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SELF-HEALING PHENOMENA ON CORRODING STEEL IN SIMULATED PORE WATER AND MORTAR, SUBSTANTIATED VIA CYCLIC VOLTAMMETRY AND SURFACE ANALYSIS

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Abstract.

The application of polymeric nano-particles was investigated as an approach to control corrosion and/or self-heal corrosion damage on steel in simulated alkaline medium and reinforced mortar. The "self-healing agent", present in the closed inner volume of PEO-b-PS vesicles was Ca-based and chosen as such due to the natural predominance of Ca in the investigated system. The vesicles' concentration was 0.0024 wt.% in the model medium and 0.025 wt.% per cement weight for the case of mortar. Therefore, a "self-repair" or "self-healing" of the steel product layer solely due to the Ca-component is not realistic in view of these minimal concentrations. The most plausible mechanism is the nature of incorporation of the Ca-containing vesicles in the product layer, enhanced chloride binding effects and adsorption on active sites on the steel surface. A more uniform and stable surface layer, initial pitting formation and propagation, but consecutive "healing", are evidenced by surface analysis and electrochemical response i.e. largely reduced anodic and corrosion currents and no further pit propagation are observed when Ca-containing vesicles are present in the model medium. Corrosion products-free steel/cement paste interface is relevant for the reinforced mortar, containing Ca-rich vesicles in contrast to vesicles-free and empty vesicles-containing matrix.

Key words: *corrosion; concrete; polymeric nano-particles; CVA; SEM; XRD; XPS*

1. INTRODUCTION

Reinforced concrete has the potential to be durable and capable of withstanding a variety of adverse environmental conditions. However, one of the major difficulties in the engineering practice, originating at the nano/micro level, is the multi-dimensional nature of steel corrosion. In the frame of a recent approach to corrosion control in reinforced concrete, the application of polymeric nano-materials was studied. Among other formations, polymeric micelles of 50 nm size (from the di-block polymer PEO-b-PS) were investigated at an extremely low concentration of 0.025 wt.% per cement weight. The results show superior performance with respect to corrosion resistance and bulk matrix properties of the micelles-modified cement-based systems [1-4]. The outcomes are due to phenomena as nucleation sites effect, accelerated chloride binding and barrier effects. Further, these type of nano-materials were hypothesized to possibly lead to self-repair of Cl-induced corrosion damage within altering their structural morphology and/or composition.

The next step of the above approach was to employ nano-materials as carriers of Ca-containing compounds (calcium being chosen due to its' natural predominance in the investigated systems).For establishing the effects on corrosion resistance, stabilized (kinetically frozen) PEO113-b- PS760 vesicles (220 nm) were investigated as "empty" and Ca-containing ones [1-5]. The aim of these studies was to investigate the possibility for maintained positive effects on the cement-based microstructure, along with increased corrosion resistance and self-healing (or repair) of corrosion damage, resulting from Ca-based "core" release. The tests were performed in model pore solutions (vesicles concentration of 0.0024 wt.%), prior to studies in reinforced mortar (vesicle concentration as previously for micelles i.e. 0.025 wt.% per cement weight). This paper summarizes some main outcomes as follows: some results from the investigation on corrosion resistance of St37 steel electrodes in cement extract, modified with the above defined vesicles [5]; visualization of the positive effects with respect to corrosion resistance in reinforced mortar and steel/cement paste interface (for more details on the electrochemical behavior of reinforcing steel, please see [3]; finally, this work substantiates the improved corrosion resistance via evidence of self-healing effects through correlating electrochemical performance (mainly cyclic voltammetry) and steel surface analysis.

2. EXPERIMENTAL

2.1 Materials

Model environment and reinforced mortar: for cement extract (CE) as a simulated pore solution and for the reinforced mortar, respectively, OPC CEM I 42.5N was used. The pH of CE is 12.6 – 12.9, chemical composition is: Ca – 201 mg/l; K – 3.85 mg/l; Na – 1.33 mg/l; Al – 4 mg/l and Fe - < 1 mg/l; a portion from the prepared 0.5 g/l vesicles solutions was added to CE (or added as mixing water for mortar). The final concentration was 0.0024 wt. % in CE and 0.025 % by weight of cement in mortar. Corrosion-inducing factor was 1% NaCl for CE and external 5% NaCl as corrosion-inducing medium for the mortar. The reinforced mortar specimens were cast in w/c ratio 0.5, c/s ratio 1:3, cured in a fog room (20°C, 98 % relative humidity) for 28 days and further lab conditioned.

Steel*:* St37electrodes of surface area 4 cm2 were used for tests in CE; Construction steel FeB500 HKN (109 cm2) was centrally embedded in the mortar specimens. All steel bars and St37 electrodes were equally treated prior to treatment in the relevant solutions and/or casting in the mortar specimens (grinding, polishing, acetone cleaning and water rinsing for St37 and acetone cleaning and water rinsing for FeB500 HKN prior to casting). Three replicates per condition were tested. Sample designation is as follows: group CE – control cases; CEn – corroding cases; CEV and CEVC stand for the non-corroding cases of steel in CE and mortar, modified with "empty" and "Ca-containing" vesicles, whereas CEVn and CEVCn stand for the corroding, vesicles-containing cases respectively.

Polymeric vesicles: Vesicles were prepared via dialysis from PEO113-b-PS760 block-polymer [1-5]. In order to distinguish between "barrier" effects and "self-healing" due to Ca-release, both "empty" and Ca-containing vesicles were used. Their hydrodynamic radius was approximately 220-250 nm, identified by dynamic light scattering (DLS) measurement and transmission electron microscopy (TEM).

2.2. Methods

Electrochemical methods: Autolab-Potentiostat PGSTAT 30 (Metrohm, NL) was used. Potentio-dynamic polarization (PDP) and Cyclic voltammetry (CVA) were employed, using a common 3-electrode cell arrangement (saturated calomel electrode, SCE, as reference electrode). PDP was in the range of -0.2V to +1.0V vs open circuit potential (OCP) at a scan rate 0.5 mV/s; CVA scans were in

the potential region of −1.4V to 0.6V at a scan rate of 5 mV/s (all electrochemical measurements are as generally employed for the systems under study).

Surface analysis:. X-ray photoelectron spectroscopy (XPS) was carried out in the UHV chamber of an electron spectrometer ESCALAB-MkII VG Scientific with a base pressure of about 1×10−10 mbar (during the measurement 1 ×10−9 mbar). The photoelectron spectra were obtained using unmonochromatized Al Kα (hν = 1486.6 eV) radiation. The instrumental resolution measured as the full width at a halfmaximum (fwhm) of the Ag3d5/2, photoelectron peak is about 1 eV. The energy scale is corrected to the C1s (peak maximum at 285 eV) for electrostatic sample charging. The fitting of the recorded XPS spectra was performed, using a symmetrical Gauss-Lorentzian curve fitting after Shirley-type subtraction of the background. Except scanning the steel surface after 7 days i.e. product layers formed on the steel electrodes in each relevant condition, consecutive mechanical polishing of equal pressure and time duration was performed in depth of the layer in the vacuum chamber of the spectrometer. This technique was chosen in order to avoid influence on the chemistry of the formed layers, which would otherwise be relevant if Ar sputtering was used. The XPS measurements resulted in quali- and quantifying of the composition of the product layers in depth i.e. for each specimen, four in depth scan results were recorded.

3. RESULTS AND DISCUSSION

3.1. Corrosion behavior of St37 steel electrodes in model solution (cement extract).

All electrochemical measurements were performed on defined time intervals (e.g. 1h, 2h, 24h, 3d, 7d) after OCP stabilization. For reinforced concrete, concrete pore solution respectively, simulated here as cement extract (CE), the steel surface is considered to be passive if OCP is equal or more anodic than -270 mV SCE. When chlorides (or other corrosion-inducing factors) are present, passivity is lost, localized corrosion initiated and OCP readings shift to more cathodic values. Figure 1 depicts OCP evolution for all investigated cases in cement extract.

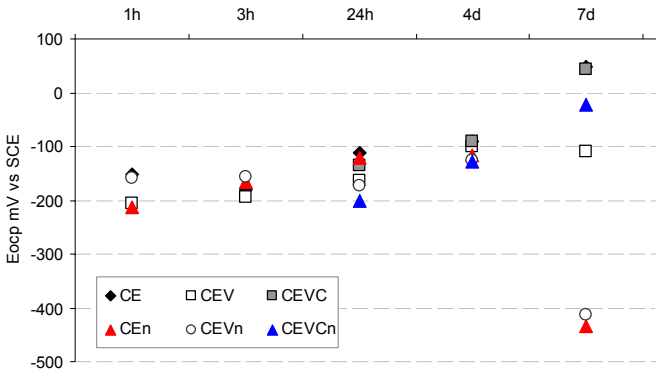


Fig.1 Evolution of OCP values for steel electrodes in cement extract with time of treatment: CE – control; CEV and CEVC – controls with empty and Ca-bearing vesicles;

CEn – corroding; CEVn and CEVCn - corroding with empty and Ca-bearing vesicles

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As can be observed, the OCP values fall in the region of passivity and shift towards more noble potentials at the end of the test for all specimens, except CEn and CEVn. For the latter two cases corrosion initiated at the end of the testing period. This result is as expected for specimens CEn (corroding steel in vesicles-free CE). The OCP readings for steel, treated in vesicles-containing CE exhibit pronounced differences, depending on the vesicles' composition. Empty vesicles (specimens CEVn) do not result in noble potentials (approx. – 400 mV recorded after 7 days i.e. corrosion initiation). In contrast, the presence of Ca-bearing vesicles in the CE results in maintaining steel passivity (approx. -20 mV were recorded for specimen CEVCn after 7 days treatment). Figure 2 depicts the calculated polarization resistance values (Rp) for steel electrodes treated in all investigated solutions after 24h, 4d and 7d (after IR correction, the latter derived from impedance spectroscopy).

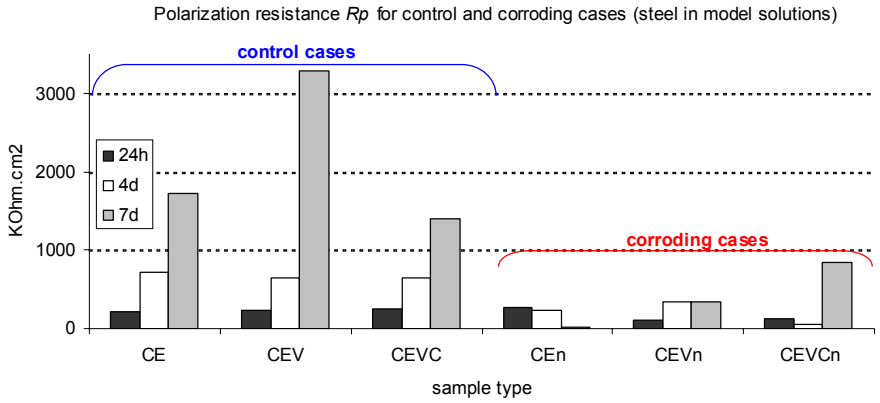


Fig.2 Polarization resistance values, derived from PDP tests with time of treatment for control and corroding cases

As seen from the plot, a trend of increasing Rp (increased corrosion resistance) was observed within treatment for the control cases (CE, CEV and CEVC), which is a general outcome within the stabilization of the steel passive layer in alkaline medium as cement extract. For the corroding cases (CEn, CEVn and CEVCn), Rp values are significantly lower and maintain this trend, except for specimen CEVCn, for which initially low but increasing Rp values were recorded, whereas this is not the case for specimens CEn and CEVn. Obviously, the Ca-bearing vesicles introduce altered properties of the product layer on the steel surface, which differ from these in specimens CEVn. In other words, barrier effects (empty vesicles, specimen CEVn) can be distinguished from chemical re-structuring on the steel surface and/or in the bulk volume of the environment (Ca-bearing vesicles, specimen CEVCn). An example (as in-direct visualization) of initial corrosion initiation and further steel surface layer "repair" is evident from the PDP response for specimens CEVCn with time – Fig.3.

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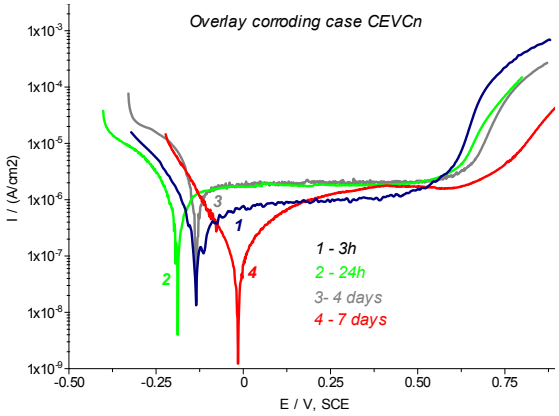
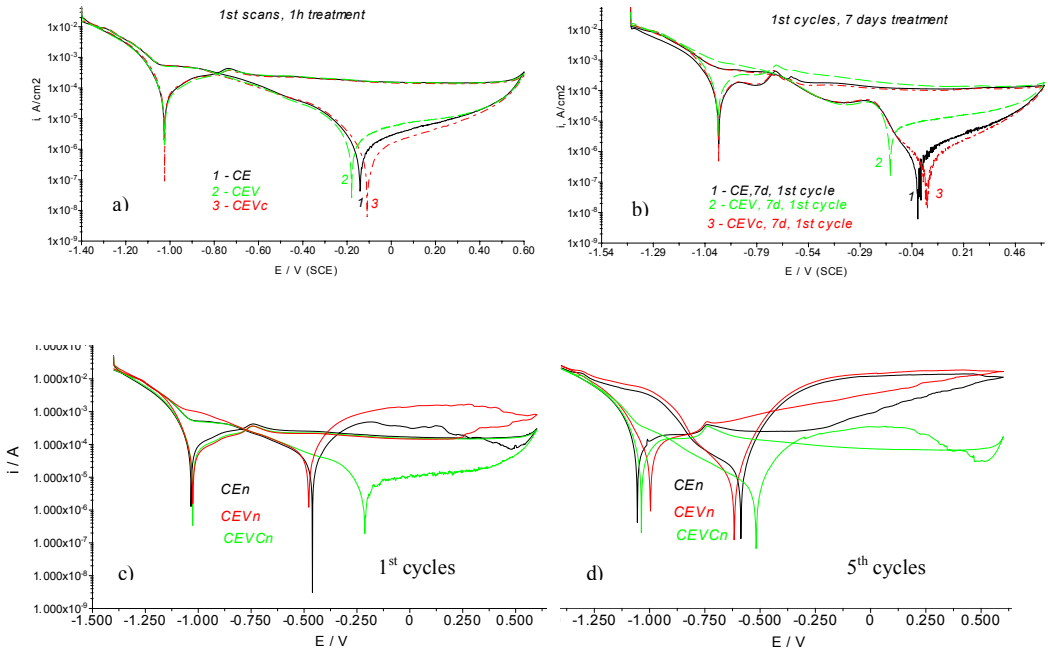


Fig.3 PDP response for specimen CEVCn with treatment for 3h, 24h, 4days and 7 days.

The initially low corrosion current and anodic currents for 3h, line 1 in Fig.3, further increase with chloride-induced corrosion – curves 2 and 3, accompanied by cathodic shift of corrosion potential. After 4 days treatment (line 3), corrosion potential (Ecorr) shifts back in anodic direction; after 7 days a more pronounced difference is observed (Ecorr around 0mV), accompanied by significant decrease in corrosion current (line 4, Fig.3) and lower anodic currents around Ecorr. The result can only be denoted to attempts for "self-repair" or "self-healing" of the product layer, since if only barrier effects were present a more significant "drop" in anodic currents would be recorded in the potential region of 0.12 to 0.45 V.

The above discussed results and considerations are actually proved by cyclic voltammetry (CVA), from which electrochemical behavior in terms of pitting initiation, propagation and attempts for steel re-passivation can be obtained.



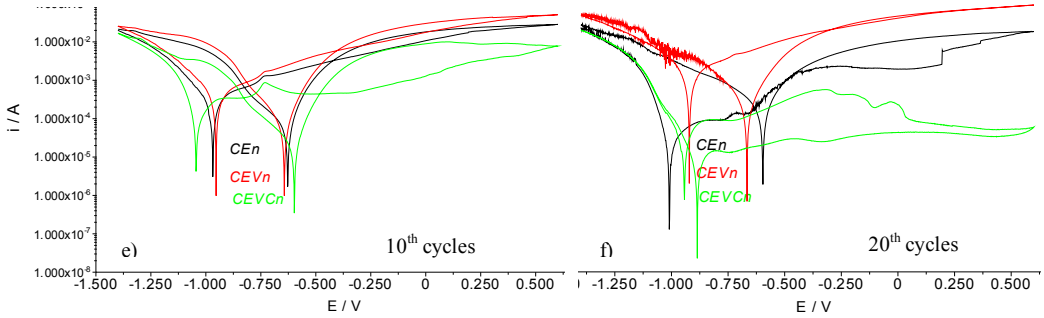


Fig.4 (a) CVA scans (1st cycles) for control specimens (CE, CEV and CEVC) after 1h treatment (stabilization) and (b) – after 7 days treatment; (c-f) 1st, 5th, 10th and 20th cycles for all corroding specimens (CEn, CEVn and CEVCn) after 1h treatment (stabilization) in the relevant solutions.

For the control (non-corroding) conditions, passive behavior is observed within the full scale of the tests for both 1h and 7 days treatment (Fig.4a)b)). Both forward and reverse scans present very low current densities in the potential region of -0.6 V to 0 V – generally the passive region for steel (St37) in this environment in the FW scan. Slightly higher currents can be observed for specimens CEV and CEVC in the reversed scans, compared to specimens CE. This is denoted to diffusion limitations with respect to the vesicles adsorption on the steel surface and further de-sorption with polarization (i.e. initial barrier effects), rather than chemical and structural alterations in the product layers due to the presence of vesicles (both empty and Ca-bearing ones). The result is due to initially increased heterogeneity of the passive layer and oxygen diffusion limitations, leading to impeded formation of a stable passive layer. Since these cases (Fig.4a)b)) are control such, these alterations are not of a large significance with respect to corrosion behavior; for pronounced positive effects of the vesicles (if any in control conditions), treatment for longer time intervals is needed.

As far as the corroding cases are concerned, a well distinguished positive effect of the Ca-bearing vesicles is observed. Fig.4c) presents an overlay of the 1st cycles: well visible is pitting formation for both CEn and CEVn specimens at potentials around – 0.37V, whereas no pitting formation is observed for specimen CEVCn. With cycling – Fig.4d), pitting is initiated also in specimens CEVCn at potentials more anodic than those for CEn and CEVn (approx. 100 mV difference), although currents in both forward and reversed scans remain the lowest for specimens CEVCn. Similar observations hold within further cycling (Fig.4a): at the end of the test, however, re-passivation behavior is relevant for specimen CEVCn – Fig.4f. The close proximity of the corrosion potential in the FW and reverse scans at the end of the test needs further investigation (incl. longer treatment). It is most likely related to restructuring of the steel product layer in the presence of Ca-bearing vesicles.

The electrochemical response of the steel electrodes in model environment i.e. cement extract, is further elucidated by surface analysis (XPS), including quali- and quantification of the product layers in depth, partial results of which will be briefly given in what follows.

3.2. Surface analysis – XPS results for steel electrodes treated for 7 days in CE.

XPS was performed on the surface of all specimens (after 7 days treatment). The product layers' composition was recorded on the "as treated" surface as well as in depth of the layers. Fig.5 presents the ionizations of O1s and C1s on the top surface layers (depth "0", Fig. 6) and the ionizations for Fe2p3/2 and Ca2p in depth of the product layer (depth "4", Fig.6). Figure 6 summarizes the XPS

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results and gives a schematic for the in-depth investigation (detailed presentation of XPS results is not subject to this work and will be separately reported).

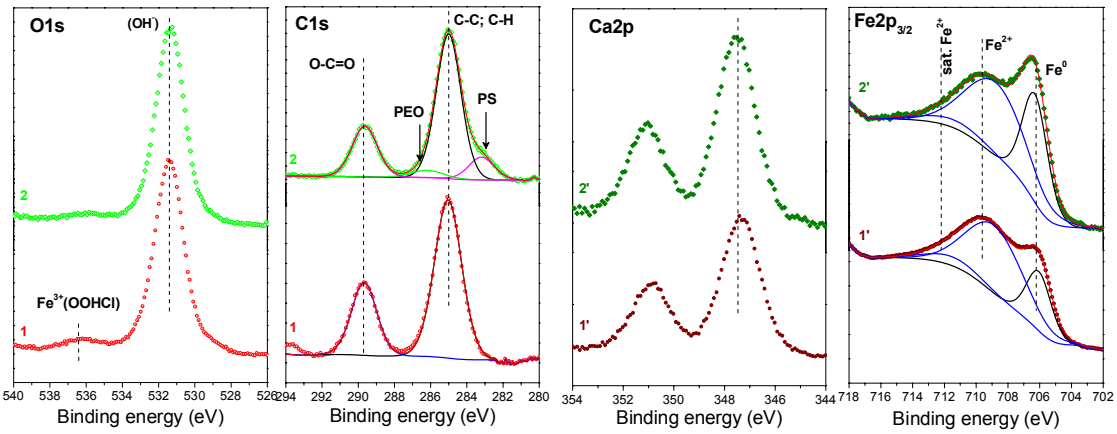


Fig.5 XPS ionizations for O1s, C1s (dept "0", see also Fig.6) and Ca2p and Fe2p3/2 (in depth, "4") of the layers.

Since the interest with respect to the above discussed electrochemical behavior is mainly in terms of the corroding specimens (vesicles free and Ca-containing), Figs. 5 and 6 present the results for specimens CEn and CEVCn only (the atomic percentages of Ca, Cl and Fe, recorded for the control specimens CE are depicted in Fig.6 (right) for comparative purposes). The amounts of carbon on the surface and in depth of the layers are denoted to both carbonates and polymeric particles for the case of specimen CEVn and CEVCn and only denoted to carbonates for specimens CEn. Analysis of the peaks for the relevant ionizations (examples given in Fig. 5, C1s and Fe2p3/2) allows differentiation of the relevant contributions. For the surface layers (dept "0", Fig.6) the following is observed: with respect to carbon, the highest percentage is recorded for specimen CEVCn, followed by CEVn and CEn (Fig.6, left) i.e. surface adsorption of vesicles is most-likely relevant (see features in C1s, Fig.5). Chloride containing iron oxides/hydroxides are characteristic for the surface of specimens CEn (Fig.5, O1s). The iron content for specimens CEn is the highest (Fig.6, right) and denoted to significant corrosion product accumulation on the surface of CEn. The calcium content for specimens CEn is also the highest on the surface (Fig.6, left) but decreases in dept of the layer (Fig.6, right) i.e. only surface adsorption and physical binding of Ca is relevant for specimens CEn, rather than Ca-substitution in the formed product layer. In contrast, for specimens CEVCn, the highest Ca content in dept of the product layer, highest Cl content and lowest (from the corroding cases) Fe content were recorded (Fig. 6, right). The results denote for the formation of a stable iron oxide layer, including Ca-substituted such, in depth of the layer (Fig.5, Ca2p and Fig.6, right) and enhanced chloride chemical binding.

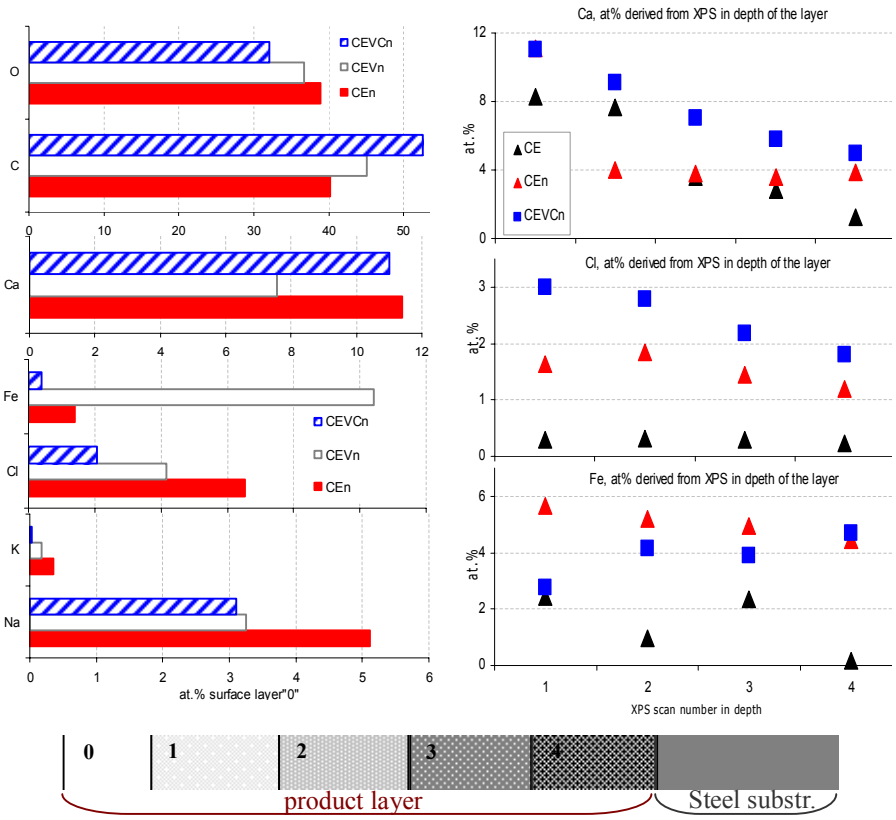


Fig.6. (left) Atomic concentrations in the outermost surface of the product layer (dept "0") and in depth of the layers (right).

With respect to iron oxides and hydroxides, all specimens exhibit a mixture of these with a larger portion of the latter in the outermost (dept "0") sections of the layers (pronounced peak at 531.6 eV in O1s, corresponding to OH-) and a larger portion of the former (oxides) in depth of the layers (hematite/magnetite based layers as evident from the characteristic features of Fe2p3/2). As also observed, metallic iron appears in dept of the layers as well (~706 eV), which is as expected within product layer removal. The morphological (not hereby presented, partly reported in [8]) and chemical alterations in the product layers formed on the steel surface in the presence of Ca-containing vesicles result in a "self-repair" or "self-healing" effects and enhanced chloride binding, which in turn result in increased corrosion resistance with time of treatment. In contrast, for steel treated in vesicles-free or "empty" vesicles containing solutions, chloride-containing iron-oxy/hydroxides and lower amount of Ca-containing compounds are relevant, which results in pitting formation and propagation and inability for surface layer re-passivation, as evidenced by CVA tests.

3.3. Corrosion behavior and steel/cement paste interface in vesicles-modified reinforced mortar specimens.

The influence of "empty" and Ca-bearing vesicles on corrosion performance and steel/cement paste interface was investigated in reinforced mortar. As previously introduced, the vesicles concentration (both empty and Ca-bearing ones) was 0.025 wt.% per cement weight. The electrochemical performance within 300 days of treatment is reported in detail in [3]. With regard to the aims of the

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present work, this section briefly summarizes visual evidences for the positive effects of Ca-bearing vesicles in terms of "self-healing" and "self-repair" of the steel surface, as previously recorded and above discussed for model solutions.

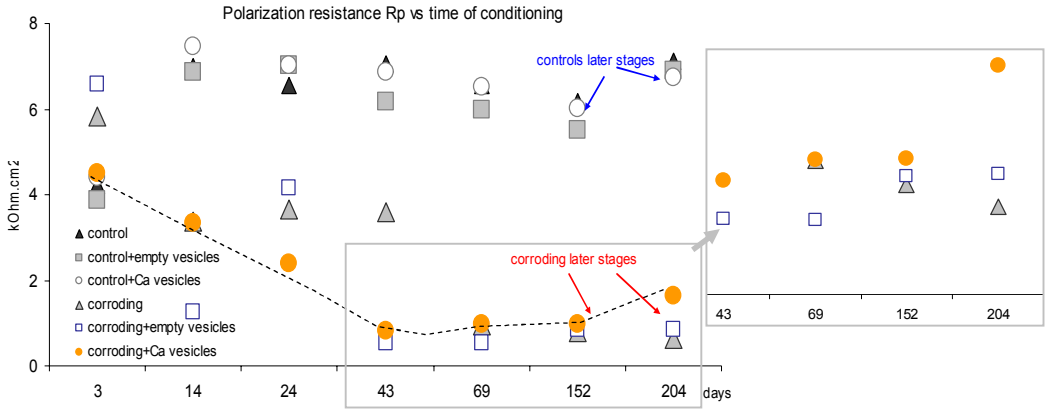


Fig.7 Evolution of OCP values (steel in reinforced mortar) with time of conditioning – 3 days- 204 days. Corrosion medium for the corroding specimens – external 5% NaCl solution

Figure 7 depicts the Rp values recorded in the frame of 204 days. As seen from the plot, passivity is relevant for all control cells, evident from the significantly larger Rp values of above 6 kOhm.cm2.

For the corroding specimens: corrosion initiation was recorded within 14 days of treatment (5% NaCl as external medium was used), corresponding to approx. two to three times lower Rp values, compared to control conditions. Should be noted that not all corroding cells behave analogically with time: for example the vesicle-free mortar presents low, but stable values until 43 days, after which an even more significant drop in corrosion resistance was recorded. Similarly, the empty vesicles-containing mortar presents fluctuation of Rp values, which stabilize in the very low resistance limits after 24-43 days. In contrast, for the reinforced mortar, modified with Ca-bearing vesicles, the Rp values gradually decrease, but depict an increasing trend after 43 days. At the stage of 204 days, these latter specimens are characterized with 1.5 times higher corrosion resistance, compared to the vesicle-free and empty vesicles-containing mortar. In other words, similarly to the previously discussed influence of Ca-bearing vesicles on steel corrosion in cement extract, the same trend of behavior appears to be present in reinforced mortar. The influence of Ca-bearing vesicles is evident here as well, being more pronounced on later stages as 300 days (not hereby presented, for more elaborated discussion and presentation on electrochemical performance for the full scale test, pls. see [3]). The responsible mechanism, leading to increased corrosion resistance is again enhanced chloride binding in the bulk cement-based matrix on first place and subsequently in the product layer on the steel surface. This is the case, since chloride apparently reached the steel reinforcement (corrosion was initiated, Fig. 7) but impeded and halted later on, as evidenced by direct observation of the steel surface and adjacent cement paste – Figure 8.

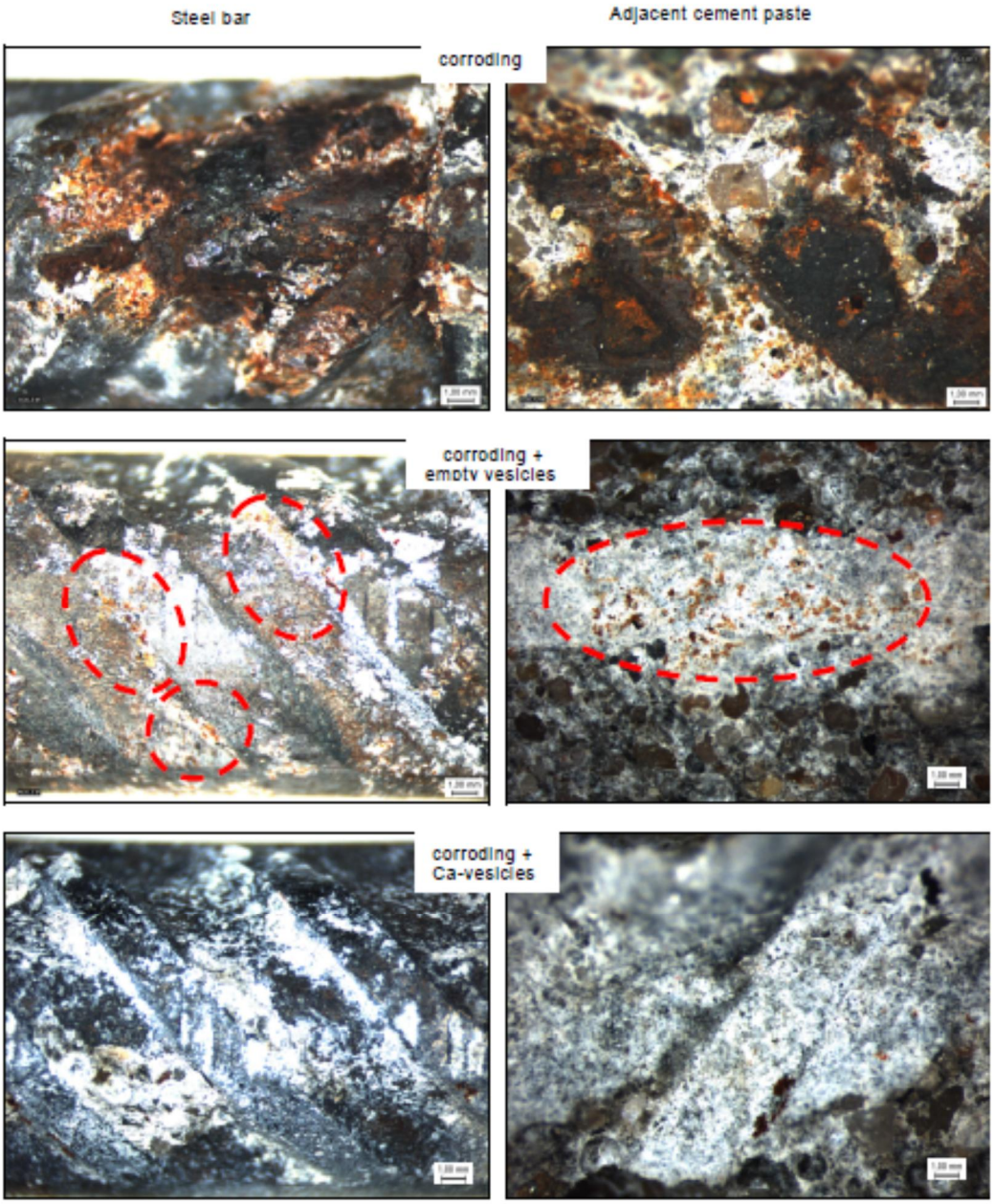


Fig.8 Light microscopy of the product layer on the steel surface (after 300 days of conditioning) – left column and the adjacent cement paste (right column) after breaking open the reinforced mortar specimens: vesicles-free specimen (top), empty vesicles-containing specimen (middle) and Ca-bearing vesicles-containing specimen (bottom).

As seen from the light microscopy investigation (also proved via electron microscopy, [3,8]), a significant corrosion damage was observed in the vesicles-free specimens (Fig.8, top). Corrosion products penetrated and deposited in the adjacent cement matrix (Fig, 8, top, right). For the specimens, containing "empty" vesicles, corrosion initiation was similarly recorded (Fig.7), although lower amounts of iron oxides/hydroxides were deposited in the adjacent cement paste (Fig.8, middle). In

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contrast to the previous two cases, no steel corrosion was observed in the case when the mortar matrix contained Ca-bearing vesicles (Fig.8, bottom). The above observations are supported by X-ray analysis (XRD) directly on the steel surface and on the (grinded) cement paste, previously present in the vicinity of the steel bars – Figs. 9 and 10.

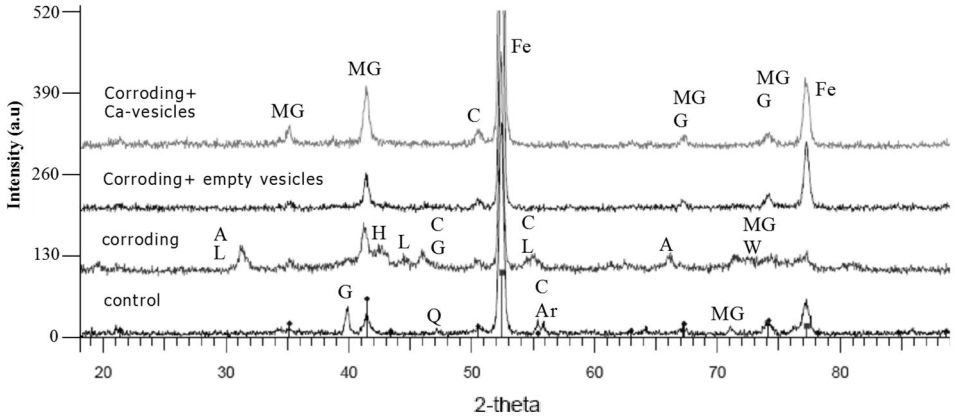


Fig.9 XRD patterns for a control specimen and all corroding specimens (*CoKa radiation*) at the conditioning time of 300 days: A akaganeite, Ar aragonite, C calcite, G goethite, H hematite, L lepidocrocite, MG magnetite and W wustite (W in MG composition) [3]

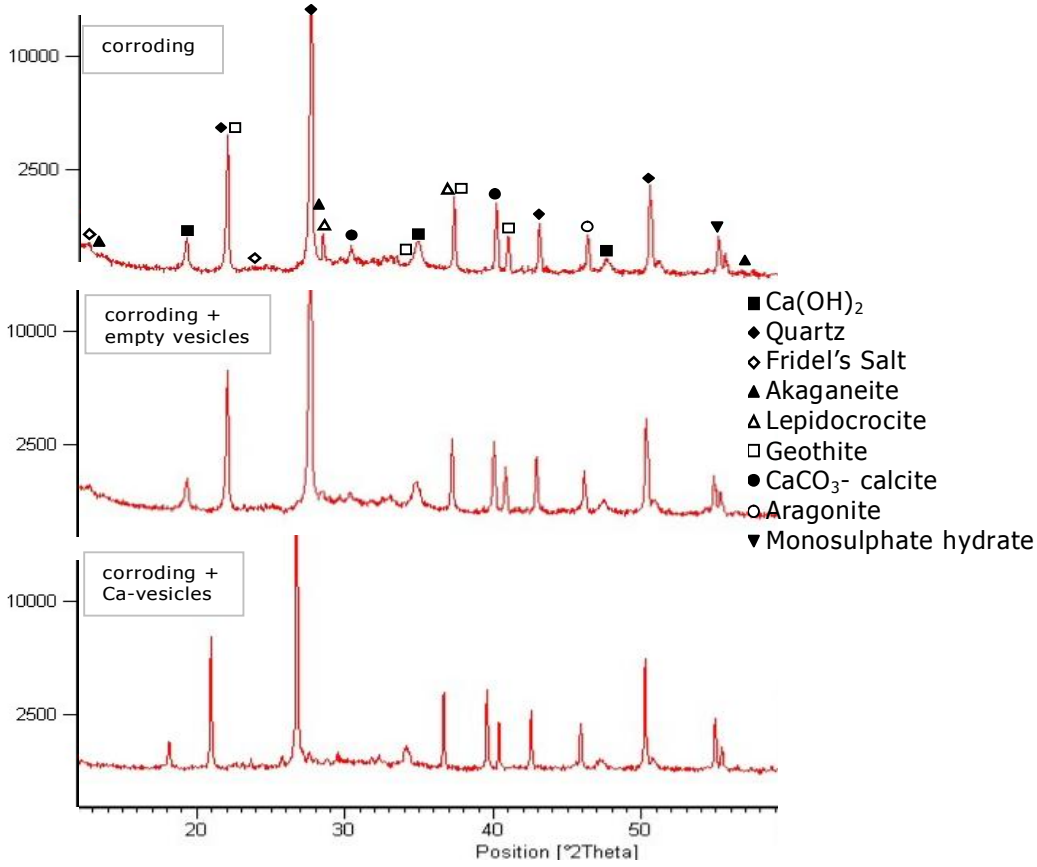


Fig.10 XRD patterns for the cement paste in teh vicinity of the steel surface for all corroding specimens, (using *Cu Ka radiation*) at the conditioning time of 300 days.

The products formed on the steel surface include a mixture of iron (oxy) hydroxides and calcite/aragonite (CaCO3), also corresponding to Ca-substituted iron oxides/hydroxides. Goethite (G) and lepidocrocite (L) are prominent corrosion products in rust layers, and akaganeite (A) is identified in corrosion products in chloride-containing environment. For the corroding specimens significant difference was observed between the vesicles-free and the vesicles-containing specimens: except for MG and G, the vesicles-free specimen shows the presence of akaganeite and lepidocrocite. For the vesicles-containing specimens a relatively clean surface was observed (the XRD patterns were similar to the control case) with predominance of the more protective magnetite. When the adjacent cement matrix was investigated, the XRD patterns do not exhibit the significant difference as recorded for the relevant steel surface. This is denoted to the fact that the cement paste was grinded in order to be tested and the contribution of iron oxides and hydroxides was masked by the larger amounts and predominance of the constituents of the cement paste. However, certain features appear to be present only in the corroding, vesicles-free case (Fig.10, top), e.g. akaganeite and lepidocrocite, explaining the observed corrosion products penetration into the cement matrix (Fig. 8).

4. CONCLUSIONS

This study reports on the influence of vesicles (PEO113-b-PS780, both as “empty” and Ca-containing formations) on the corrosion performance of steel in cement extract and in reinforced mortar. In the presence of both vesicle types corrosion resistance was increased, but the effect was significantly more pronounced when Ca-containing vesicles were involved. Clear differentiation between “barrier” effects and “self-repair” can be made: corrosion was initiated but impeded later on and no corrosion product was observed only in the presence of Ca-bearing vesicles. The positive effect was confirmed via cyclic voltammetry and by morphological observation and surface analysis of the steel reinforcement: for the vesicles-free specimens γ-FeOOH and Fe3+OOHCl, were observed, which are the predominant corrosion products in rust layers (especially for chloride-containing environment). For the vesicles-containing specimens, lower accumulation of products was recorded when empty vesicles were involved and no corrosion product formation was detected when Ca-containing vesicles were used. The steel surface layer for the vesicles-containing specimens mainly consisted of stable Fe3O4 and α-FeOOH. The results indicate that the presence of Ca-containing vesicles improves the protective properties of the steel surface layer and further ceases the initially commenced corrosion process. The concentration of 0.0024 wt.% vesicles in the model solutions and 0.025 wt.% per cement weight is minimal and therefore self-repair or self-healing of the product layer solely due to the Ca-component release is not realistic. The most likely mechanism is the nature of incorporation of the Ca-containing vesicles in the steel product layer, enhanced chloride binding effects and adsorption on active sites on the steel surface.

REFERENCES

1. Hu J., Koleva D.A., et al., Cem.Concr.Res., 42, 1122-1133 (2012)

2. Hu J., Koleva D.A., van Breugel K., J.Mater.Sci. 47 (2012) 4981-4995.

3. Hu J., Koleva D.A. et al., Corrosion Sci., 65, Pages 414-430 (2012)

4. Hu J., Koleva D.A., et. al. J. Electrochem.Soc. 158 (2011) C76.

5. Hu J., Koleva D.A., van Breugel K. ECS Transactions, 41 (16) 1-9 (2012)

6. Koleva D.A., van Breugel K., Ye G., Koenders E., ACI Mater.J. 267 (2009)101-110

7. Koleva D.A., J. Hu, Van Breugel K., J. Intern. Sci. Publ.: MMT5 (2011) 63

8. Koleva D.A., Hu J., Kolev H., van Breugel K., Proceedings of "Materials Characterisation 2013", WIT Press, Siena, Italy, June 2013.