Hybrid Composite Aggregates for Superior Corrosion Performance of Low-carbon Steel in Model Solutions

D.A. Koleva¹, Jie Hu¹, K.van Breugel¹, N. Boshkov²,
Ts. Radeva², V. Milkova²

¹Delft University of Technology, The Netherlands, Faculty of Civil Engineering & Geosciences, Dep. Mater.& Environment, Stevinweg 1, 2628 CN Delft

²Bulgarian Academy of Sciences, Institute of Physical Chemistry, Acad. G. Bonchev, Sofia 1000, Bulgaria

Introduction: This work forms part of the first initial tests in the frame of a project on Self-healing corrosion damages in reinforced concrete. The main research objective is to initially improve the properties of the steel surface and the bulk cementitious matrix, by introducing polymeric micro/nano aggregates with tailored properties. Further, only in the event of detrimental external influence (as CO₂ penetration and thus carbonation in the matrix, or Cl⁻ penetration and thus localized corrosion on the steel surface) the aggregates will participate in a self-healing mechanism, by means of releasing initially incorporated in their core certain chemical substance (e.g. CaO). The result will be restored alkalinity in the bulk matrix and repaired passive layer on the steel surface.

Motivation: Since the intended for use tailored polymeric aggregates are formations, serving far different purposes, as drug delivery for example, rather than the hereby studied phenomena in reinforced concrete, the initial investigation is related to different aspects. Some of them concern: proper choice of the polymeric formations, proper choice of the substance that they carry, size, behavior in alkaline medium etc. Additionally, their addition to concrete as a 'solid' electrolyte and the complexity of the involved hydration mechanisms, thus also particles/cement interactions, need to be well clarified in advance.

To this end, this preliminary research tries to answer the question if the hereby used hybrid formations (Fig.2) have any impact on corrosion behavior of steel in alkaline medium, with and without chlorides, and thus to make the path for further investigation in a real cement-based system. The initial tests show very promising results and hereby report on the electrochemical behavior of steel electrodes in cement extract, containing the hybrid formations, coupled with quali- and quantification of products layers before and after treatment.

Fig.1 CaO crystals, before "encapsulation" in the particles

Fig.2 Composite particles: CaO core/ polymer (triple layered) shell.

Materials and methods: The hereby investigated specimens were steel electrodes (low-carbon steel St37) with

service area of 0.7 cm². No special pretreatment of the surface was used, only grinding, polishing and acetone rinsing before testing were performed for each electrode. There were 4 types of testing solutions: two controls i.e. without hybrid aggregates (from here on, for simplicity, the aggregates will be referred to as "particles") and 2 with particles. One of the controls and one of the particle-containing solutions contained NaCl as well (1.5%), as a corrosion accelerating factor. The initial (basis) solution was cement extract (CE), prepared by mixing Portland cement CEM I 42.5 and water in a ratio of 1:1 and filtrating the suspension after 24h. Thus sample designation is as follows: CE (CE only); CEp (CE + particles); CEN (CE + 1.5% NaCl) and CENp (CE + particles + 1.5% NaCl). The composite particles were synthesized through a layer-by-layer adsorption of oppositely charged polyelectrolytes on CaO crystals (Fig.1) (PDADMAC/PAA/PDADMAC over CaO). Polyelectrolytes: poly(diallyldimethylammonium chloride) PDADM AC, 4.10⁻² g/l; Poly(acrylic acid), sodium salt, PAA, 4.10⁻² g/l. The particles concentration was 3.10⁻² g/l (demi water). In the hereby tested solutions (CE), particle concentration was 4.9.10⁻⁴ g/l. The methods involved at this stage of the experiment were: electrochemical (EIS, PDP) and steel surface analysis.

Results: Figure 3 (top) presents the EIS response in the control (CE only) solutions, with and without admixed particles. Fig.3 (bottom) depicts the EIS response for the CEN solutions (with 1.5% NaCl). As seen from the plots, the electrodes immersed in solutions with particles (samples CEp and CENp), present higher corrosion resistance, evident from the higher magnitude of impedance for both chloride-containing and chloride-free solutions. The difference is especially pronounced for the former case, whereas in the latter case, electrochemical behavior is expected to be similar, since the concentration of the particles is very low (4.9.10⁻⁴ g/l) and steel normally passivates in the highly alkaline (pH 12.6) CE (the response for all cases is after OCP stabilization of approximately 1h and is an average of 3 replicates per time interval).

Fig.3 EIS response for steel in CE (top) and CEN (bottom)

Finally, corrosion current density derived from PDP in CE (CE and CEp, without addition of chloride) was in the range of 2.04.10⁻⁷ A/cm² for CE and lower, 1.6.10⁻⁸ A/cm² for the CEp specimens. This is an on-going investigation; therefore the paper will further present a complete set of electrochemical data for intervals of 1h until 480h of treatment in all solutions and a correlation of electrochemical response with AFM, SEM and XRD results.

At this preliminary stage it can be stated, that the extremely low concentration of the particles results in a significant improvement of corrosion performance, especially in chloride-containing environment.