Preliminary Study on the Self-healing of Steel, Resulting from the Presence of Nano-aggregates in Cement Extract

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Introduction: This work presents results from a preliminary investigation on the corrosion behavior of carbon steel in cement extract (CE) in the presence of very low concentration polymeric nano-aggregates (PEO_{113}-b-PS_{70} micelles). The steel electrodes were investigated in Cl-containing CE as corrosion medium, compared to chloride-free solution as a reference case. Electrochemical measurements (EIS, Potentio-dynamic and Potentiostatic Polarization (PDP, PSP)) and surface analysis (SEM, XRD, XPS) were employed for evaluating the corrosion performance at different time intervals. The results so far indicate that a very low concentration of the micelles (0.024 g/l) improves the corrosion resistance of steel in Cl-containing cement extract at early stages. The investigation is on-going.

Materials and methods: *Steel electrodes* (low-carbon steel 37) with surface area of $0.65\ cm^2$ were used. All electrodes were equally treated prior to electrochemical measurements i.e. they were grinded with no.500 to no.4000 grinding papers and polished; further, just before immersing in the relevant solution, they were cleaned with acetone. *Cement extract*: Ordinary Portland cement CEM I 42.5 and tap water were mixed in the ratio of 1:1; the suspension was filtrated after 24h and thus a simulated pore solution (CE) received. The pH of CE is 12.6 – 12.8. *Polymeric nano-aggregates*: Used in this study were PEO_{113}-b-PS_{70} micelles, received as stabilized aggregates, concentration 0.5 g/l (demi-water). For this experiment, part of the so received solution was added to the CE (groups CN and CNC below), thus 0.0024 wt% of the micelles were present in both chloride-free and chloride containing CE. *Sample designation:* For the EIS and PDP measurements, four solutions are relevant: CE with micelles; CE without micelles; CE with micelles and NaCl; CE without micelles with NaCl. Thus the samples designation is: control groups "C" (without micelles) and "CN" (with micelles) and corroding groups "CC" (without micelles) and "CNC" (with micelles), where Cl⁻ was added to the CE in concentration 10 g/l.

Results: Fig.1 depicts the OCP evolution of the steel electrodes in the four tested solutions (i.e. control and corroding groups) after immersion of 1h, 3h, 6h and 12h, showing similar trends. An obvious positive effect in terms of more anodic potentials were derived form the micelles + NaCl containing CE (group CNC), but only at earlier stages.
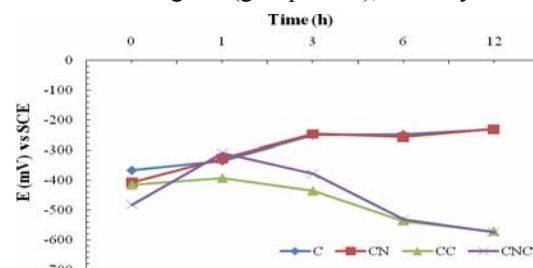

Fig.1 OCP readings for all studied conditions.

EIS measurements provide evidence for the initially enhanced corrosion resistance of steel in micelles-containing solutions, i.e. in both chloride-free and chloride-containing CE (Fig. 2, 1h and 3h response)). With time of immersion, the steel in chloride-free CE maintains passive state, the micelles adding no significant influence to the observed corrosion resistance (Bode plots, Fig.2, 6 and 12h response). For the Cl-containing solutions, a transition from higher to lower and again higher magnitude of impedance is observed.

The EIS response depicts a well distinguishable 2nd time constant for the micelles-containing solutions, denoted to a more pronounced contribution of the product layer on the steel surface, due to the presence of the micelles.
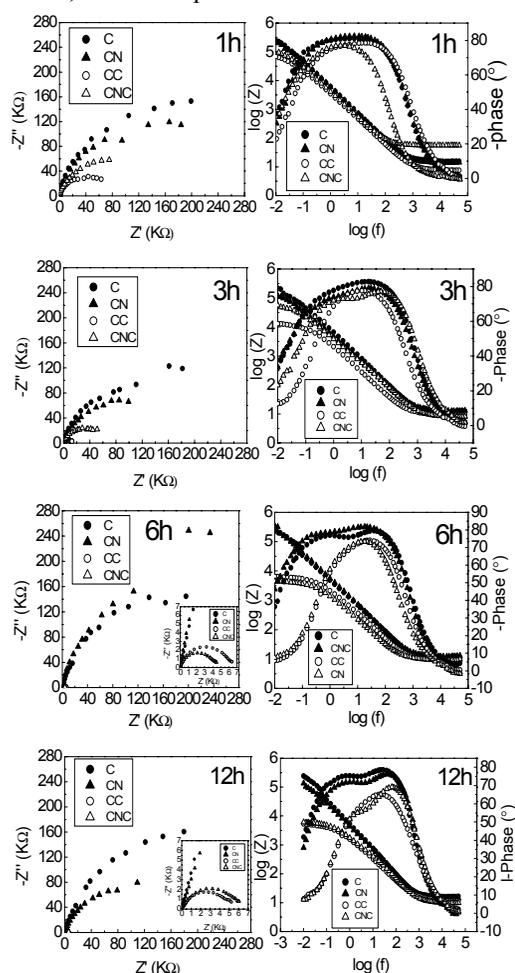

Fig.3 EIS response in Nyquist and Bode format for steel in CE solutions

PDP tests support the EIS response, showing a pronounced positive influence of the micelles at early stages (Fig.3a,b) and similar response in-between control and corroding groups later on. Corrosion current densities for the corroding groups are however very low (in the range of 0.472-35.6 $\mu A/cm^2$), which is as expected, since CE is a highly alkaline solution and chloride-induced corrosion in such environment is related to reversible pit initiation, growth and impeding of the corrosion process.
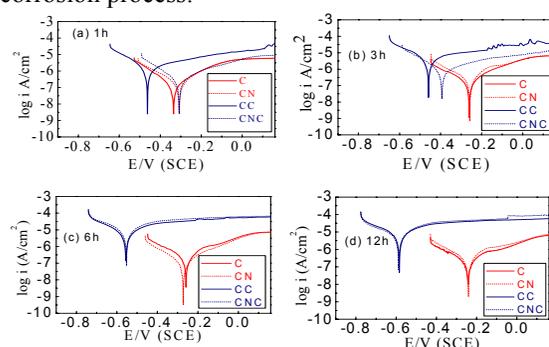

Fig.2 Potentiodynamic polarization of steel

In that sense, the micelles are obviously having positive effect, although according potential readings, the "corroding" specimens CNC behave close to the specimens CN. Cathodic OCP values however can be also relevant if there were oxygen diffusion limitations. This latter aspect may have significant contribution to the observed behavior, especially related to the EIS response.

Further, the paper will discuss the correlation of electrochemical behavior and surface analysis, shedding light on the possible self-healing of chloride-induced corrosion damage in the presence of polymeric nano-aggregates.