

# A New Approach on Corrosion Tests for Building Materials with PCM

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**Abstract:** Using Phase Change Materials (PCMs) in building structure for energy saving has been the subject of many recent studies. Utilization of PCM in building envelope provides passive thermal energy storage. These studies focus mainly on the thermal and physical characteristics of PCMs. Depending on the chemical structure of PCM used in concrete, the corrosion rate of metallic structure embedded in concrete may be accelerated. This influences durability of reinforced concrete and also service life of building. The aim of this study is to investigate corrosive behaviour of Butyl Stearate (BS) as PCM on rebar in 3.5% NaCl medium to demonstrate long-term durability of reinforced concrete. Electrochemical impedance spectroscopy (EIS) technique was used to monitor accelerated corrosion tests. EIS is introduced as a new approach for corrosion tests for building materials with PCM in this study. Open circuit potential results showed that BS had a protective effect compared to the reference sample. No corrosive activity on rebar was reported during the first nine months of measurements. Further investigations are on-going to inspect the change of corrosive behaviour with time for longer period.

## 1. Introduction

The building sector is responsible for 40% of primary energy consumption and about the same share of greenhouse gas emissions. More than half of this energy is consumed for space cooling and heating needs in buildings (Administration, 2012). Decreasing energy consumption in buildings has become very urgent to meet the ambitious targets of energy policies of many countries.

Using Phase Change Material (PCM) in building applications is a novel, sustainable and efficient solution to improve energy performance. PCMs can store and release thermal energy at a nearly constant temperature with high storage density (Kosny, 2015). One way of applying PCM in buildings is direct mixing into concrete. This method can provide cost and time effective use of passive solar energy utilization. The main advantages of using PCMs in building structure are reducing temperature fluctuations and heating/cooling energy demand, peak shifting, and keeping ambient temperature within comfort limits.

In recent studies, researchers mainly focused on the effects of PCM incorporation on thermal properties and mechanical strength of construction materials. However, the corrosive effect of PCM on reinforced concrete structure is another challenge to meet for long-term service life of buildings. Corrosion of rebar (reinforced steel) embedded in concrete strongly affects mechanical strength, service life due to higher volume of rust, which can lead to eventual breaking of concrete. Volume of oxidized steel ( $\text{Fe}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ , hydrated ferric oxide) increases by 6-7 times (Moser et al., 2012, Bensabra and Azzouz, 2013). In general, concrete protects rebar against corrosion. High alkaline media of concrete creates a passive layer on steel, and hence prevents corrosion of steel. In some cases, this passive layer may be ineffective due to damage by  $\text{Cl}^-$  ions and  $\text{CO}_2$  infiltrating into concrete. This passive layer and properties of concrete may also be affected in the positive or negative way by adding PCM.

Electrochemical Impedance Spectroscopy (EIS) is a standard characterization technique used for many materials in corrosion studies. In this study, with a new approach EIS is used for the first time to test the corrosive effects of PCM on rebar. Butyl stearate (BS), an ester with hydrophobic structure, was used for enhancing thermal performance of concrete as PCM.

Thermal and mechanical properties of BS added concrete have been investigated in our previous study (Cellat et al., 2015). Here, corrosion behaviour of BS on rebar in aggressive conditions for long-term concrete durability was investigated by EIS.

## 2. Experimental

### 2.1 Phase Change Material

For the selection of PCM with suitable temperature range for buildings, human comfort zone was taken into consideration. BS an ester with melting point of 21°C and melting enthalpy of 134.2 J/g was determined as a suitable PCM in our previous study (Cellat et al., 2015). The properties of BS as given by the supplier are given in Table 1.

Table 1. Properties of BS

Properties	Values
Grade	technical 40-60% (GC)
Impurities	butyl palmitate, residual
Refractive index	n <sub>20/D</sub> 1.443
Melting point	17-22 °C
Flash point	160 °C
Density	0.861 g mL <sup>-1</sup> at 20 °C
Molecular weight	340.58 g mol <sup>-1</sup>
Chemical formula	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COO(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>

### 2.2. Preparing Concrete Specimens

A self-compacting and high strength concrete mixture with PCM was prepared. All cementitious materials and concrete admixtures used were supplied by Kambeton Company. Steel rebars with a diameter of 0.8 cm were purchased from Icdas Steel Company. The chemical composition of steel was (wt.%) 0.20% C, 0.58% Mn, 0.21% Si, 0.013% P, 0.021% S, 0.14% Ni, 0.11% Cr, 0.02% Mo, 0.003% V, 0.21% Cu, 0.01% N and Fe in balance. Cement (Oyak Cimento, CEM II/A-M (P-LL) 42.5 R), fine and coarse aggregates (0-3 and 5-10 crushed fine aggregates), water, new generation Polycarboxylate ether (PCE) as superplasticer and technical grade Butyl Stearate (Sigma Alrich) were mixed according to TS 802 absolute volume method for C40/50 type concrete (802, 2009). Composition of the concrete for 1 m<sup>3</sup> of mixture is given in Table 2.

Table 2. Composition of concrete for 1 m<sup>3</sup> of mixture

	PCE (kg)	PCM (kg)	Aggregates <sup>1</sup> (kg)	Aggregates <sup>2</sup> (kg)	Cement (kg)	Water (kg)
Concrete	5.4	0	1076	738	450	188
Concrete with 5 % wt. BS	5.4	15	999	686	450	186

- <sup>1</sup>: 0-3 crushed fine aggregates
- <sup>2</sup>: 5-10 crushed fine aggregates

Prepared concrete mixture was fed into cubical specimen molds with dimensions of 7x7x7 cm. Cubical specimens were prepared with/without addition of BS in concrete and they were named rebar-BS and rebar, respectively. The steel was cut to a length of about 5 cm. A copper wire was connected in steel to supply electrical conductivity. Lateral surfaces of the steel were coated with polyester to expose only bottom surface of electrodes to concrete medium. The open surface of electrodes were polished with emery paper of 320, 500 and 1200 grades prior to experiments. Afterwards, they were washed with distilled water, then ethanol and finally with distilled water followed by drying with filter paper. The prepared electrodes were placed in the middle of the cubical specimens, to be equidistant to each surface of the concrete. The specimens were allowed to harden for 24 h at room conditions in the laboratory. Demoulded specimens were stored in water at 20±2°C for 28 days for curing. Cured specimens were fully submerged in 3.5% wt. NaCl (analytical grade, Sigma Aldrich) solution for electrochemical experiments. All the experiments were carried out with three parallel specimens for reproducibility.

### 2.3. EIS Measurement

The EIS was carried out with the conventional three electrodes system open to atmosphere using Ag/AgCl (3.0 M KCl) as a reference electrode and Pt sheet (with 2 cm<sup>2</sup> surface area) as the counter electrode. The prepared electrode had 0.503 cm<sup>2</sup> surface area.

EIS experiments were conducted between 100 kHz and 0.0046 Hz at open circuit potential at different immersion durations in 3.5 % wt. of NaCl solution and the amplitude was 5.0 mV using CHI 660 D electrochemical analyzer (serial number F1190). The experimental procedure is given in Fig 1. EIS experiment involves the application of a sinusoidal potential or current to the metal with a wide range of frequencies. The capacitance and resistance at the metal/solution double layer is determined from EIS data. The related metal/solution double layer and resistances are given Fig 2.

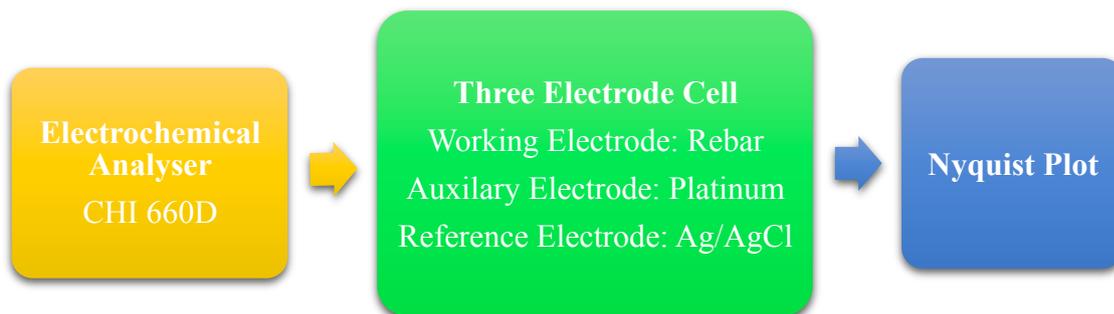


Fig. 1. Schematic view of electrochemical experimental procedure.

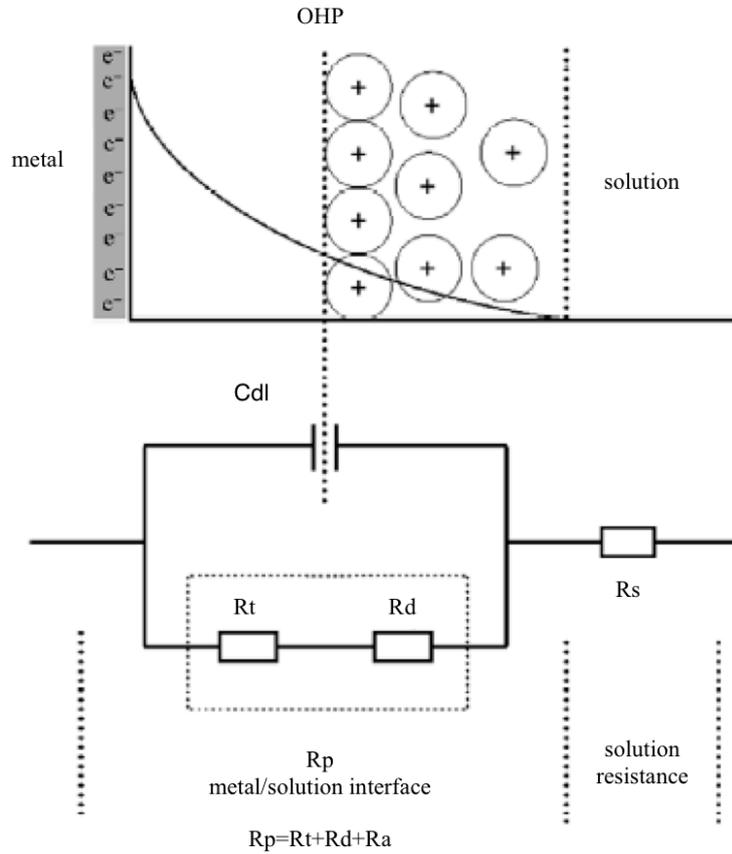


Fig. 2. A schematic representation of metal/solution double layer structure and related equivalent circuit diagram (Solmaz et al., 2008).

### 3. Results and discussion

The open circuit potential ( $E_{ocp}$ ) value is used to explain corrosion behavior of rebar in concrete (Deus et al., 2012, Itty et al., 2014). The  $E_{ocp}$  values can be used to determine regions of different corrosion probability of the BS/rebar system as follows:

- Region 1:  $E_{ocp} < -0.244$  V vs. Ag/AgCl high corrosion probability (~90%)
- Region 2:  $-0.35$  V  $< E_{ocp} < -0.094$  V vs. Ag/AgCl uncertainty of corrosion
- Region 3:  $E_{ocp} > -0.094$  V vs. Ag/AgCl a 10% probability of corrosion (Chaparro et al., 2012, Bautista et al., 2015).

$E_{ocp}$  values of rebar-Ref and rebar-BS in 3.5% wt NaCl solution for 270 days are presented in Fig. 3. This figure shows that the  $E_{ocp}$  of rebar-Ref and rebar-BS shifted to negative potential in the first 15 days of immersion time. After 15 days,  $E_{ocp}$  moved toward positive potential direction for both specimens. Rebar-BS showed excellent  $E_{ocp}$  stability between 30 and 150 days with 10% probability of the corrosion region but, rebar-Ref switched significantly between uncertainty of corrosion and high corrosion probability regions. This behavior of the rebar-BS indicates that protective film layer occurred on rebar surface. In the last 120 days, rebar-BS moved to negative potential showing the same behavior as the rebar-Ref between uncertain corrosion and high corrosion probability regions. This can be explained with the passive layer forming on the rebar surface by decomposition of BS.

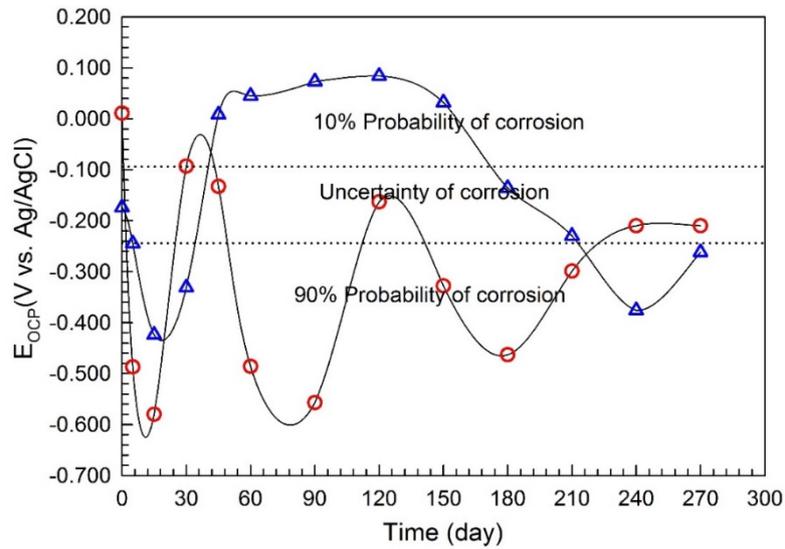


Fig. 3. Open circuit potentials of rebar-Ref (○) and rebar-BS (△) in 3.5 % wt. NaCl solution.

The EIS is a useful technique to investigate the corrosion process of rebar in 3.5% wt. NaCl solution. EIS can also be used to understand the diffusion process of the chloride ion to rebar surface (Ribeiro et al., 2015).

The Nyquist plots obtained with EIS that show the frequency response of rebar-Ref and rebar-BS after 270 days in 3.5 %wt. NaCl solution are given in Fig. 4. Rebar-BS and rebar-Ref both have one depressed semicircle at high frequency region, followed by a straight line in the low frequency region. The high frequency capacitive loop of rebar is related to the charge transfer resistance ( $R_t$ ) for corrosion process occurring on rebar surface and the accumulation resistance ( $R_a$ ). For rebar-BS, in addition to  $R_t$  and  $R_a$  film resistance ( $R_f$ ) should be considered in the high frequency loop.

The low frequency straight line is attributed to diffusion-controlled corrosion of the rebar. The diffusion resistance ( $R_d$ ) is the resistance against the diffusion of different species like chloride ion and corrosion products within concrete pores. The diffusion of the chloride ion from the solution through concrete pores to rebar surface results in corrosion. The soluble corrosion products are also transported from the metal surface through concrete into the solution (Ye et al., 2013). The  $R_p$  is the sum of all the resistances (Solmaz et al., 2008, Erbil, 1988).

The  $R_p$  values calculated from Bode plots for rebar-Ref and rebar-BS were determined as  $9791.5 \Omega \text{ cm}^2$  and  $14772.5 \Omega \text{ cm}^2$  for 270 days, respectively. These  $R_p$  values demonstrate that a protective BS film was formed on the rebar surface at the end of 270 days.

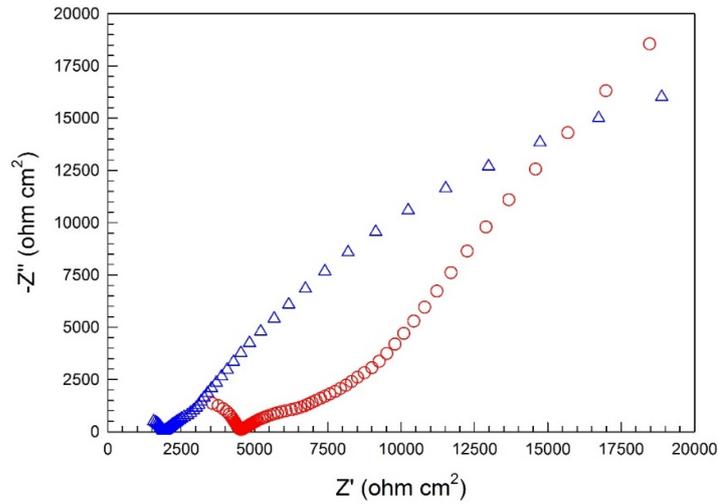


Fig. 4. Nyquist plot of rebar-Ref (○) and rebar-BS (△) in 3.5 wt. % NaCl solution at room temperature after 270 days immersion.

The solution resistance ( $R_s$ ) is investigated to envision pore capacity of concrete that will allow ions to pass from solution to rebar surface. When the porosity of concrete increases,  $R_s$  value would decrease allowing fewer ions to get to the electrode surface. The  $R_s$  values calculated from Bode plot for 270 days is presented in Fig. 5. While rebar-BS has lower  $R_s$  than rebar-Ref at the end of 45 days, both of electrodes show the same  $R_s$  trend between 45 and 180 days. The last 90 days, they demonstrated different  $R_s$  values. It can be concluded that porosity of rebar-BS concrete decreased between 210 and 270 days. Although  $R_s$  value of rebar-BS decreased, the protective hydrophobic BS film that was formed protected and increased  $R_p$  at the end of 270 days.

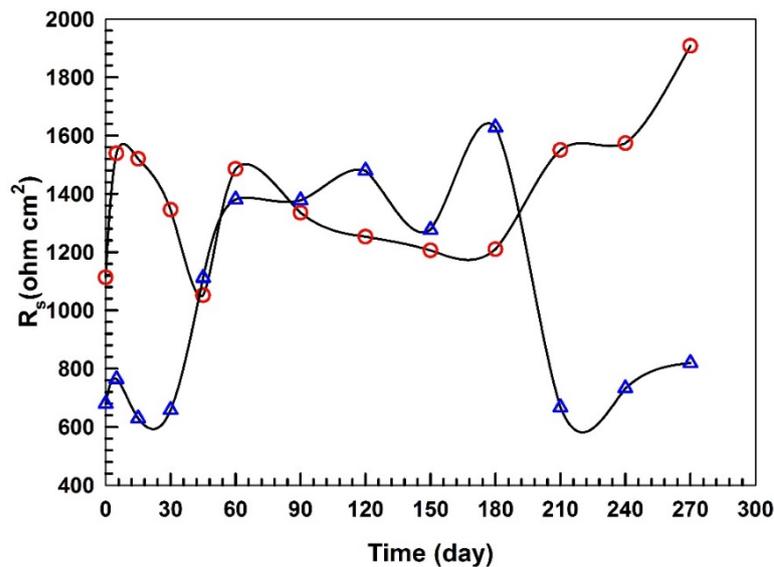


Fig. 5.  $R_s$  of rebar-Ref (○) and rebar-BS (△) in 3.5 wt. % NaCl solution at room temperature for 270 days immersion.

#### 4. Conclusions

In this study EIS was first applied in determining the corrosive effect of PCM use in concrete mixes for passive building applications. The conclusions based on electrochemical measurements can be summarized as follows:

- $E_{ocp}$  values of rebar-BS was very stable and stayed within the low probability corrosion region during 150 days
- The  $R_p$  values of rebar-Ref and rebar-BS were determined as  $9791.5 \Omega \text{ cm}^2$  and  $14772.5 \Omega \text{ cm}^2$  for 270 days, which confirms protective film formation of BS on rebar.
- The  $R_s$  of rebar-BS decreased in the last 90 days, which shows that BS increases the porosity of concrete.
- BS can be recommended to be utilized as PCM for thermal enhancement of concrete safely with limited corrosive effects

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