

A rapid method to test the effectiveness of corrosion inhibitors in reinforced concrete

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INTRODUCTION

Corrosion of steel reinforced concrete (RC) is one of the major deterioration mechanisms causing economic and social losses [1]. The rate of corrosion depends strongly on the location of the structure. The major deterioration problems of RC structures are chloride-induced corrosion; sulfate-induced corrosion and carbonation. Another trigger of corrosion in RC is stray current [2].

For the last decades, the service life of RC structures is being considered in two phases: initiation and propagation of corrosion. The protection from the initiation phase is mainly achieved by designing of specific quality concrete. Various types of inhibitors are used for the mitigation of corrosion propagation. The high alkaline of pore solution passivates the steel embedded into the concrete. As long as the composition of the pore solution in concrete remains constant, the steel rebars are passivated. Whereas the passivated layer at the steel is destroyed, the propagation phase begins.

Currently, there are numerous strategies available for increasing the service life of reinforced structures exposed to severe environmental conditions, including the use of (a) low-permeability (high-performance) concrete, (b) chemical corrosion inhibitors, (c) protective coatings on steel reinforcement (e.g. epoxy-coated or galvanized steel), (d) corrosion-resistant steel (e.g. stainless steel), (e) non-ferrous reinforcement (e.g. fiber-reinforced plastics), (f) waterproofing membranes or sealants applied to the exposed surface of the concrete, (g) cathodic protection (applied at the time of construction), and (h) combinations of the above.

Corrosion inhibitors mostly act on the steel surface. The first mentioned of inhibitors in RC was examined in the late 1950s. Since then the most conventional inhibitor is calcium nitrite [3], but organic compounds are also known.

The standard methods for estimation of the efficiency of the chemical admixture against the corrosion in concrete are time-consuming (ASTM G109 - 07). However, industry and academia are always looking for a reliable accelerated test for this purpose. This paper is focused on the development of such an accelerated test providing the results within less than 10 days. The feasibility and efficiency of the proposed method are checked by testing two commercially available corrosion inhibitors.

MATERIALS AND METHODS

Materials

CEM I 52.5N supplied by Nesher Cement, Israel, is used for this study. Its mineral and chemical compositions are presented in Table 1.

Table 1. Mineral and chemical compositions of cement.

Mineral composition	wt.-%	Chemical composition	wt.-%
Alite	61.02	CaO	62.16
Belite	12.95	SiO ₂	19.02
C ₃ A cubic	5.86	Al ₂ O ₃	5.42
C ₄ AF	12.42	Fe ₂ O ₃	3.82
Bassanite	1.87	MgO	1.31
Anhydrite	0.28	TiO ₂	0.53
Portlandite	1.83	K ₂ O	0.37
Calcite	2.25	Na ₂ O	0.22
Arcanite	0.97	P ₂ O ₅	0.4
Aphthitalite	0.55	Mn ₂ O ₃	0.05
		SO ₃	2.48
		IR	0.76
		FL	2.8
		LOI total	2.93

Inhibitors

Two commercially available inhibitors were taken. The first one was migrating corrosion inhibitor based on amine carboxylate (MCI-2005, Cortec Corporation); the second one was based on calcium nitrite (Sika CNI), which helps to anodic protection by creating a passivation layer (Fe₂O₃) by electrochemical reaction between NO₂⁻ and Fe₂⁺. Sika CNI contains a minimum of 30 % calcium nitrite by mass. Both meet all ASTM C1582 requirements.

Preparation of mortar samples

Cement was mixed with water, natural quartz sand ($D_{max} = 2.36$ mm) and admixtures in a pan mixer and then cast in molds 50x50x50 mm. Water/cement ratio was 0.55; mixture proportions and properties are shown in Table 2. After 24-hour of hydration in sealed molds samples were immersed in water for 28 days (23 ± 2 °C). Compressive strength of the samples (with standard deviation) is shown in Table 3. Air contents and flow of hydraulic cement mortar of the samples was tested according to ASTM C109 / C109M, ASTM C185 - 15a and ASTM C1437 - 15.

Table 2. Mixture proportions and properties of mortar compositions

Materials		Specific gravity	Relative Mass	Unit weight [kg/m ³]	Air content [%]	Flow diameter [mm]
Reference	Sand	2.6	3.00	2,165	5.2	172
	Cement	3.1	1.00			
	Water	1.0	0.55			
MCI-2005 0.6/1000 Liquids	Sand	2.6	3.00	2,261	1.9	172
	Cement	3.1	1.00			
	Water	1.0	0.55			
	Admixture	1.185	0.0015			
CNI 10/1000 Liquids	Sand	2.6	2.97	2,146	7.1	166
	Cement	3.1	1.00			
	Water	1.0	0.525			
	Admixture	1.3	0.0283			

Table 3. Development of compressive strength of mortars in time

Sample	Compressive strength [MPa]				
	1 day	3 days	7 days	28 days	90 days
Reference mortar	15.4 ± 0.72	31.3 ± 1.16	33.5 ± 2.41	44.1 ± 0.11	48.9 ± 1.20
Mortar with MCI-2005	13.4 ± 0.42	30.7 ± 1.80	33.9 ± 1.38	42.1 ± 1.95	42.9 ± 2.60
Mortar with CNI	9.10 ± 0.07	24.5 ± 0.48	30.5 ± 1.00	38.8 ± 2.95	44.9 ± 1.05

Accelerated test

To simulate the natural corrosion that occurs in RC structures, the specimens were exposed to the corrosive environment in the laboratory. The corrosion acceleration system is presented in Figure 1 (a) and consists of a plastic container filled with 5% NaCl solution (pH = 6.2...7.1). The specimens are 6 reinforced concrete cubes placed over wooden spacers and immersed in a solution, so that the top of the samples is higher than the surface of the solution by about 1 cm. The rebars protruding from the concrete samples are used as an anode, connected to a positive terminal, and the stainless-steel plates (cathode) are connected to the negative terminal of the direct current (DC) power supply. The process starts by applying a constant voltage to the system, which is set at 3.6 and 7.2 volts. The electric current passing through the samples is measured every 1 minute and the values are saved in the data logger. The experiment ended after crack width reached 0.10...0.15 mm; these values correspond to upper limits set by international standards in RC structures exposed to chloride attack. Figure 1 shows a schematic diagram of the system and a photo of the experimental system from one of the trials.

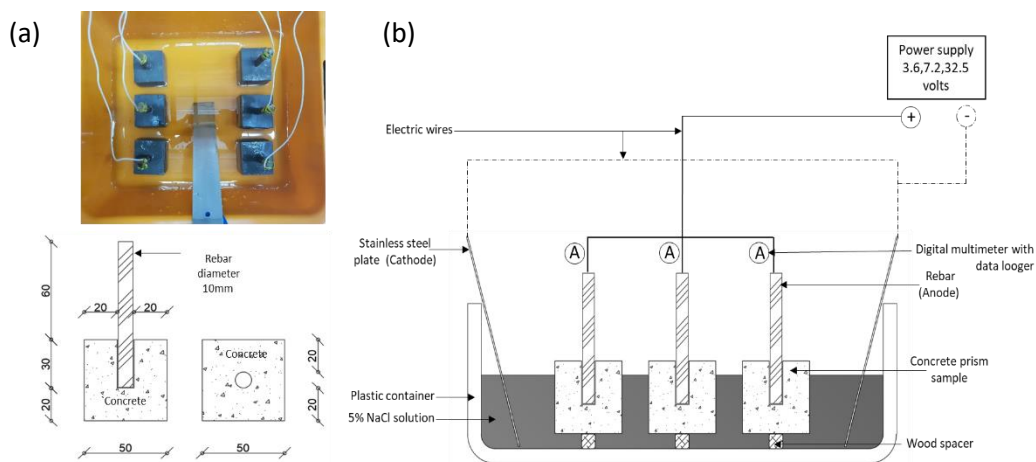


Figure 1. Corrosion acceleration system (all dimensions are in mm)

RESULTS

It was found that the introduction of a CNI inhibitor dramatically decreases the early-age strength (Table 3). However, after 90 days of hydration the strength is close to that of the reference. MCI-2005 admixture has also a negative influence on the early-age strength, but to lesser extent than CNI. Moreover, MCI-2005 notably reduces the air content, which is also directly related to the strength properties. In any case, all the samples exhibit similar 28-days strength, that allows comparing the influence of the inhibitors.

The samples are subjected to a constant electrical voltage, while electrical resistance (ER) develops over time (Figure 1). The measurement proceeds until the drop of ER, which indicates

the appearance of cracks along the rebar. As ER decreases, crack opening increases, until it reaches a steady state. Table 4 shows the times of crack formation in the samples tested with the electric voltage of 3.6 and 7.2 V, respectively. It can be seen, that CNI is not an effective inhibitor. This can be explained by the fact that the presence of chloride and sulfate ions can damage the passivation layer, so there is faster cracking development, than in the reference sample. Similar results have been already described elsewhere [4]. With the increase of electrical voltage, the effect of the inhibitors decreases. It is worth to note that the strength of the sample has a significant influence on the time of crack formation. A confirmation of these results is found in the work of Montes, Bremner and Lister [5]. The natural electrical voltage measured in our work was 0.17 ± 0.1 V, which corresponds to regular concrete. For such a small voltage both types of corrosion inhibitors are expected to serve better.

Table 4. Cracking time in mortar samples under 3.6 and 7.2 volts

Sample	Reference		MCI-2005		CNI	
	3.6	7.2	3.6	7.2	3.6	7.2
Voltage in the system [V]						
Average time to crack [min]	6,534.5	3,961.5	8,812.5	4,234.5	4,936.5	3,861.0
Percentage [%]	100	100	135	106.8	75.5	97.5

CONCLUSIONS

The rapid laboratory method to test the effectiveness of corrosion inhibitors in reinforced concrete has been proposed. The observations from testing two types of corrosion inhibitors yielded the following conclusions:

- The proposed method is user-friendly and allows easy and quick estimation of the efficiency of corrosion inhibitors.
- The reliable results can be obtained within 10 days.
- At a voltage of 7.2 volts, the effect of the inhibitor is negligible, and the strength of the concrete is act as the determining factor.
- It is shown that increasing the voltage reduces the duration of the experiment, while the reliability of the results decreased. The optimum voltage for the present series of experiments is considered 3.6 V. This voltage might be reduced further to 1.2 V (the upper threshold in ordinary reinforced concrete) the future experiments, which in turn is going to increase the precision of the results.

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