

The Influence of PEO₁₁₃-b-PS₇₈₀ Vesicles on the Corrosion Performance of Carbon Steel in Simulated Pore Solution

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This study presents the results from a preliminary investigation on the corrosion behavior of carbon steel in cement extract (CE) in the presence of very low concentration (0.0024 wt. %) polymeric nano-aggregates (PEO₁₁₃-b-PS₇₈₀ vesicles). Two types of vesicles were studied: vesicles with a CaO-containing core and vesicles with an “empty” core. The results from the electrochemical measurements (Electrochemical Impedance Spectroscopy (EIS) and Potentio-dynamic Polarization (PDP)) indicate that the presence of the CaO-containing vesicles lead to a significantly increased corrosion resistance of the steel, but no pronounced effect was observed for the “empty” vesicles. However, steel surface analysis indicates that the presence of both vesicles type results in a more homogeneous and compact product layer.

INTRODUCTION

Well known is that in reinforced concrete, corrosion of the steel reinforcement is one of the main reasons for degradation in concrete structures [1-3]. The two main corrosion-inducing factors are chloride and carbon dioxide [4]. Upon arrival at the steel/cement paste interface, chlorides cause depassivation of the steel rebar and locally the pH can drop to below 6, resulting further in fast corrosion propagation [5]. Carbon dioxide reacts with the calcium-bearing compounds in the concrete matrix, resulting in the formation of calcium carbonates and thus, leading to a pH drop in the pore solution to below 9 i.e. general corrosion of the reinforcing steel takes place [6].

Numerous methods and techniques are known, still under investigation or successfully applied to minimize or prevent reinforcement corrosion: e.g. protective coatings and sealers [7, 8], cathodic protection [9, 10], concrete realkalinization [11, 12] and corrosion inhibitors [13-15]. With respect to the application of polymeric nano-aggregates for corrosion control in cement-based systems, literature reports are limited.

In our previous investigation, the influence of admixed Polyethylene oxide (PEO)-block-Polystyrene (PS) micelles (PEO₁₁₃-b-PS₇₀ micelles) on the global performance and microstructural properties of cement-based materials and corrosion performance of reinforced mortar was studied [16-22]. The investigations showed very promising results: in plain mortar, although the compressive strength of the micelles-containing mortar was almost unaffected, the presence of a very low concentration of micelles (0.025 % by weight of dry cement) in the mortar mixture exerted influence on microstructural properties e.g. significantly reduced porosity and pore network connectivity, compared to the micelles-free mortar matrix. Additionally, the coefficient of water permeability was 3 orders of magnitude lower for the micelles-containing specimen, compared to the micelles-

free specimen. The NaCl permeability for the micelles-containing specimen was also found to be significantly lower than the micelles-free specimen [18, 20].

In cement extract (as a model alkaline medium, representing the concrete pore water), a very low micelles concentration (0.0024 wt. %) was able to increase the corrosion resistance of steel in the presence of chlorides. However, the significant effect only appeared at early stages [16, 17, 22].

In reinforced mortar, although the admixed micelles only had a slight effect on steel corrosion resistance, their presence resulted in a positive effect in terms of impeding corrosion products accumulation and further propagation when very high (5 wt.%) chloride concentrations were involved [19, 21].

The experimental results so far indicate that the influence of admixed micelles is mainly on the microstructure and water permeability of the cement matrix and their effect on the steel corrosion performance is minimal. To this end and within further objectives of the still on-going investigations, except the polymeric aggregates (i.e. micelles), self-healing agents were involved. In this work, PEO₁₁₃-b-PS₇₈₀ vesicles, which are formations already carrying an “active” compound, were added to a simulated pore solution (alkaline medium). The alkaline solution served as a corrosion medium for investigating the steel corrosion performance. Both “empty” and “charged” (with a self-healing agent) vesicles were investigated. The corrosion performance of the steel electrodes was studied via electrochemical measurements (Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP)) and surface analysis (SEM and EDX) techniques.

MATERIALS AND METHODS

Materials: Polymeric Vesicles: Used in this study were PEO₁₁₃-b-PS₇₈₀ vesicles (both with an “empty” core and a CaO-containing core). The vesicles in aqueous media with a concentration of 0.5 g/L (demi-water) were obtained by the dialysis method. The hydrodynamic radius of the vesicles was approximately 220-250 nm, identified by dynamic light scattering (DLS) measurement, as shown in Fig.1.

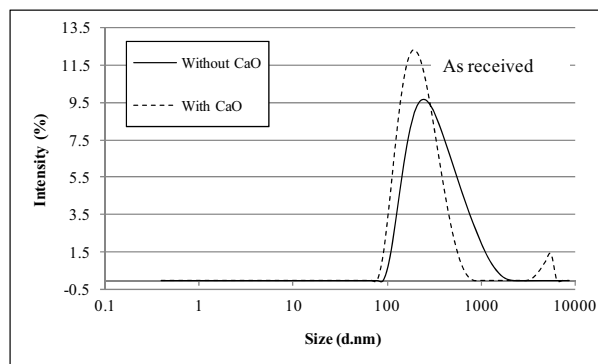


Fig.1 Dynamic light scattering (DLS) of the vesicles solutions as received

Cement extract and steel electrodes: The cement extract (as a simulated pore solution) was prepared from Ordinary Portland cement CEM I 42.5 N and tap water by mixing in the weight ratio of 1:1; the suspension was filtrated after 24h rotation and thus a simulated pore solution (CE) was received. The pH of CE is 12.6-12.9. For chloride-containing CE, Cl⁻ was added with a concentration of 10 g/l. The aqueous solution of

PEO₁₁₃-b-PS₇₈₀ vesicles was added to part of the cement extracts, thus 0.0024 wt. % of the vesicles were present in chloride-free and chloride-containing cement extracts.

Low-carbon steel 37 with surface area of 4 cm² was used. All electrodes were equally treated prior to electrochemical measurements i.e. they were grinded with no.500 to no.4000 grinding papers and rinsed with acetone just before immersing in the relevant solution. The sample designation in this work is shown in Table 1.

Table.1 Sample designation in this study

Groups	Designation	Vesicles (Empty core)	Vesicles (CaO core)	Cl ⁻ (10g/L for CE)
Control Groups	OPC			
	OPCV	×		
	OPCVC		×	
Corroding Groups	OPCn			×
	OPCVn	×		×
	OPCVCn		×	×

Methods: Electrochemical methods: Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) were employed, using a common 3-electrode cell arrangement (SCE as reference electrode). The EIS measurements were performed at open circuit potential (OCP); the PDP measurements were performed after OCP stabilization in the range of -0.2 to +1.0 V vs OCP at a scan rate 0.5 mV/s; The EIS measurements were carried out in the frequency range of 50 kHz to 10 mHz by superimposing an ac voltage of 10 mV. The used equipment was EcoChemie Autolab-Potentiostat PGSTAT30, combined with FRA2 module, using GPES and FRA interface.

Surface analysis: The morphology and composition of the product layers, formed on the steel surface as a result from the relevant conditioning for each group type (the conditioning time was 168h, because the difference in electrochemical responses were most significant at this stage) were investigated using scanning electron microscopy (SEM), coupled with energy dispersive X-ray (EDX) analysis. SEM and EDX investigations were performed with an environmental SEM, ESEM Philips XL 30, equipped with EDX detector. The chemical composition and distribution of products, associated with corrosion (for corroding groups) and/or passivation (for control groups), were determined (qualitatively and semi-quantitatively) by energy dispersive X-ray analysis (EDX).

RESULTS AND DISCUSSION

Open circuit potential (OCP) and Potentiodynamic curves (PDP)

Fig.2 presents the OCP readings for all specimens at different time intervals (readings are the average value of 3 replicates per condition; deviations are also shown in the plot). As depicted in Fig.2 that for the control specimens (immersed in CE without chloride), the OCP values were always more anodic than -250 mV (SCE) for all specimens, meaning that the steel reinforcement was in passive state. For the corroding specimens (immersed in CE in the presence of chloride), more cathodic potential were recorded for the vesicles-free specimen OPCn from 24h immersion stage and onwards (which is as expected); specimen OPCVn ("empty" vesicles were present in CE) behaved similarly to specimen OPCn, with already corrosion initiation at 168h, evidenced by the OCP values below -400mV; for specimen OPCVCn (CaO-containing vesicles were present in CE),

the steel electrode was in passive state until the end of the test (168h) and behave similarly as the control cases (specimens OPC, OPCV and OPCVC).

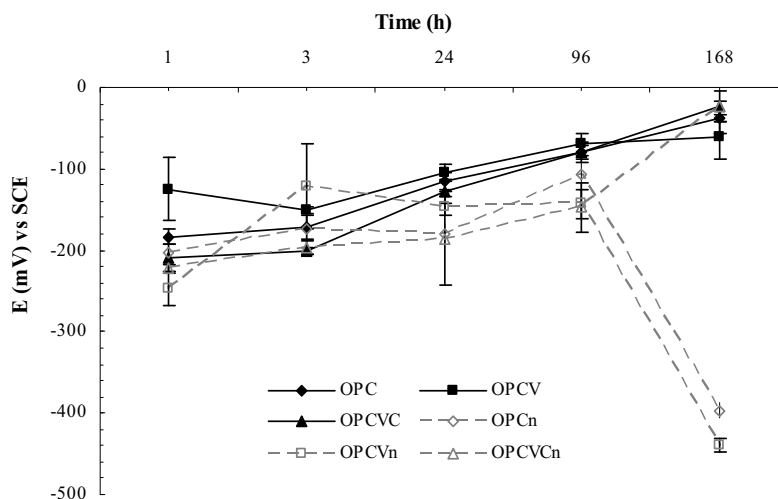


Fig.2 OCP readings of steel electrodes for all specimens with treatment of 1h-168h

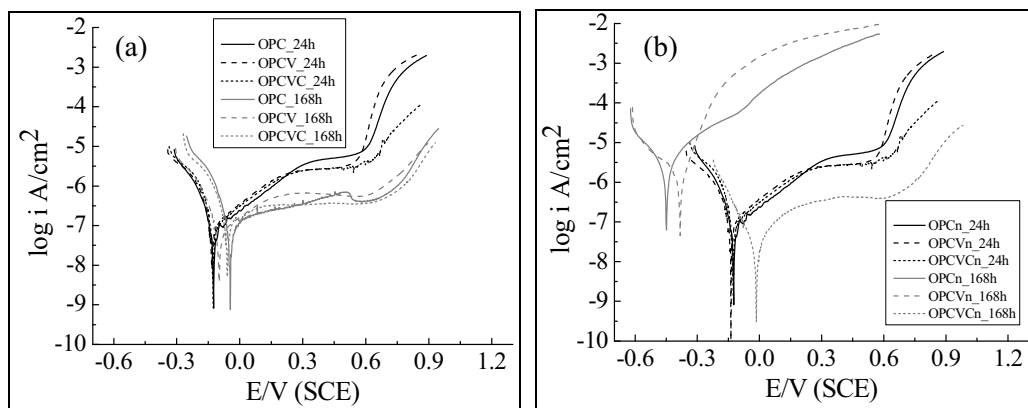


Fig.3 Potentio-dynamic polarization curves for steel electrodes as a comparison of 24 and 168h response: (a) control cases, (b) corroding cases

The potentio-dynamic curves for all specimens after 24h and 168h are shown in Fig.3. Very anodic corrosion potential and very low corrosion and anodic current densities were observed for the control specimens (Fig.3a) for both 24 and 168h. In contrast, cathodic corrosion potentials (between -380mV and -470mV) and increased current densities were relevant for corroding specimens OPCn and OPCVn after 168h treatment (Fig.3b), except for the group OPCVCn, which behaved as the control groups (i.e. with a more anodic corrosion potential and lower current densities, compared to the other two corroding specimens). The data derived from OCP and PDP was further confirmed by electrochemical impedance spectroscopy (EIS).

Electrochemical impedance spectroscopy (EIS)

Fig.4 depicts the EIS response in Nyquist and Bode format of the steel in cement extract (vesicles-free and vesicles-containing solutions) in both control (Fig.4 (a)) and corroding specimens (Fig.4 (b)) at the time interval of 24h and 168h. The control specimens exhibited high corrosion resistance (very high magnitude of $|Z|$ for all control

specimens in Fig.4 (a)), which indicate that a stable passive layer was formed on the steel surface in chloride-free environment (as expected). The vesicles caused no significant influence on the observed corrosion resistance. For the corroding specimens, the data derived from EIS measurement provide evidence for the enhanced corrosion resistance of specimen OPCVCn: as seen in Fig.4 (b), at early immersion stage (i.e. 24h), the corrosion resistance of the steel electrode was similar for all corroding specimens; however, after 168h treatment, compared to specimens OPCn and OPCVn, the magnitude of impedance $|Z|$ was significantly higher for specimens OPCVCn; phase angle for specimens OPCVCn was significantly higher, approx. 85 deg (compared to the other corroding specimens, between 55 and 60 deg). Here again, the corroding group OPCVCn behaved similarly to the control specimens (responses for the control specimens at 168h time interval in Fig. 4 (a)).

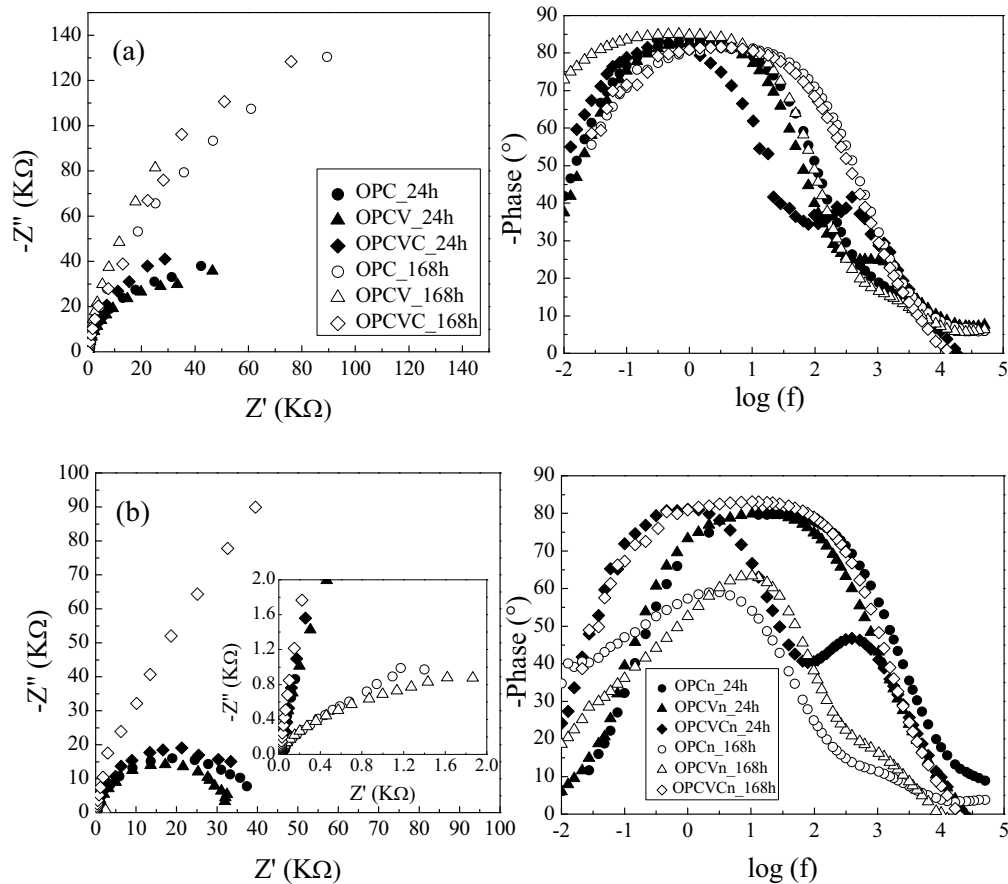


Fig. 4 EIS response for (a) control cases and (b) corroding cases after 24h and 168h treatment

Therefore, the electrochemical results indicate that the presence of CaO-containing vesicles in cement extract lead to a delay of corrosion initiation and significant corrosion resistance improvement of the investigated steel electrodes. Because the steel electrodes treated in corrosion medium in the presence of “empty” vesicles behaved similarly to the vesicles-free specimens (pls. see responses for specimens OPCn and OPCVn in Fig.3 (b) and Fig.4 (b)), the positive effect of CaO-containing vesicles is well seen. In other words, the observed increased corrosion resistance is not only related to the influence of the

vesicles themselves on the barrier properties of the layer (as has been previously observed for steel electrodes in the presence of micelles [16, 17, 22]), but is also related to the presence of CaO in their core.

Morphology

Fig.5 and Fig.6 show the morphology observation and EDX analysis of steel surface for control specimens and corroding specimens at 168h respectively (the difference in electrochemical behavior were most apparent at this stage).

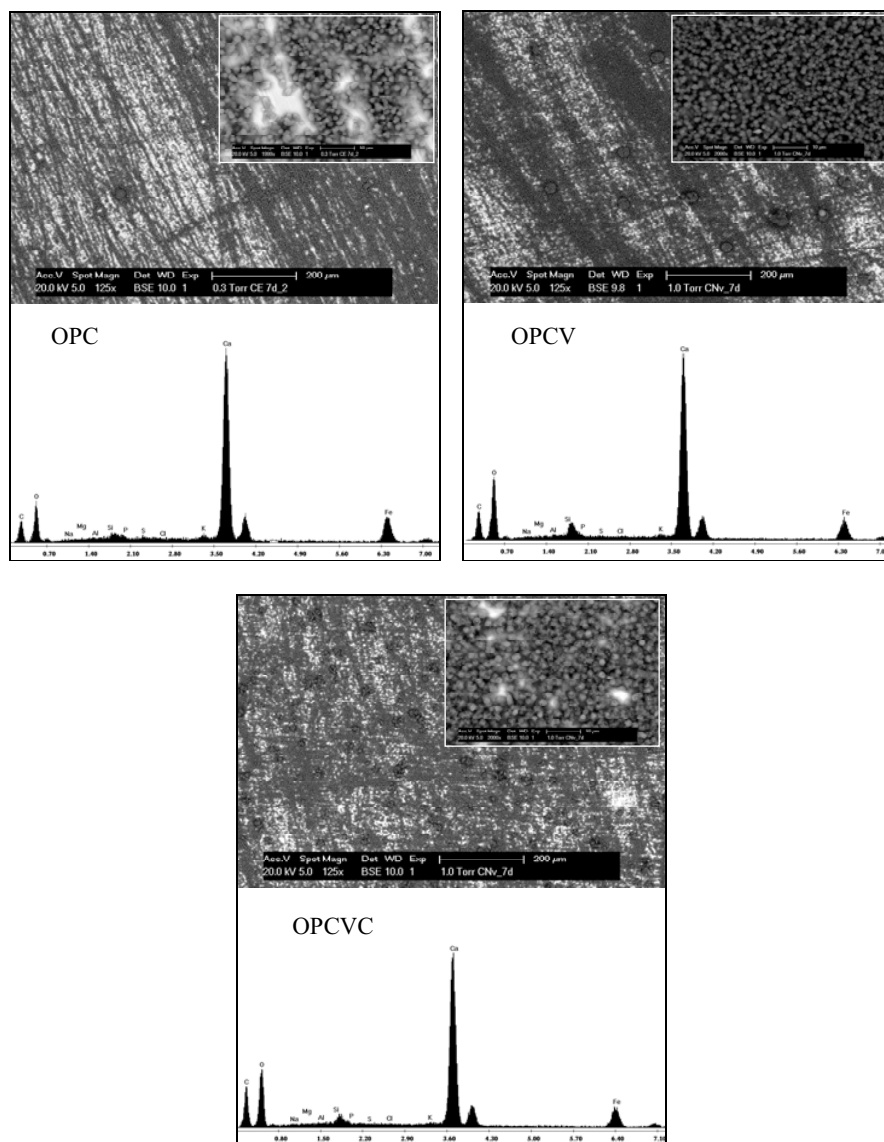


Fig.5 Morphology observation and EDX analysis of steel surface for control specimens at 168h

For the control specimens (Fig.5), similar morphology and composition were recorded for all specimens except that the product layer for the vesicles-containing

specimens were visually more homogeneous and compact, This also corresponds to the similar corrosion behavior of the control specimens at this stage (Fig.3 (a) and Fig.4 (a))

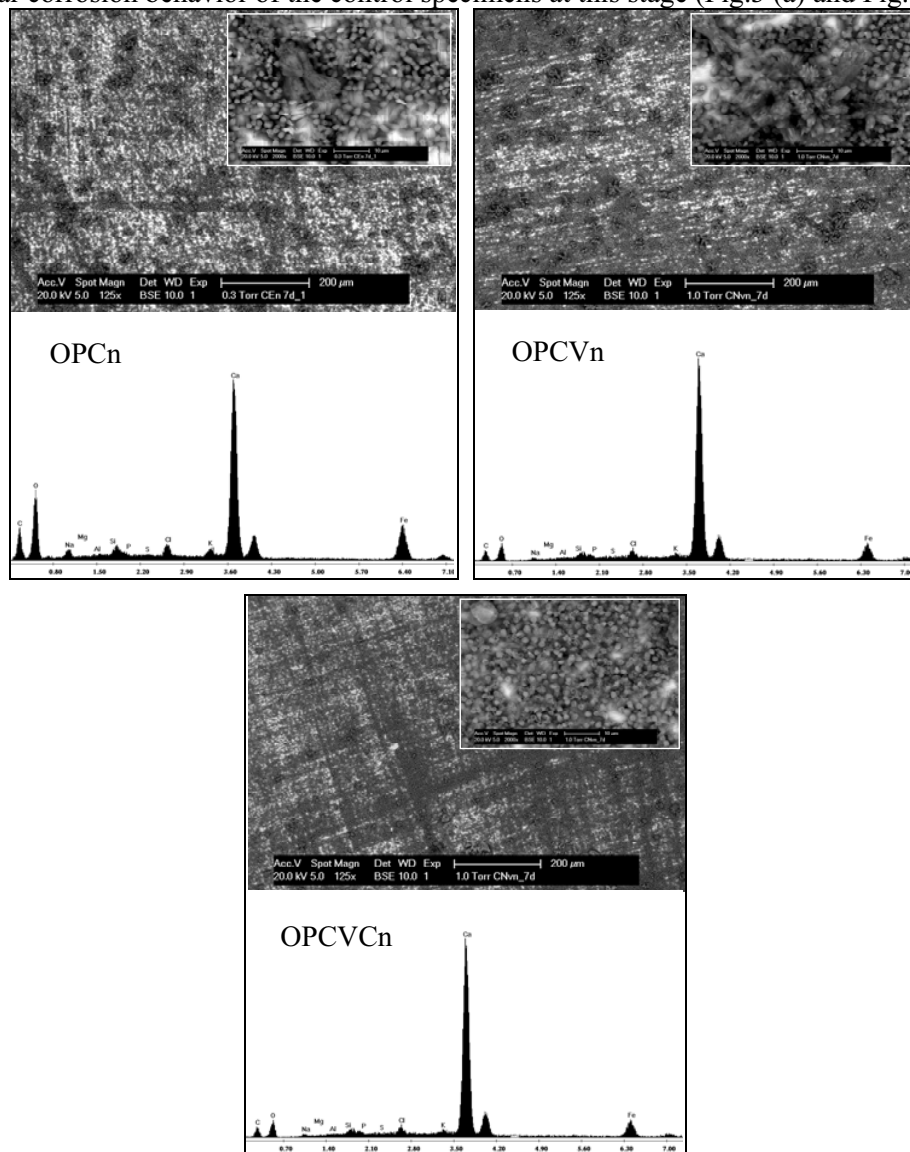


Fig.5 Morphology observation and EDX analysis of steel surface for corroding specimens at 168h

For corroding specimens, similar trend as the control specimens was observed: the vesicles (both with an “empty core” and a CaO-containing core) lead to more homogeneous and denser layer on the steel surface. Further, the chloride concentration on the steel surface for the vesicles-containing specimens (especially for the CaO-containing vesicles) was most likely lower (considering the EDX spectrums in Fig.5), which would mean better properties of the product layer and an increased corrosion resistance of the steel. A thorough XPS analysis (including in depth of the product layers) actually proves the above statements and will be reported as a separate work.

Based on the experimental results, the following can be summarized: in simulated pore solution, the “empty” vesicles didn’t show significant effect on the corrosion

behaviour of the steel; however, the CaO-containing vesicles are able to significantly delay or minimize the Cl⁻-induced corrosion initiation on the steel surface (Fig.2, Fig.3 (b) and Fig.4 (b)).

Significantly enhanced barrier properties of the formed product layers (as previously proved in the presence of micelles [16, 17, 22]), were hereby also observed, but the major contribution to increased corrosion resistance seemed to be the presence of CaO in the core of the studied vesicles. Since the concentration of both types of vesicles is very low in the simulated pore solution (0.0024 wt. %), the concentration of CaO compound reserved in the core of the CaO-containing ones is extremely low and is unlikely to be solely responsible for the observed behaviour. Therefore, the most plausible reason related to the improved corrosion performance of steel, treated in model medium where CaO-containing vesicles were present is a core (CaO) release due to the local pH drop in the vicinity of the steel surface (resulting from chloride induced corrosion initiation) and local product layer repair.

CONCLUSIONS

In this work, the corrosion behavior of steel in cement extract (CE) in the presence of polymeric PEO₁₁₃-b-PS₇₈₀ vesicles was investigated. Morphological observations and surface analysis indicate that for the vesicles-containing specimens (both CaO-containing and "empty" such), the product layers formed on the steel surface are denser, more homogeneous and compact. However, a pronounced difference in corrosion behaviour was recorded for the steel electrodes treated in the presence of the two vesicle types: electrochemical tests reveal that a very low concentration of CaO-containing vesicles (0.0024 wt. %) delays corrosion initiation and significantly increases the corrosion resistance of the steel. The most plausible mechanisms are related to: barrier effect of the vesicles; diffusion limitations to chloride ingress and counteraction of the Ca-containing core and chloride ions (corrosion delay respectively) and a repair of the layer resulting from the CaO release due to local pH drop on the steel surface.

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