perpendicular to the reinforcement forming a barrier. The inhibitor migrates to the concrete capillary structure, first by liquid diffusion via the moisture that is normally present in concrete, then by its vapor pressure [1], [2].

1. Preparatory work for samples

Steel reinforcement type PC52 was cut in 130 mm long specimens. The composition of mild steel used is presented in **Table 1**.

Table 1 PC-60 type reinforcement steel composition

Steel Mark	C	Mn	Si	S	P	Cr	Ni	Mo	Ti	V	W	Other Elem.
PC60	≤ 0.27	≤ 1.7	≤ 0.65	0.04	0.04	0.3	0.3	-	-	0.1	-	Cu= 0.3

The rods were cleaned and after cleaning, their weights (initial weight) were taken in an electronic balance with accuracy of four decimal because the weight of the corrosion product comes in milligrams.

The rods used for electrochemical tests are connected by stainless steel wires at one end, then was sealed with epoxy material for avoiding galvanic corrosion. Then the rods are placed in cylindrical mould at 20mm of their bottom and the concrete is added so to have 20mm cover at the top. The composition of concrete is presented in **Table 2**.

Table 2 Concrete admixture composition

Materials	Concrete class	
	C25/30(Bc30)	
	Gravimetric	Volumetrical
	Kg/m ³	parts
Cement CEM II/A-LL 32,5R	675	1
Sand 0-3mm	650	0,75
Sand 3-7mm	650	0,75
Wather	230	0,45

2. Samples testing

The specimen was cylindrical with 170mm high and 60mm diameter. The concrete specimens were kept at room temperature for 24 hours and then demoulded for placing them in water for curing. After 28 days of curing, the samples were subjected to alternate wetting (3.5% solution of sodium chloride)-drying (at room temperature), so as to get accelerated corrosion. In **Figure 1** are presented the samples immersed in NaCl 3.5% solution.



Figure 1 Samples immersed in NaCl 3.5% solution

3. Samples measurements

- Weight loss test is a destructive technique in which the rods are weighed before embedding into the concrete and after the corrosion attack. Periodically the concrete specimens are broken open and rods are taken out for weighing. The weight difference is a measure of corrosion rate.
- SEM investigation were performed using “electron-scan microscope “TESCAN VEGA LMU”
- Electrochemical measurements were performed using Princeton Applied Research electrochemical system model 2273 coupled with an electrochemical cell with three electrodes - working electrode (test sample), auxiliary electrodes of graphite and reference electrode (calomel). Test temperature was 25°C. The following types of electrochemical measurements have been made:
 - Potentiodynamic determinations to emphasize the carbon steel corrosion susceptibility in concrete specific environment from the concrete/ steel system, with/without inhibitor addition.
 - Electrochemical impedance measurements (EIS) in boric acid / sodium borate solution on specimen with/without inhibitor addition and maintained in 3.5% sodium chloride solution.

Results and discussion

In this work the several electrochemical measurements have been made.

Potentiodynamic measurements were made to emphasize the influence of inhibitors on the carbon steel corrosion susceptibility in concrete specific environment from the system concrete/steel in presence of sodium chloride. Overlapping the curves corresponding to specimen with concrete uninhibited and inhibited with ethanolamine and diethanolamine respectively have obtained the following results (**Figure 2**, **Figure 3** and **Figure 4**). Measured potentiodynamic polarization curves indicated that by addition of the inhibitor the passive region appeared. In both cases the experimental results indicate that migrating corrosion inhibitor offers an effective inhibiting system for protecting reinforced concrete.

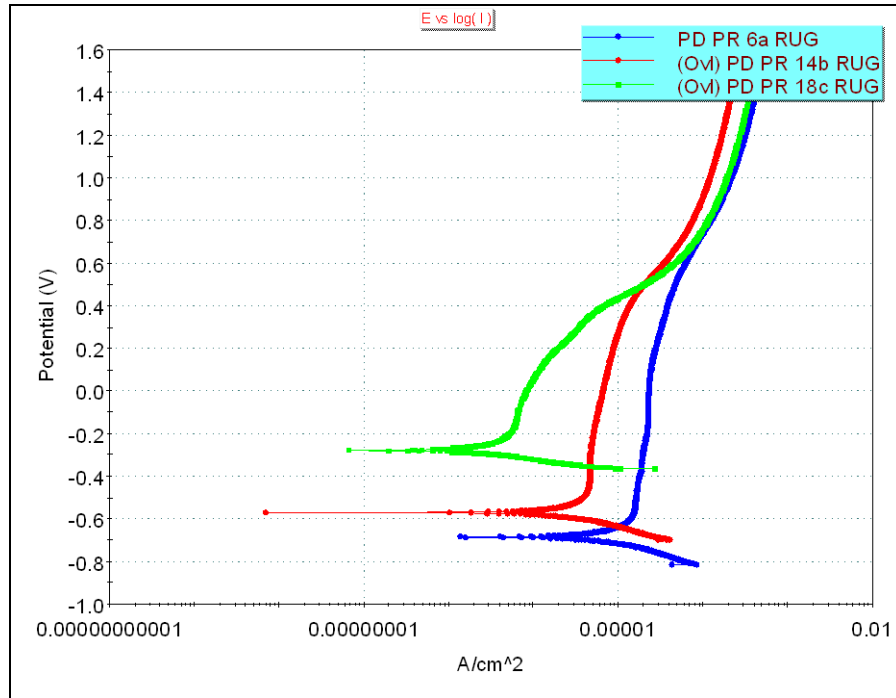


Figure 2 PD curves corresponding of samples with steel in concrete: a) without inhibitor(blue), b) with ethanolamine(red),c) with diethanolamine (green), prior tested 60 days by wetting(in 3.5% NaCl solution) –drying

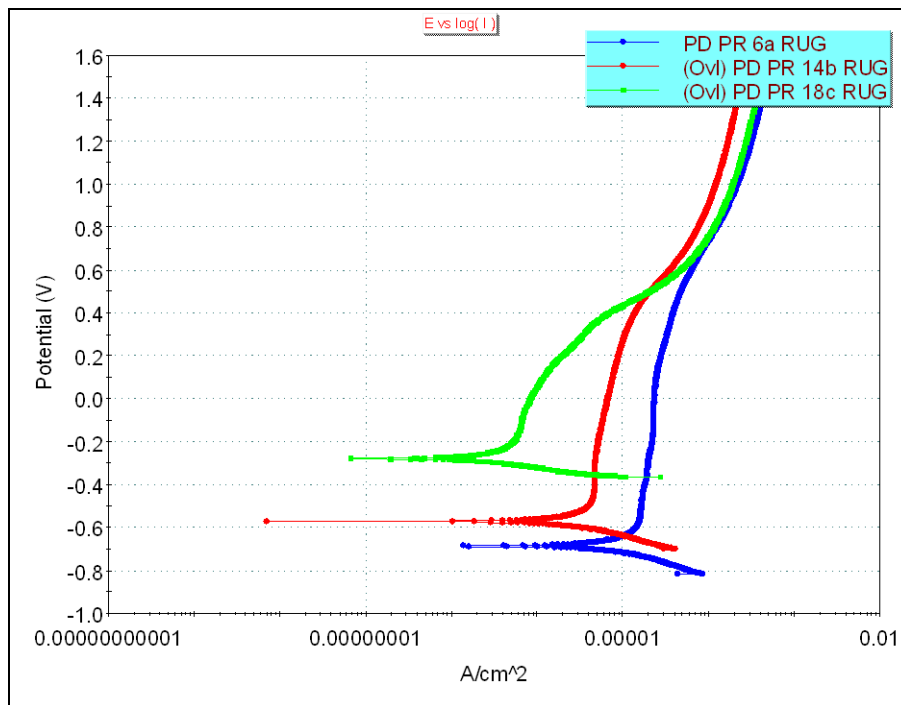


Figure 3 PD curves corresponding of samples with steel in concrete mixed with ethanolamine, prior tested for:a)45 days(blue,) b)60 days(red),90 days(green) by wetting(in 3.5% NaCl solution) –drying

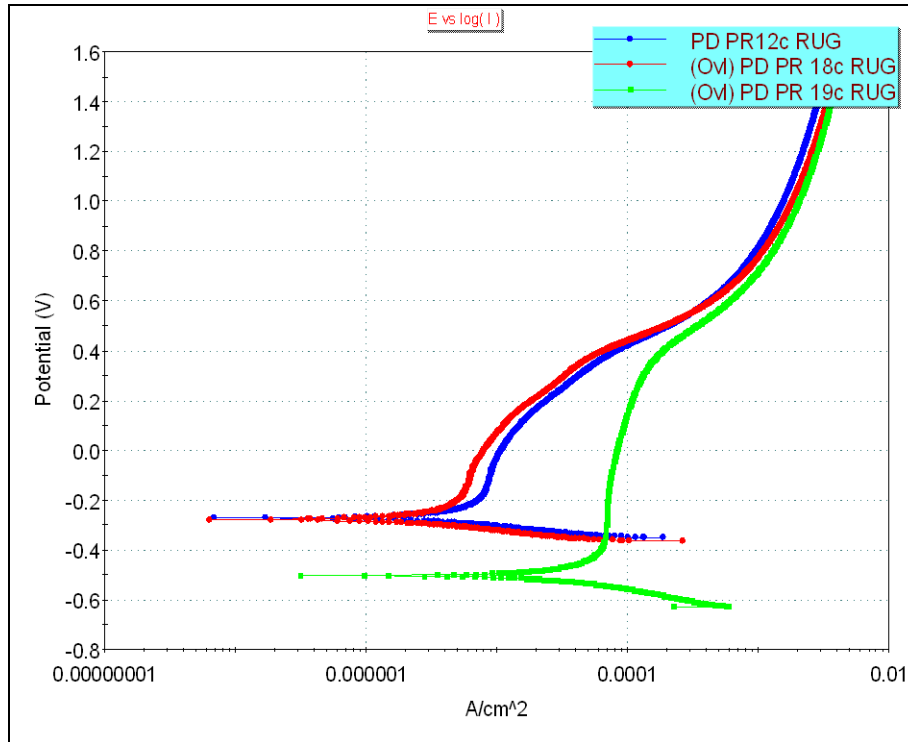


Figure 4 PD curves corresponding of samples with steel in concrete mixed with diethanolamine, prior tested for: a) 45 days (blue) b) 60 days (red), 90 days (green) by wetting (in 3.5% NaCl solution) – drying

There are many findings about the film forming ability of organic inhibitors: the thickness and composition of the protective film depends on the concentration of the inhibitor. Inhibitors of this type were reported to be adsorbed on the mild steel surface in layers of 2-10nm thickness [3]. Therefore, a possible way of reducing corrosion is blocking active areas on the surface of the metal by molecules adsorbed.

Electrochemical impedance spectroscopy is an important method to characterize many electrical properties of materials and their interfaces. Therefore, this technique is widely used for determining the corrosion susceptibility of steel reinforcement in concrete, too.

For the majority of the specimen, equivalent circuit corresponding to the best fitting is with three time constants and a diffusion element (also used by SHI XianMing and others[4]) (R (C (R (Q (R (C (RW)))))). For some of the concrete specimen, such as that which was uninhibited and tested for 60 days, the EIS data can be fitted using a simple equivalent circuit, with two time constants (without the intermediate frequency loop which characterizes the corrosion products). For the best comparison of the circuit parameters evolution (R and C) over testing period we used the same equivalent circuit presented in **Figure 5**.

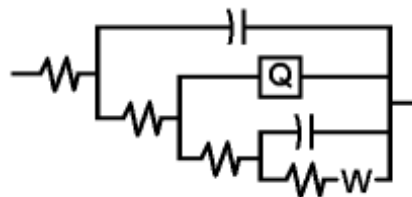


Figure 5 Equivalent circuit

Analogous with SHI XianMing and others [4], we considered that this electrochemical system consists in three interfaces: electrolyte -concrete interface, steel-concrete interface, and steel - electrolyte respectively.

Figure 6 shows Nyquist diagram which best accentuate partition into three interfaces.

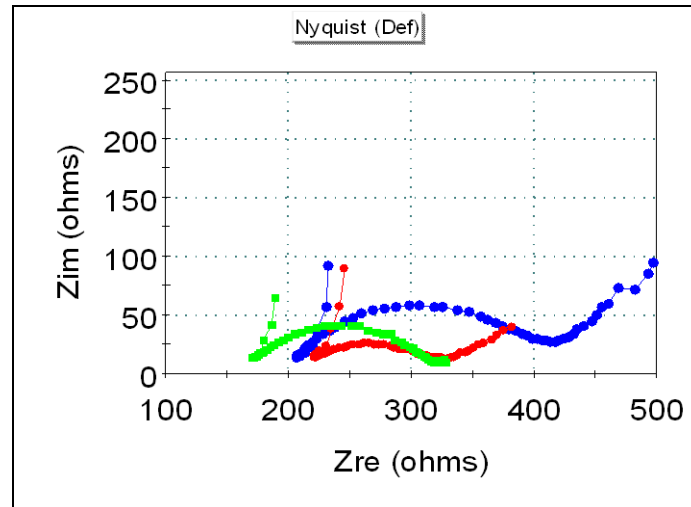


Figure 6 Nyquist curves corresponding of samples with steel in uninhibited concrete inregistered after testing: a) 45 days (blue) b) 60 days (red), 90 days (green) by wetting(in 3.5% NaCl solution) – drying

The high frequency loop can be assigned to properties of interface electrolyte- concrete, with R_1 and C_1 as the electrical resistance and capacitance of concrete mixture. Further evolution of these parameters over time for the samples subjected to wetting (in 3.5% NaCl solution) / drying (at room temperature) cycles, can be attributed to a permanent changing of pore fluid chemistry and cement hydration with participation of chloride or inhibitor.

Intermediate frequency loop can be assigned to properties of steel-concrete interface, R_2 and C_2 representing the electrical resistance and capacitance of the interfacial film which consists mainly of corrosion products.

Low frequency loop can be attributed to steel-electrolyte interface properties with R_3 and C_3 representing the charge transfer resistance of steel (mainly polarization resistance) and double layer capacitance of the inhibitor film on the steel surface, as well as the Warburg impedance which characterizes the diffusion of species through the interface.

The addition of the inhibitor increases the polarization resistance of steel, with reduction of corrosion rate of steel after subjecting the samples to several successive wetting (in 3.5% NaCl solution)/drying (at room temperature) cycles.

Images of secondary electrons illustrating the topography of the surface and deposits form by SEM analyses have been obtained. Have been subject to the SEM examination the specimen tested by alternate cycles wetting (in 3.5%NaCl solution)/drying (at room temperature) for 60 days. The steel samples were removed from the concrete and then their surface was examined. Through the examinations carried out, we keep trace of, to make a comparison between one steel rebar removed from concrete specimen without inhibitor and another steel sample removed from concrete specimen inhibited with diethanolamine.

Figure 7 presents SEM image for steel sample removed from the concrete specimen uninhibited and prior tested by wetting / drying.

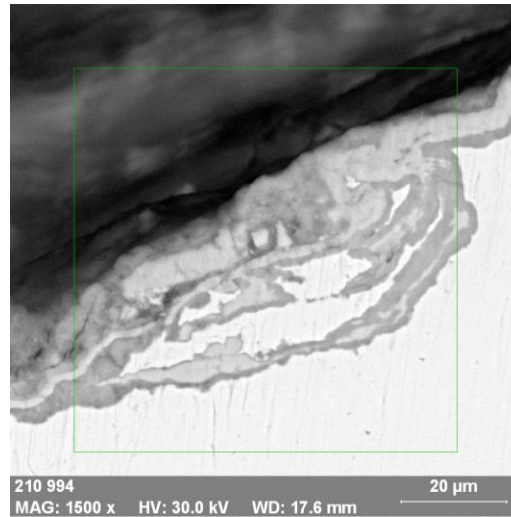


Figure 7 SEM images for steel sample removed from the concrete specimen uninhibited and prior tested by wetting (in NaCl 3.5%)/ drying

Figure 8 presents obtained data as a spectrum of surface chemical composition by EDS investigations.

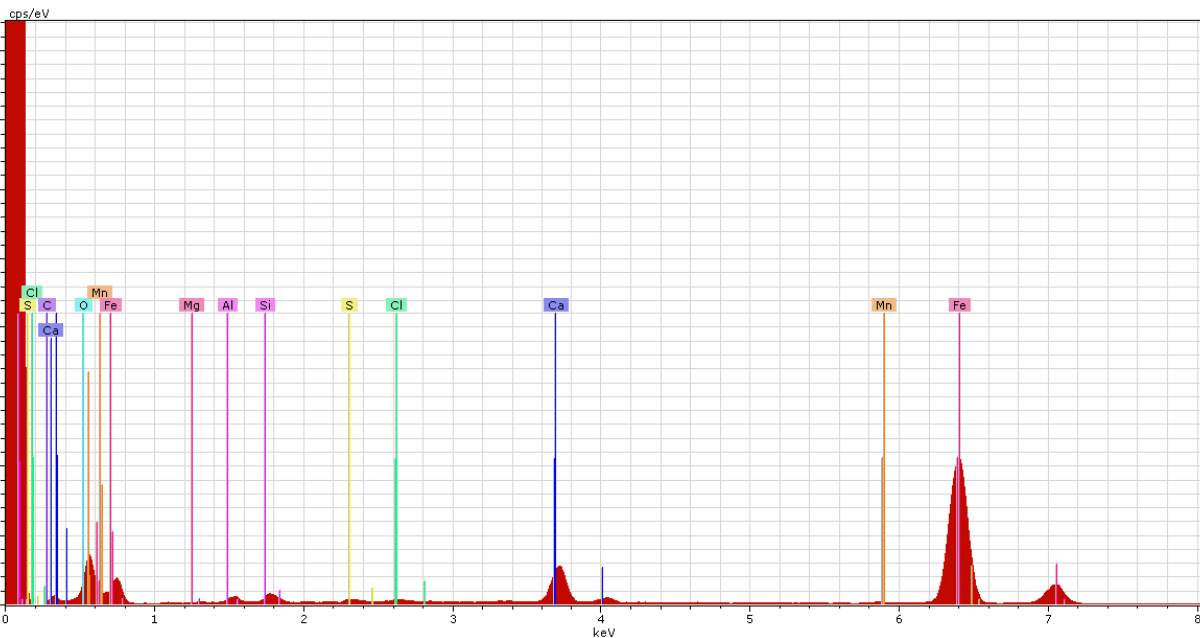


Figure 8 Spectrum of surface composition EDS for steel sample removed from the concrete specimen uninhibited and prior tested by wetting (in NaCl 3.5%)/ drying

By the presence of chlorine on the surfaces of the steel removed from the concrete specimen without inhibitor is confirmed its influence in corrosion production, and the results are in accordance to their obtained from electrochemical measurements.

In **Figure 9** is presented the SEM image for surface morphology of carbon steel rebar previously embedded in concrete with inhibitor diethanolamine and tested by wetting (in 3.5% NaCl solution)/drying (at room temperature).

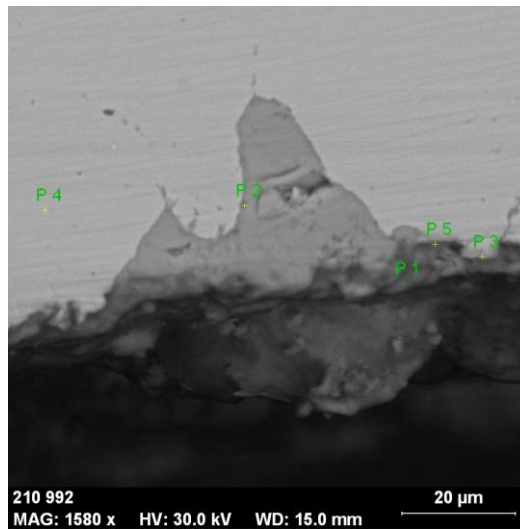


Figure 9 SEM images for steel sample removed from the concrete specimen inhibited with diethanolamine and prior tested by wetting (in NaCl 3.5%)/ drying

For the same sample **Figure 10** shows the spectrum of surface composition EDS. In this case it is observed the absence of chlorine and at same the time, presence of nitrogen small percentage. The provenance source is assumed to come from the amino group composition of the inhibitor. For inhibited specimen, it can be assumed that the inhibitor has a tendency to migrate to the surface of the concrete steel, thus controlling the corrosion propagation induced by sodium chloride (through Cl⁻ ions disturbance from the steel-concrete interface).

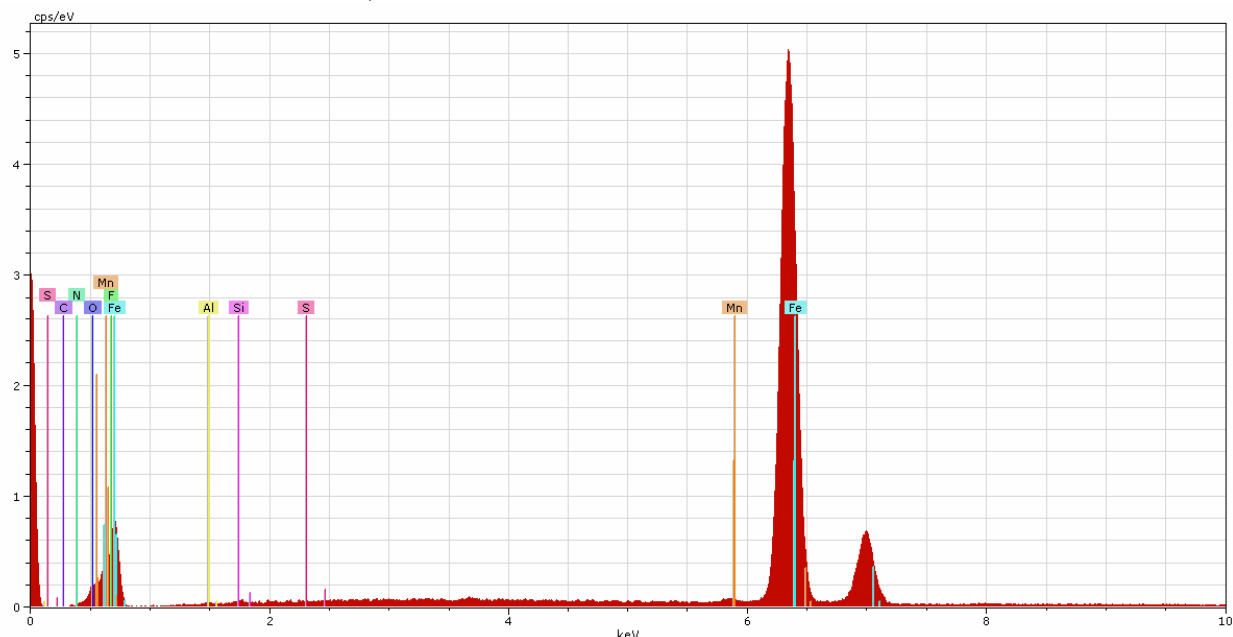


Figure 10 Spectrum of surface composition EDS for steel sample removed from the concrete specimen inhibited with diethanolamine and prior tested by wetting (in sol de NaCl 3.5%)/ drying

From the weight loss, the corrosion rate is calculated by the formula given below [1]:

$$\text{Corrosion rate} = KW/ATD(\text{mm/yr}) \quad (1)$$

Where: K is 8.76×10^4 , a constant; W is the weight loss in grams; T is exposure time in hours; A is the surfaces area in $[\text{cm}^2]$.

The results of gravimetric measurements and inhibition efficiency E% calculated are represented in **Table 3**. These results are consistent with observations made after other investigations.

Table 3 Inhibition efficiency determined by gravimetric measurements

Specimen Cod	Test. Time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corroz. rate (mm/yr)	Inhib. Efficiency (E%)
1 (without inhibitor)	45	77.8512	77.6966	0.1546	287043037.2	
8 (ethanolamine)	45	80.9800	80.9136	0.0664	123283684.8	57.05045
11(diethanol-amine)	45	78.9241	78.9061	0.0180	33420276.0	88.35705
2 (without inhibitor)	60	84.4970	84.3356	0.1614	399557966.4	
9 (ethanolamine)	60	81.5631	81.4918	0.0713	176508568.8	55.82404
12 (diethanol-amine)	60	82.0932	82.0740	0.0192	47531059.2	88.10409
4 (without inhibitor)	90	80.9609	80.7602	0.2007	745272154.8	
10 (ethanolamine)	90	76.5504	76.5270	0.0234	86892717.6	88.34081
13(diethanol-amine)	90	81.7180	81.3300	0.1153	428150869.2	42.55107

Conclusions

- According published information, MCI presents the following characteristics when used in concrete for corrosion protection:
 - They are effective in corrosion protection of steel in concrete when used as an admixture or by surface impregnation and can be used in small dosages;
 - There are compatible with all additives and ingredients used in concrete mixes;
 - MCI do not affect concrete properties, are environmentally friendly, are not reactive and adsorb onto the rebar surface.
 - Amines are fast migrating and have a high speed shifts towards embedded reinforcement.
- The results obtained from the electrochemical measurements are confirmed by inhibition efficiency (E%) gravimetric determined, and certify that studied inhibitors are effective in corrosion protection of steel in concrete. Between the two studied inhibitors, diethanolamine presents a better efficiency over the long term in relation to ethanolamine.
- From the spectrum of surface composition EDS (for inhibited specimen), it can be assumed that the inhibitor has a tendency to migrate to the surface of the concrete steel, thus controlling the corrosion propagation induced by sodium chloride (through Cl^- ions disturbance from the steel-concrete interface).
- The presence in the spectrum of surface composition EDS of chlorine on the surfaces of the steel removed from the concrete specimen without inhibitor, confirm its influence in corrosion production.

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