

Evaluation of Corrosion in Steel Reinforced Concrete with Brick Waste

Julieta D. Chelaru, Maria Gorea

Abstract—The massive demolition of old buildings in recent years has generated tons of waste, especially brick waste. Thus, a concern of recent research is the use of this waste for the production of environmentally friendly concrete. At the same time, corrosion of the reinforcement steel rebar in classical concrete is a current problem. In this context, in the present paper a study was carried out on the corrosion of metal reinforcement in cement mortars with added brick waste. The corrosion process was analyzed on four compositions of mortars without and with 15%, 25% and 35% brick waste replacing the sand. The brick waste has majority content in SiO_2 , Al_2O_3 , FeO_3 and CaO . The grain size distribution of brick waste was close to that of the sand ($d_{\max} = 2 \text{ mm}$). The preparation method of the samples was similar to ordinary mortars. The corrosion action on the rebar in concrete, at different brick waste concentrations, was investigated by electrochemical measurements (polarization curves and electrochemical impedance spectroscopy (EIS)) at 1 month and 26 months. The results obtained at 26 months revealed that the addition of the brick waste in mortar improved the anticorrosion properties in the case of all samples compared with the etalon mortar. The best results were obtained in the case of the sample with 15% brick waste (the efficiency was $\approx 90\%$). The corrosion intermediary layer formed on the rebar surface was evidenced by SEM-EDX.

Keywords—EIS, steel corrosion, steel reinforced concrete, waste materials.

I. INTRODUCTION

CORROSION of steel rebar is the main cause of failures of reinforced concrete [1]. Because reinforced concrete is one of the most used materials in the field of buildings, its destruction involves significant financial losses. On the other hand, the massive generation of the waste from building by demolitions is a large subject in the recent years [2], [3]. A sustainable development of modern society involves its reducing by recycling. Lately, a lot of research focused on the use of waste from civil construction to replace sand or aggregates in different proportions [2]-[5]. Also, a current concern of research is to find innovative solutions for protection against corrosion of reinforcements with low economic and low environmental impact [6]-[10]. In this context, the aim of this paper is to investigate the corrosion of steel rebar in mortar prepared with different concentrations of brick waste (0%, 15%, 25%, and 35%). The corrosion behavior of the steel rebar in these mortars at different concentrations of brick waste was investigated by electrochemical methods (polarization measurements and EIS).

J. D. Chelaru and M. Gorea are from the Chemical Engineering Department, Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, RO 400028, Romania (phone: 40-264-593833; fax: 40-264-590818; e-mail: julieta.chelaru@ubbcluj.ro, maria.gorea@ubbcluj.ro.).

The Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Analysis (EDX) was used to illustrate the intermediary layer formed on the rebar surface.

II. MATERIALS AND METHODS

A. Mortar Samples' Composition

The four compositions of mortar without and with 15%, 25% and 35% brick waste (BW) were studied. The BW, having composition as shown in Table I, was collected from an old, demolished building in Cluj-Napoca, Romania.

TABLE I
CHEMICAL COMPOSITION OF BW

Oxide	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
% wt	64.86	0.54	18.0	5.19	4.62	1.6	0.95	2.5

Loss on ignition = 1.74%

The BW contains a high percentage of SiO_2 (64.86%) and alumina oxide (18%) along to alkaline-earth oxides (CaO , MgO) and alkaline oxides (Na_2O , K_2O). Alkaline-earth oxides and alkaline oxides can be solubilized in aqueous solutions increasing the pH of the system. Increasing the pH of the system leads to corrosion protection of the reinforcement.

The experimental mortars were prepared in a laboratory cement mixer. The composition of the mortar samples is shown in Table II.

TABLE II
COMPOSITION OF TESTED SAMPLES

Sample	Cement [%]	Sand [%]	BW [%]	Water [mL]
S0	25	75	-	225
S15	25	60	15	225
S25	25	45	25	225
S35	25	30	35	225



Fig. 1 The mortar samples: (a) generally view; (b) cross section

The raw mortar samples were poured into metallic molds with 40 mm × 40 mm × 160 mm in size. The steel rebar with 6 mm diameter was embedded in middle of mortar samples (Fig. 1). The samples molds with mortar were maintained in RH 95% during 24 hours. For the corrosion tests, the samples were removed from the mold and cured in humidity atmosphere.

B. Electrochemical Tests

The corrosion behavior of steel rebar was investigated at 1 month and 26 months. Before and between the electrochemical measurements, the samples were maintained in a humid atmosphere (RH 55%). In order to ensure conductivity between the electrodes, before the corrosion tests, the samples were immersed in electrolyte (NaCl 3%). The electrochemical corrosion measurements were performed on a PC-controlled electrochemical analyzer PAR 2273 (Princeton Applied Research, USA) using a three electrodes cell containing a working electrode (WE - rebar with an exposed area of 9.5 cm²), a saturated Ag/AgCl/KCl electrode as reference electrode, and a Pt counter electrode.

The open circuit potential (OCP) for WE immersed in the corrosive solution was monitored for 1 hour. Then, EIS spectra were recorded in the frequency ranging from 10 kHz – 10 mHz with a disturbance voltage of ± 10 mV at 30 points/decade. The impedance data were fitted with R(QR) and R(CR)W equivalent electrical circuits, using the ZSimpWin V3.21 software. Immediately after the EIS measurement, the potentiodynamic polarization curves were recorded by scanning in a potential range of ± 20 mV and of ± 200 mV vs. OCP (for Tafel interpretation) with a scan rate of 0.166 mV/s. The testing temperature was 21 °C ± 2 °C.

C. SEM-EDX Analysis

SEM analysis was performed with a Scanning Jeol JEM5510LV (Japan) coupled with Oxford Instruments EDX Analysis System Inca 300 (UK) at 15 kV and spot size 39 μm.

III. RESULTS AND DISCUSSIONS

A. Corrosion Tests

In order to determine the corrosion behavior of steel rebar in different compositions of mortar, the experiments were started with recording the OCP of the samples in time. The OCP was measured vs. Ag/AgCl/KCl_{sat} and become relatively constant after one hour. The OCP values were situated between -425 mV and -492 mV for samples preserved in humid conditions for 1 month, respectively between -6 mV and -81 mV for samples preserved for 26 months.

Electrochemical Impedance Spectroscopy (EIS)

The EIS plots were recorded immediately after OCP in order to investigate the behavior corrosion of steel rebar in different compositions of mortar. The results are presented in Fig. 2. The Nyquist plots for samples that were maintained for 1 month in humid conditions indicated that the impedance spectra exhibit one depressed capacitive loop (Fig. 2 (a)). The impedance spectra were analyzed for all samples by fitting the experimental data with an equivalent electrical circuit that

contain only one R-C couple (Fig. 2 (a)); R_{ct} representing the charge transfer resistance and, C_{dl} the double layer capacity, at the rebar steel | electrolyte interface. The values of C_{dl} were calculated using (1):

$$C = (R^{1-n} \cdot Q)^{\frac{1}{n}} \quad (1)$$

where: Q is the constant phase element that replaced the capacitive element due to the roughness and inhomogeneities of the coatings; coefficient n represents the depressed feature of the capacitive loop in Nyquist diagram ($0 < n \leq 1$).

Analyzing the Nyquist plots in the case of samples maintained for 26 months in humid conditions, it can be noticed a completely different behavior compared with samples maintained for 1 month. The impedance spectra were analyzed for all samples by fitting the experimental data with a R(CR)W equivalent electrical circuit. The presence of Warburg impedance indicates that the electrochemical reactions are controlled by diffusion phenomenon (Fig. 2 (b)). The R_{Ω} represents the electrolyte resistance between the reference electrode and the work electrodes surface, in the case of both equivalent electrical circuits used. To understand the electrochemical process occurring at the WEs surface, the parameters for all samples were obtained by using the proposed equivalent electrical circuits. The quality of fitting procedure was evaluated by the chi squared (χ^2) values, which were of the order 10⁻⁴. The results are shown in Table III.

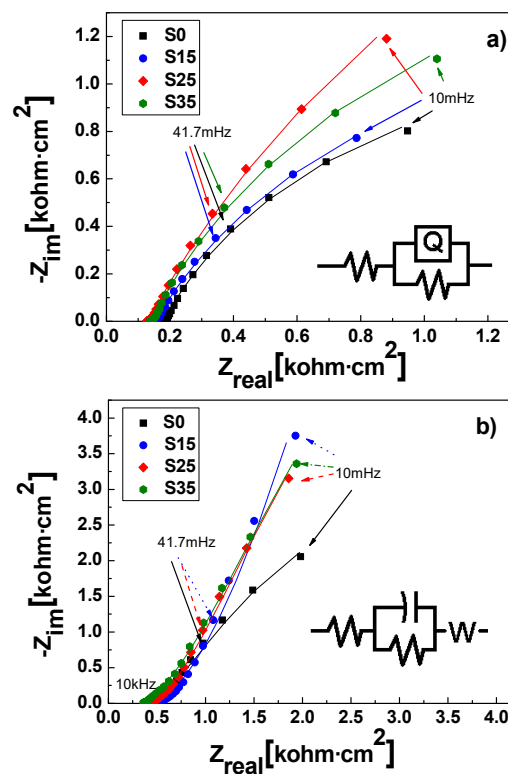


Fig. 2 Nyquist impedance diagrams for the rebar electrodes at: (a) 1 month, (b) 26 months, immersed in 3 wt.% NaCl; the lines represent fitted data

TABLE III
THE ELECTROCHEMICAL PARAMETERS

Time	S*	R_{Ω} [$\text{k}\Omega \cdot \text{cm}^2$]	Q [MF]	C [MF]	N	R [$\text{k}\Omega \cdot \text{cm}^2$]	$W \cdot 10^4$ [$1/(\Omega \cdot \sqrt{\text{Hz}})$]
1 month	S0	0.179	14.21	-	0.76	2.871	-
	S15	0.154	18.95	-	0.74	3.375	-
	S25	0.132	17.20	-	0.76	7.612	-
	S35	0.142	12.13	-	0.78	4.247	-
26 months	S0	0.441	-	13.38	-	2.82	25.55
	S15	0.414	-	6.69	-	126	22.11
	S25	0.443	-	7.76	-	16.26	25.38
	S35	0.368	-	7.54	-	17.33	22.13

*sample

Analyzing the data from Table III obtained after 1 month, it can be observed that the polarization resistance ($R = R_p$), which is an indicator of corrosion resistance, can be practically assimilated to the charge transfer resistance, and it is not influenced by the BW concentrations. In contrast, after 26 months, the R_p values are increased for all samples with BW. The highest R_p was observed for addition 15% BW ($R_p = 126 [\text{k}\Omega \cdot \text{cm}^2]$).

The Potentiodynamic Polarization Curves

To determine the corrosion current density (i_{corr}) and the corrosion potential (E_{corr}), the potentiodynamic polarization curves were recorded in the potential range of ± 200 mV vs. OCP (Fig. 3).

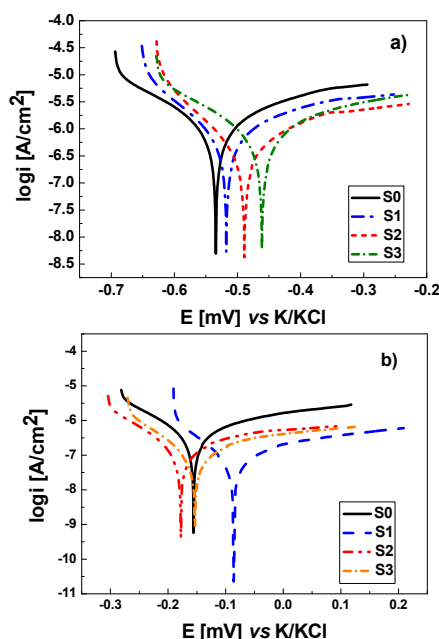


Fig. 3 Polarization curves (± 200 mV vs. OCP) recorded for rebar imbedded in mortar: (a) 1 month and (b) 26 months

For all mortar samples, the results obtained by Tafel interpretation of the polarization curves are presented in Table IV. Based on these results, it can be observed that after maintaining the samples in a humid atmosphere for 1 month,

the values of i_{corr} are very close in all cases. This behavior assumes that the addition of BW has no influence on the corrosion properties for a short period of time. On the other hand, analyzing the results obtained after 26 months, it can be observed that the values of i_{corr} indicated a pronounced decrease for all samples that contained BW. The highest corrosion resistance ($R_p = 90.47 \text{ k}\Omega \cdot \text{cm}^2$) and the lowest corrosion current density ($i_{\text{corr}} = 0.08 \mu\text{A}/\text{cm}^2$) were noticed at 15% concentration of BW. This agrees with the results obtained from the EIS measurements.

TABLE IV
CORROSION PROCESS PARAMETERS FOR STUDIED SAMPLES

Time	Sample	E_{CORR} [mV]	i_{CORR} [$\mu\text{A}/\text{cm}^2$]	R_p [$\text{k}\Omega \cdot \text{cm}^2$]	η [%]
1 month	S0	-539	1.74	20.01	-
	S15	-521	1.15	21.78	34
	S25	-491	1.18	31.98	32
	S35	-465	1.22	29.96	30
26 months	S0	-161	0.77	55.30	-
	S15	-91	0.08	90.47	89
	S25	-183	0.21	66.90	72
	S35	-158	0.18	71.96	77

In Table III are presented also the values of the anticorrosion efficiency obtained by addition the BW in mortar. The efficiency in case of all concentration of BW was determined with (2):

$$\eta = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} [\%] \quad (2)$$

where i_{corr}^0 and i_{corr} are current density for the sample without and with BW, respectively. As it can be observed, the inhibition is pronounced for all samples with BW after 26 months maintained in humid conditions. The highest efficiency was obtained in case of 15% BW ($\eta = 89\%$).

B. SEM-EDX Analysis

SEM-EDX analysis was used for illustrating the intermediary layer between steel rebar and mortar matrix (S0 and S15). The steel rebar samples are presented in Fig. 4. Visual examination on the surface of the rebar embedded in mortar does not show corroded areas. However, the area directly exposed to the external conditions presents a severe corrosion. The results of the SEM-EDX analysis are presented in Figs. 5 and 6.



Fig. 4 Rebar samples for SEM-EDX analysis

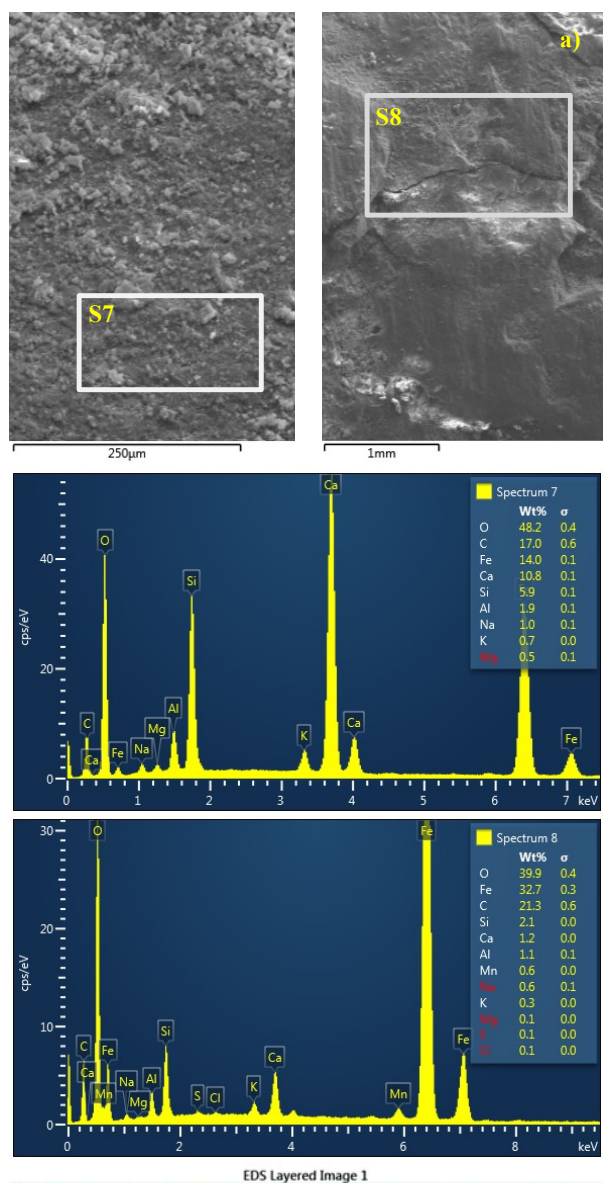


Fig. 5 SEM-EDX analysis of the S0 sample

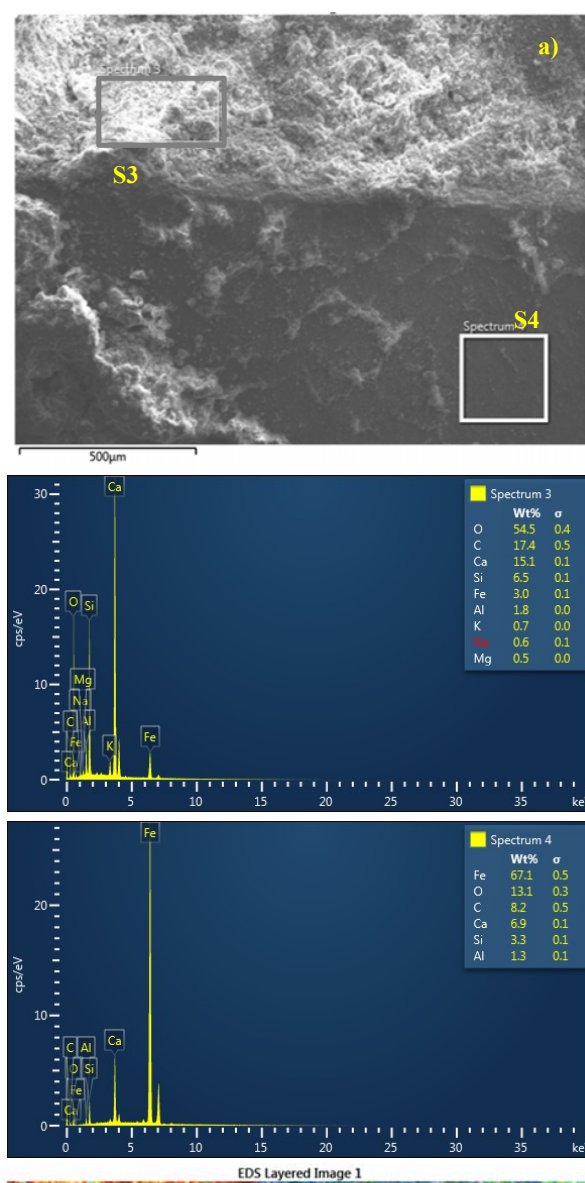


Fig. 6 SEM-EDX analysis of the S15 sample

By analyzing the distribution of elements (Fig. 5 (b)) the intermediate layer between steel and concrete can be observed. Also, on the steel surface, predominate Fe and C with small amounts of Ca are observed. The presence of the Ca, in the form of hydroxide, increases the pH of the system and provides protection against corrosion to the reinforcement.

In case of the rebar embedded in concrete with 15% WB, based on the SEM-EDX the presence of a high quantity of Ca compared with the etalon concrete can be observed (0% WB). Also, the presence of alkalis which dissolve easily, maintained the pH at high values, which gives the system a good anticorrosive property. The results obtained by SEM-EDX analysis are consistent with the corrosion tests.

IV. CONCLUSIONS AND FUTURE WORK

Based on the electrochemical investigations (EIS and potentiodynamic polarization curves measurements), it can be concluded that in the case of the addition of the BW in the mortar composition, the anticorrosion properties of the rebar are improved. The best efficiency was noticed in case of addition 15% of BW ($\eta \approx 90\%$).

SEM-EDX analysis for rebar embedded in etalon concrete showed that the intermediary layer formed around on the rebar contains calcium hydroxide, which increases the pH of the system ensuring protection against corrosion of the reinforcement. In the case of concrete with BW, the presence of alkaline hydroxides, maintaining the pH at a high value, provides a high anti corrosion protection of the reinforcement.

The results are promising, so research will continue in the near future. Also, the corrosion behavior of the reinforced concrete with BW will be tested in petrochemical industry conditions. The corrosion test will be conducted in real residual water from the exploitation of crude oil from Transylvania, Romania.

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