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Effects of migrating inhibitors on corrosion of reinforcing steel covered with repair mortar

G. Batis [a,*], A. Routoulas [b], E. Rakanta [a]

[a] NTUA Chemical Engineering Department, Materials Science and Engineering Section, 9 Iroon Polytechniou, 15780 Athens, Greece
[b] TEI Piraeus, Physics, Chemistry & Materials Technology Department, 250, Petrou Rally and Thivon, 122 44 Athens, Greece

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Abstract

The present study concerns the investigation of the protective effect of migrating corrosion inhibitors, against rebar corrosion, in specimens of repair fiber reinforcement mortars, in relation to these containing corrosion inhibitors. The strain gauge (SG) measurement technique was used for fast corrosion measurements, under anodic potential application in corrosive environment of 3.5% wt NaCl solution. The corrosion protection effectiveness was also tested by galvanic current measurements between different categories of specimens in order to estimate the galvanic corrosion between repaired and non-repaired areas. According to these investigations the positive effect of the migrating corrosion inhibitors in fiber-reinforced mortars against corrosion of the rebars is evident, providing a prevention of steel rebars' corrosion in the cases of repairing concrete structures. The presence of fiber reinforcement in repair mortar specimens prevents the microcracking effects, resulting in decrease of concrete cracking due to reinforcement corrosion.

Keywords: Reinforcement corrosion; Reinforcement protection; Migrating inhibitors; Repair mortars; Strain gauges; Fiber reinforcement

1. Introduction

The corrosion protection of the reinforcing steel in a new concrete structure is dependent on interconnected factors such as:

- The high pH value (pH 12.5–13) of the pore solution of concrete which causes the passivation of the embedded rebars, due to the creation of tightly adherent thin film of oxides [1] (Fe_2O_3 or γ-Fe_2O_3).
- The concrete is a natural protective barrier between the reinforcement steel and the external corrosive environment [2].

Diffusion of the porous concrete matrix by chloride ions or carbon dioxide CO_2 leads to the destruction of passivation on the embedded rebars, resulting in the initiation of steel corrosion.

The qualitative characteristics (composition, hydration level, porosity, chloride diffusion coefficient) of the concrete layer covering the steel affect the corrosion rate.

The time of corrosion initiation depends on external factors as well (cracks in the concrete, depth of the steel cover, chloride ions concentration) [3].

The strain gauge (SG) technique, used in this study, for a fast monitoring of corrosion is based on the appearance of swelling stresses on the area of steel rebars into the concrete. The purpose of the appearance of swelling tension is the formation of corrosion products, (Fe_3O_4, Fe_2O_3, FeO(OH)), which have higher specific volume than iron (Fe).

For the measurement of the swelling tension mentioned above, special SG sensors were embedded into the mortar specimens during their preparation [4,5].

The repair of damaged reinforced concrete structures is made by a new range of ready-mixed mortars offered. These materials consist of polymer-modified mortars containing migrating corrosion inhibitors.

The migrating corrosion inhibitors are of great interest for the repair of reinforced concrete since they can migrate through concrete via diffusion. Upon contact

* Corresponding author. Tel.: +301-7723-186; fax: +33-1-7723-184.
E-mail address: batis@chemeng.ntua.gr (G. Batis).

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with reinforcing steel they form a monomolecular protective layer which reduces corrosion by protecting the anodic as well the cathodic areas of the rebars [6,7]. However, in some applications, lower efficiencies in protection levels have been reported [8].

Microcracks also are affecting the mortars, accelerating the corrosion of the steel rebars. The presence of reinforcement fibers in the mortars is therefore affecting positively the shearing force between rebars and mortar, during the development of swelling stresses because of the corrosion and the relevant retardation of corrosion [9].

After a traditional repair of corroded reinforcements in a concrete structure due to chloride attack, the reinforcing bars often show a new corrosion at the edges of the repair. For this reason, the presence of migrating corrosion inhibitor in the area of the reinforcing steel and repair mortar is necessary. The inhibitor migrates through the concrete around the repair and its near surroundings to provide protection of the reinforcing steel not treated.

The positive influence of reinforcement fiber mortar in steel protection against corrosion is expected to be better in cases of using migrating corrosion inhibitors.

2. Materials and methods

2.1. Materials

The cement used in this work was a Greek cement (OPC). The chemical composition and physical properties are given in Table 1.

The aggregate used was a Greek sand of 250 μm < d < 4 mm diameter. The steel rebars used meet Greek specifications of Hellenic Organization for Standardization ELOT 971/94 corresponding to DIN 488/84.

Their chemical composition (% wt) was the following: C: 0.18, Mn: 0.99, S: 0.047, P: 0.023, Si: 0.15, Ni: 0.09, Cr: 0.09, Cu: 0.21, V: 0.002, Mo: 0.021.

Drinking water from Athens water supply network and INHIB-M, (corrosion inhibitor alkanolamines based on), were also added to the specimens preparation.

The finished repair mortar used, is a cement formulation, consisting of ready-mixed, fiber-reinforced powder and liquid resin (a water dispersion of special non-toxic polymers) containing migrating corrosion inhibitors VCI type (volatile corrosion inhibitors). They could be applied by trowel or spray rendering machine, with 2 kg/m^2 consumption per mm coating thickness.

3. Specimens casting

3.1. Specimens for SG measurements

The mortar test specimens were in the form of 80 mm × 80 mm × 100 mm prisms. The steel bars were machined on a lathe to the final diameter of 10 mm. They were washed with water, immersed for 15 min in a strong HCl solution with inorganic corrosion inhibitor, then washed with distilled water, alcohol and acetone and then weighed to an accuracy of 0.1 mg (ISO/DIS 8407.3). The shape and dimensions of specimens are shown in Fig. 1. The bars were embedded in the mold up to a depth of 15 mm. Thus the area of bars exposed to corrosion equals to 27.5 cm^2. Copper wire cables were connected to each steel bar for the electrochemical measurements. The specimens were covered with epoxy resin Araldite to protect the connection of steel with

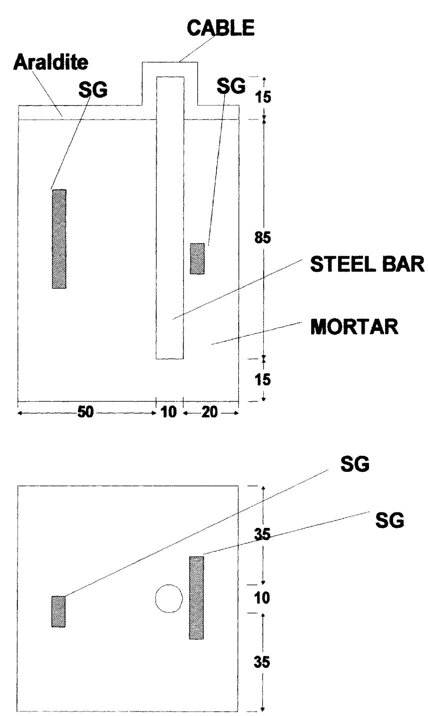

Fig. 1. Dimensions of specimens.

Table 1
Chemical composition (%) and physical characteristics of cement OPC

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	$CaO_{(f)}$	LOI	SP.GR	Blaine	(% water demand)
20.67	4.99	3.18	63.60	2.73	0.37	0.29	2.44	2.41	2.52	3.15	3990	27.6

copper cable against corrosion. Mortar specimens were stored in the curing room (20°C, 100% humidity) for 7 days and were immersed in the corrosive environment 3.5% wt NaCl solution.

3.2. Specimens for galvanic current measurements

The test specimens considered for the galvanic current measurements were 80 mm long, 80 mm wide and 100 mm high. They contained four identical steel bars in the position shown in Fig. 2. Copper wire cables were connected to each steel bar for the electrochemical measurements. Prior to the preparation, the surface of the steel bars was cleaned of rust according to ISO/DIS 8407.3 and weighed. Thereafter, the bars were placed in molds, as shown in Fig. 2, where the mortar was cast and stored at ambient conditions (20°C, 50% humidity) in the laboratory for 24 h. Then the specimens, after being demolded, were cured in tap water for 24 h. Finally, the specimens were stored for an additional 24 h at ambient conditions and thereafter the part shown in Fig. 2 was insulated with epoxy resin Araldite.

The proportions of materials used and specimens' code name are given in Table 2.

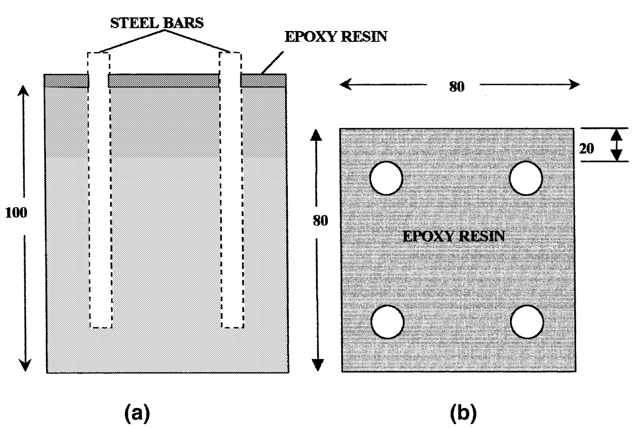

Fig. 2. Schematic representation of reinforced mortar specimens: (a) lateral view; (b) upper view.

4. Methods

The characteristics of SG sensor used are shown in Table 3 and the type is KM-30-120 of KYOWA. Distances and directions between the SGs are shown in Fig. 1.

In each specimen two SG sensors were embedded. One of them (horizontally mounted) measured the swelling of the specimen due to cumulative action of corrosion and other parameters (creep, wetting), which change the specimen's volume. This sensor was placed near the rebar. The second one (vertically mounted) was compensating the parameters of specimen volume variation except corrosion and it was placed far from the rebar [5,10].

For the acceleration of corrosion process of the reinforced specimens, which were immersed in 3.5% NaCl solution, impressed anodic potentials 1, 1.5 and 2.5 V, were applied for several days. Higher potentials 3, 4.5, 6 and 7.5 V were applied for the corrosion of resistant specimens. The test set-up, including a potentiostat for applying the anodic potential, the SG bridge-amplifier circuit and the multimeter for SG resistance measurements, is shown in Fig. 3.

The application of the anodic potential to the specimen by the potentiostat is made by means of a counter electrode, $80 \times 100 \times 20$ mm graphite auxiliary electrode and a saturated calomel reference electrode (SCE).

Before the application of impressed anodic potential to the specimen immersed in 3.5% wt NaCl solution, the output voltage of each SG is measured, in order to have the initial values as SGT_0 and SG_0^* [volume changes compensation (T) and corrosion (*)]. After the application of the anodic potential to the specimens in the given time (t), the output voltage of SG amplifier for each SG (SGT_t, SG_t^*) was measured at daily intervals and plotted against time.

The difference $(SGT_t - SG_t^*) - (SGT_0 - SG_0^*)$ corresponds to the compensated strains in mortar, caused by reinforcement corrosion. Considering strain gauges characteristics (resistance 120 Ω, gauge factor 1.8) and Wheastone bridge-amplifier circuit data (0.1 Ω

Table 2
Categories of specimens – composition ratio (wt)

Code name	OPC	Sand	Water	Inhibitor M	Remarks
SGO	1.0	3	0.5	–	–
SGM	1.0	3	0.5	0.01	–
SG38	–	–	–	0.01	Specimens made with repair mortar
SGS	1.0	3	0.5	–	3.5% NaCl solution used instead of water
SGSM	1.0	3	0.5	Inhibitor M sprayed	3.5% NaCl solution used instead of water

Table 3
Strain gauge characteristics

Sensing alloy	Backing	Operating temperature range (°C)	Resistance (Ω)	Gauge factor	Dimensions (mm)
Cu–Ni	Acryl	0–150	120	1.8	30 × 10 × 3

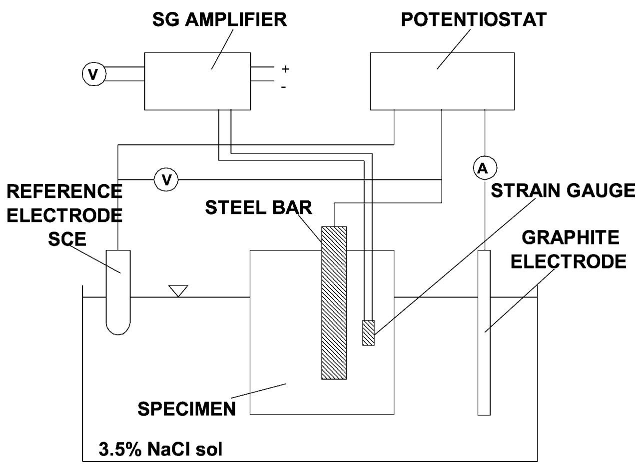

Fig. 3. Schematic diagram of the corrosion test set-up.

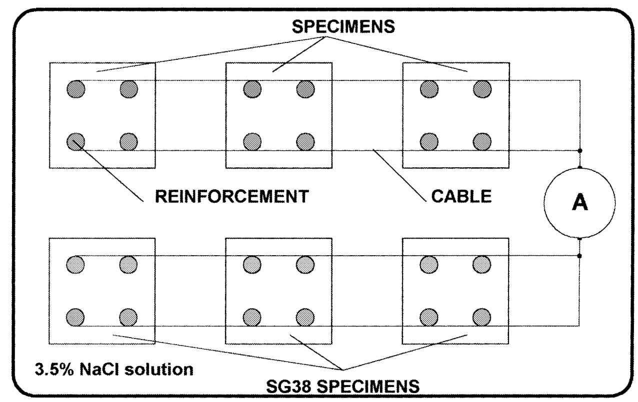

Fig. 4. Schematic diagram of galvanic current measurement set-up.

resistance change creates 600 mV SG value) it can be assumed the conversion: 1 mV of SG value measured = 0.94 μ strain.

At the end of the corrosion test the specimens were broken to reveal the steel rebar and the corrosion rate was determined by the mass loss of the reinforcing steel rebars.

For the examination of the corrosion inhibitors and proprietary repair mortar effectiveness, porosity was measured by mercury porosimeter (Carlo Erba, Mod. Milestone 2000).

Due to the fact that in the construction under proprietary repair mortars are used at the problematic points and not in the whole surface two different conditions regarding the degree of protection are created. An important issue in this repair is the formulation of galvanic micro- or macroelements which causes the most important failures in the construction. For this reason the creation of galvanic microelements was examined by measurements of current density, between ready-mixed mortar specimens, when combined with those of the other categories.

The mortars which were used for the experimental set-up were:

(a) Cement mortar without any kind of addition (SGO).
(b) Cement mortar with corrosion inhibitor addition (SGM).
(c) Cement mortar containing 3.5% wt NaCl solution instead of water (SGS).
(d) Cement mortar containing 3.5% wt NaCl solution instead of water and sprayed with corrosion inhibitor (SGMS).
(e) Ready-mixed repair mortar (SG38).

Three specimens from the category of ready-mixed mortar with interconnected steel bars were electrically connected with three specimens of each of the other categories (a)–(d). The galvanic current developed through the different specimen categories was measured by an ammeter as shown in Fig. 4.

The bottom 20 mm of the mortar specimens was immersed in 3.5% wt NaCl solution.

5. Results and discussion

The test results obtained for the given categories of specimens by the SG technique are illustrated in Figs. 5 and 6.

The specimen SGS, containing 3.5% wt NaCl solution in the mortar mass, shows a rapid expansion and mortar cracking due to corrosion, within 1 day of the anodic potential application.

During the first 20 days of the anodic potential application we observe a low rate of expansion of the specimen SG, which turns out in rapid expansion after 25 days, due to mortar cracking, caused by rebar corrosion.

Regarding the other specimens, an evident expansion (caused by corrosion) is not observed, excluding that appearing at the final stage of anodic potential appli-

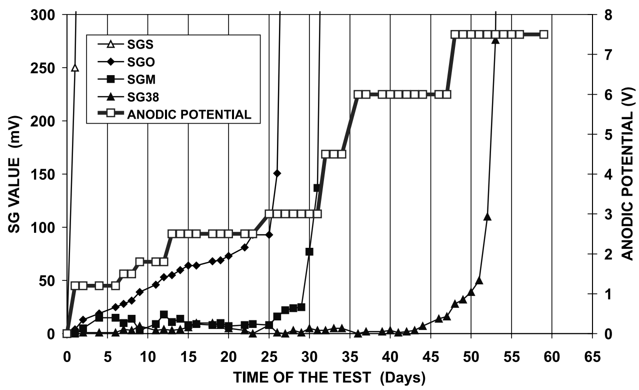

Fig. 5. SG values versus time of the test for different specimens.

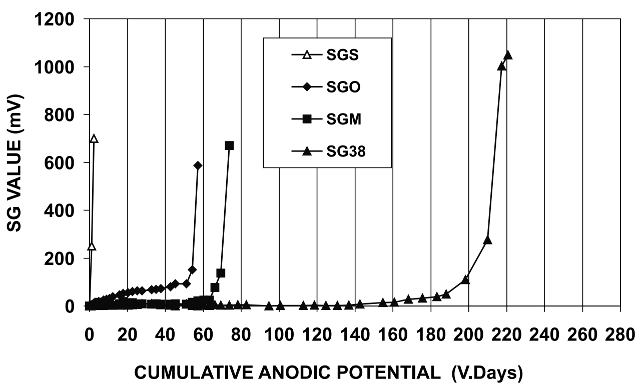

Fig. 6. SG values versus anodic potential applied for different specimens.

cation. The most probable explanation for this very low corrosion rate is the fact that the corrosion process is controlled by the inhibitor presence, forming a corrosion protective film in the rebar surface.

The time of corrosion initiation as indicated by an increase in the SG value for the specimen SGM is the 27th day. However, cracks were noted after 30 days. Regarding specimen SG38, corrosion initiation was noted after 45 days and the specimen cracked after 50 days.

Taking into account the stages of higher anodic potential applied in some specimens and in order to achieve a comparison between the various specimens' corrosion rates under the same conditions, the SG measurement results were also plotted against the integrated anodic potential in Fig. 6. It is observed that the cracking of specimens SGS, SG, SGM, SG38, is obtained at 2, 55, 72 and 200 V days, respectively.

It is evident that the specimen SGS presents the lower corrosion resistance compared with all other specimens, due to the high initial chloride concentration and that the fiber-reinforced mortar specimen SG38 containing an migrating corrosion inhibitor presents extremely high corrosion resistance.

Furthermore, the time between corrosion initiation and mortar cracking is more (5 days) in specimen SG38, made with fiber-reinforced mortar, as compared to the specimen SGM (3 days). This could be attributed to the improvement of tensile strength, due to fiber reinforcement and lower cracks development.

The correlation between SG measurements up to cracking and the rebars' mass loss caused by corrosion for the tested specimens is shown in Fig. 7 and Table 4. We observed that the full area of the steel bars was corroded, but the corrosion was mainly oriented to the bar side facing the graphite electrode (see Fig. 3).

A sufficient correlation provided between SG rates in mV/day and rebars mass-loss rates in mg/day for all specimens proves that the SG sensor elongation before cracking is affected by the formation of the corrosion products and consequently SG measurements correspond to the corrosion caused in steel rebars. SG measurements also record cracking of mortar resulting from the reinforcements' corrosion.

The corrosion rate in specimen SGO (without corrosion inhibitor) under anodic potential application was 109 mg/dm^2 day. The use of corrosion inhibitor M decreased the corrosion rate to 90.4 mg/dm^2 day. The corrosion inhibitor M is a mixed (anodic and cathodic) inhibitor that is physically adsorbed on the steel reinforcement surface [11].

The combined use of fiber reinforcements and corrosion inhibitor M (SG38) has effectively decreased the corrosion rate to 30 mg/dm^2 day. The positive effect of simultaneous use of corrosion inhibitors and fiber-reinforced polymer mortar has been reported by other investigators [12].

The total porosities (measured with Carlo Erba 2000 mercury porosimeter) of the mortar of specimens SG38 and SGO–SGM–SGS were 10.9% and 13.55–13.67–13.34%, respectively.

The total porosity of repair mortar specimen was lower than that of others. There is not a significant

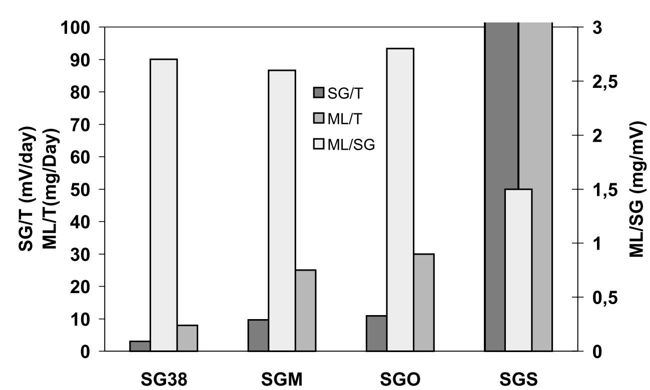

Fig. 7. Mass loss – SG values comparison for different specimens.

Table 4
Comparison of SG values – mass loss of rebars for different specimens

Specimen code	Mass loss (mg)	SG rate before cracking (mV/day)	SG value (mV)	Cumulative anodic potential (V. days)	Corrosion time (days)	Corrosion rate (mg/dm^2 day)
SGS	750	250	750	2	2	1364
SGO	750	10.9	600	55	25	109
SGM	746	9.7	700	72	30	90.4
SG38	429	3	1100	220	52	30

difference in the porosity of specimens SGO, SGM, SGS, due to the same proportion of materials used. The addition of corrosion inhibitor or chlorides does not affect effectively the total porosity.

Consequently, the lower porosity of SG38 specimen is a major factor of the lower corrosion rate obtained during the test.

In the case of construction under repair, although ready-mixed repair mortars' durability is critical, the important issue is the formulation of galvanic corrosion cells between parts of the steel reinforcements embedded into repair mortar and old concrete. For this purpose the galvanic currents between the repair mortar and cement mortars (SG38–SGO, see Table 2) were measured, as well the galvanic currents between repair mortar and mortars containing corrosion inhibitors (SG38–SGM). The evolution of galvanic currents versus time is shown in Fig. 8.

Mortar specimens with corrosion inhibitors present around 25% lower currents (low chances of forming galvanic cells). Experimental results of mass-loss measurements support our opinion that the corrosion decreases by about 30%. The variation of galvanic currents could be attributed to the mortar resistivity changes.

The evolution of galvanic currents versus time between repair mortar and common mortars including 3.5% wt NaCl solution (SG38–SGS) is shown in Fig. 9. The comparison is also for mortar specimens including

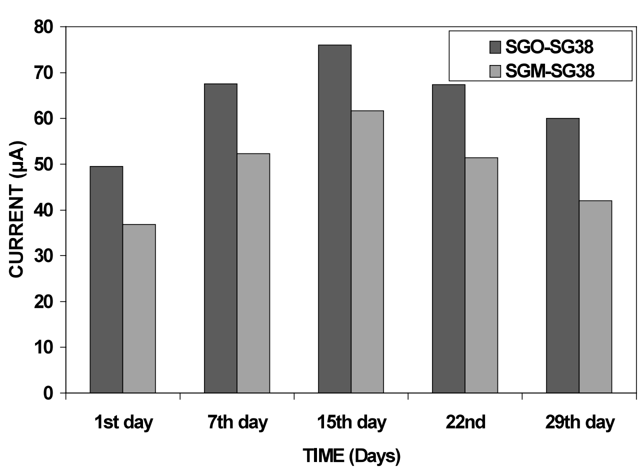

Fig. 8. Galvanic current versus time for specimens SGM, SGO.

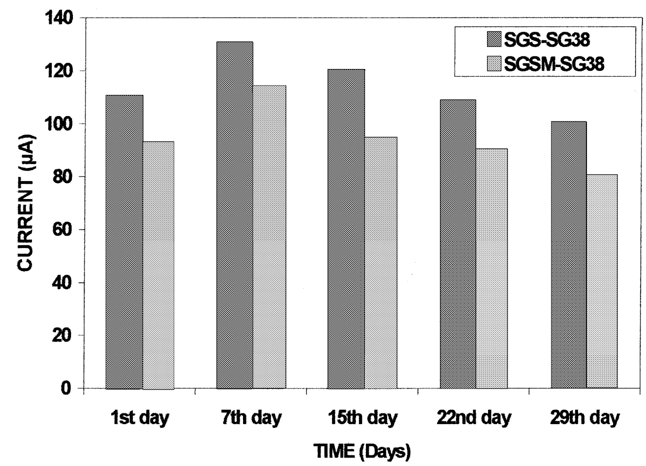

Fig. 9. Galvanic current versus time for specimens SGSM, SGS.

3.5% wt NaCl solution and corrosion inhibitor (SG38–SGSM). There is also a galvanic current decrease of about 20% in specimen including inhibitor.

The results confirm that, in the cases of topical repairs by mortars containing corrosion inhibitors, the presence of the same corrosion inhibitor in the repaired area decreases the formulation of galvanic corrosion cells.

6. Conclusions

Based on the results of corrosion measurements the following conclusions can be drawn:

- All the categories of specimens containing corrosion inhibitor exhibited lower rebars' corrosion as compared to that without inhibitor.
- The correlation between SG and mass-loss measurements for all categories of specimens provides comparative results of corrosion evaluation.
- Specimens made with fiber-reinforced mortar containing corrosion inhibitor exhibited the best corrosion protection results. This can be attributed to the combined straightening of protective passive layer and the lower mortar porosity. The positive effect of fiber reinforcements is proven by the slow rate of cracking, due to the tensile strength improvement by the fibers.

- The presence of migrating corrosion inhibitor provides lower galvanic currents between different mortar specimens, resulting in better protection of the steel rebar against corrosion.
- For the better corrosion protection of an existing concrete structure, the repairing process may include the use of migrating corrosion inhibitor, as well in the repair mortar as in the rebars and the surrounding concrete.

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