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Bio-based admixture with substances derived from bacteria for the durability of concrete

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20.1 Introduction

Cementitious materials are sensitive to many physical, chemical and biological factors responsible for their degradation (Feugeas, 2008; Roux, 2008; Ollivier and Vichot, 2008). One of their most frequent degradation mechanisms is reinforcement corrosion. Although the high-alkaline environment of concrete allows for the formation of a passive and protective oxide film on the surface of carbon steel used in concrete as reinforcement, an abundance of literature can be found concerning problems of concrete structure degradation due to reinforcement corrosion. As a matter of fact, the protective layer can be destroyed by the decrease in alkalinity of concrete (carbonation of the cover concrete) (Chang and Chen, 2006; Johannesson and Utgenannt, 2001; Pade and Guimaraes, 2007) and/or through entrance of chlorides,

leading to pitting of passivated reinforcing steel (Ahmad, 2003; Basheer et al., 2001). The environmental conditions, such as CO₂ concentration and presence of chlorides, are not the only phenomena to be taken into account. The physical and chemical nature of concrete is also important, since the aggressive species must penetrate through the concrete pores to reach the reinforcement. Different ways of rebar protection from corrosion have been suggested:

- Increase the concrete cover on the steel rebar in the concrete (standard exposition class Eurocode 2) (Zhang and Lounis, 2006; EN 1992, 1997).
- Cathodic protection of rebars by deposition of a zinc layer on the surface of the steel, or by application of a direct current from a graphite mesh anode to the surface to be protected (Glass et al., 1997; Hassanein et al., 2002; Koleva et al., 2009).
- The use of corrosion inhibitors (Ormellese et al., 2008, 2009). This method can eventually be combined with cathodic protection (Efim, 2002; Whitmore, 2004).

Corrosion inhibitors such as monofluorophosphate (MFP) are sprayed or painted on mature concrete surfaces (Chaussadent et al., 2006), or added to the fresh concrete mix. Many of these inhibitors contain components that are not eco-friendly (Roust et al., 2010).

Corrosion inhibitors have been used successfully to preserve steel structures for many decades. More recently, they have been applied in the field of construction to preserve historical monuments and concrete constructions suffering from rebar corrosion. In their state-of-the-art report, Söylev and Richardson (2008) focused on the most commonly used inhibitors, such as aminoalcohol, calcium nitrite, and sodium monofluorophosphate. They analyzed the effectiveness of corrosion inhibitors regarding mechanical performances, protection against corrosion in chloride-contaminated and carbonated concrete, penetrability of the inhibitor, influence on workability of fresh concrete and hardened concrete properties, and, finally, long-term behavior for real structures. They made conclusions with regards to the ability of those products to delay the corrosion initiation of rebars exposed to chloride attack and carbonation. The inhibition efficiency appeared to be less significant once corrosion was initiated, mainly due to the difficulty of penetration of the inhibitors through the pores of the concrete. This is why the development of admixtures as corrosion inhibitors has developed as an alternative with higher efficiency. Moreover, the growing demand for corrosion inhibitors that are biodegradable and less toxic than the current formulations turns researchers towards the development of eco-friendly admixtures providing a sustainable protection against corrosion.

This study presents the performance of a bioadmixture, containing bacterial extracellular substances, with regard to the corrosion inhibition efficiency in different solutions representative of concrete. Three interstitial solutions obtained with standard cements CEM I, CEM II, and CEM III were tested with and without bioadmixture. The inhibiting effect of bioadmixture addition in synthetic solutions containing chlorides was also investigated and highlighted the inhibiting effect of the biomolecule against chloride-induced depassivation of steel.

20.2 Types of corrosion inhibitors in concrete

It is not an attempt to describe all the kinds of corrosion inhibitors used for protection or repair for concrete structures. These can be classified according to their application methods, or their mechanism of protection, or their content. Here, only corrosion inhibitors that can be used as admixtures or applied on the hardened concrete surface are considered with regard to their content and their ecological impact. These type of corrosion inhibitors can induce an increase in the corrosion potential of the rebar and act as anodic inhibitors. When they act on the oxygen reaction of the reinforcement and reduce the corrosion rate by a decrease in corrosion potential, they are cathodic inhibitors. Mixed inhibitors are able to reduce the corrosion rate without a significant change in the corrosion potential, thanks to their action on both anodic and cathodic sites of the steel.

Admixtures based on alkali metals or on alkaline earth metal nitrates (Fujita and Kashima, 1982; Kudo and Ibe, 1976; Rosenberg and Gaidis, 1981, 1986; Whitaker, 1974) have disadvantages linked to the ecological and toxic risks associated with nitrates. Admixtures containing alkanolamines and alcohols trihydrates or tetrahydrates have been described (Fellows and Eckler, 1988) for the protection of steel, but their application to mineral building materials like cementitious materials has not been described in the literature. Other water-soluble hydroxylamine-based products (Martin and Miksic, 1987) react with carboxylic acids to reduce their volatility before acting as corrosion inhibitors. As for many migrating corrosion inhibitors, the main problem consists of controlling the concentration of inhibitor needed at the level of the embedded steel. Elsener et al. demonstrated that the inhibitory action of migrating corrosion inhibitors was not detectable by measurements of corrosion currents (Elsener et al., 2000). It is assumed that the inhibitors do not diffuse deep enough into the cement matrix to be active at the metal-cement interface. Another patent (Standke and McGettigan, 2003) discloses the use of organosilane and/or organosiloxane-containing inhibitors as admixture in concrete or to be applied on hardened concrete. No results were found concerning the use of these products as admixture in fresh concretes, particularly with regard to potential modifications in the rheology of these. The same remarks can be made about the patents by Furman et al. (2005) and Miksic et al. (1997, 1998). Their formulas are based on sodium gluconate and sodium molybdate (Miksic et al., 1997, 1998) with aluminum nitrate, cyclohexylammonium benzoate, ethylammonium benzoate, ammonium and dimethyl ethanolamine (Furman et al., 2005) assumed to inhibit possible alkali-reactions in concrete. Some inhibitors were proposed as admixture with rheology-modifying properties of fresh concrete (Miksic et al., 2002). They contain alkaline earth lignosulfates in addition to ammonium benzoates and sodium glucoheptonates which give plasticizer properties to the product. No indication concerning mechanical behavior of these cured concretes was given. One patent (Miksic et al., 2006) describes the composition and method of using fiber-reinforced mortars to repair reinforced concrete structures. Corrosion inhibitors used as admixture in these mortars contain am-

monium benzoates, sodium and potassium sebacates. They are assumed to diffuse into the hardened concrete to reach the rebars. Other patents (Arfael et al., 1993; Berke and Hicks, 1997; Berke et al., 1996, 2002) disclose inhibitors containing calcium nitrite and stearate, nitrate or alkaline earth metal nitrite combined with components modifying the rheology of fresh concrete (for instance superplasticizers), or the setting time of the concrete (accelerators or retarders). The 20 patents mentioned offer products that can be used as admixtures in fresh concrete or applied to hardened concretes. Regarding the corrosion inhibitors applied to mature concrete, the main issue concerns the ability of the active ingredient to diffuse from the cover to the reinforcement. This kind of inhibitor mostly acts as a barrier against ingress of aggressive agents in water, rather than through a direct interaction between the inhibitor and the rebars. These products are able to clog the porous network of concrete and consequently decrease the rate of capillary imbibition of the concrete, without having reached the reinforcement located more deeply in the concrete. In the case of mature concrete repair, the solution consisting of the use of mortar with corrosion inhibitors in their composition present the same problem of diffusion control, whatever the chemical composition of the corrosion inhibitor.

Corrosion inhibitors as admixtures present an easily implemented solution to improve the durability of concrete. It could be claimed that a new concrete, correctly designed, should not face problems of rebar corrosion but, with regard to the increasing demands on the time of use and the potential recyclability of concrete, admixtures with corrosion inhibition provide additional safety for concrete to withstand degradation due to aggressive environments.

Concrete is known to bear high compressive stresses but its tensile strength is limited. In the tension zone, concrete will always exhibit cracks. This explains why it has been estimated that, in Europe, 50% of the annual construction budget is spent on the rehabilitation and repair of existing structures (Tittelboom et al., 2011).

Using admixture as a corrosion inhibitor provides the advantage of acting directly on the reinforcement without having to diffuse through the concrete porosity. It is worth pointing out, however, that there are contradictory results in the literature about the influence of such products on concrete properties (Söylev et al., 2008), depending on their chemical composition, their concentration, their compatibility with other admixtures, their effect on properties of fresh and hardened concrete are susceptible to variation. It is therefore of great importance to check the possibility of harmful effects arising from the use of those admixtures. Furthermore, the majority of inhibitors described in the current patents containing chemical substances, few of them are not eco-friendly with regard to the criteria for Environmental and Health Data Sheets.

20.3 Case study: bio-based admixture from bacterial extracellular substances

20.3.1 *Bio surfactant as bio admixture*

Many admixtures (chemical admixtures and mineral admixtures) are used to improve the rheological properties of fresh concrete and to influence the behavior of hardened concrete (Palacios and Puertas, 2005; Şahmaran et al., 2006; Černý et al., 2006; Izaguirre et al., 2009).

Bioadmixtures attract increasing scientific interest, as a result of the increasing demand for inhibitors displaying substantially improved environmental properties (Zhor and Bremner, 1996; Plank, 2004; Riedel and Nickel, 2000; Orts et al., 2007). Bioadmixtures generally result from industrial biotechnological processes (e.g., welan gum) (Sonebi, 2006). They are extracted from fermentation processes by culturing fungi or bacteria (e.g., extracellular polysaccharide) (Roux et al., 2010), or include polymers with significant biodegradability (e.g., polyaspartic acid) (Amjad, 2011).

The application of bioadmixtures in the cement-based industry is relatively recent. Kahng used the extracellular production from *Paenibacillus sphaericus* as a viscosity-modifying bioadmixture for cement mortar (Kahng et al., 2001). Khayat and Yahia investigated the effects of combined bioadmixtures of welan gum and naphthalene-based water reducer on the rheological properties of cement grouts (Khayat and Yahia, 1997). Lignosulfonate is a plasticizer which improves the workability of concrete (Wang et al., 2012). Patural studied the effect of cellulose ethers as bioadmixture on both water retention and rheological properties of cement-based mortars (Patural et al., 2011).

The present study concerns the development of environmentally friendly products to be incorporated into concrete (admixtures) in accordance with REACH requirements and simultaneously fulfilling two conditions: limiting biocontamination of the surface of concrete and improving the corrosion resistance of the reinforcement. The efficiency against biocontamination of cementitious surfaces has been analyzed previously (Chagnot et al., 2015). Furthermore, standardized tests have permitted the validation of this product as admixture for concrete (He et al., 2014), leading to the elaboration of concretes that are more eco-friendly and more resistant to natural environments than traditional Portland cement concrete (CEM I) (Roux et al., 2013). The work presented below focuses on the improvement of durability of concrete structures by protecting their reinforcement from corrosion.

The active ingredients of the admixture consist of bacterial exo-products. They are eco-friendly and in agreement with the criteria for establishing Environmental and Health Data Sheets (SDS).

Many bacteria are able to produce amphiphathic substances, i.e., “biosurfactants,” which are potentially interesting compounds in many fields of study, due to having both hydrophilic and hydrophobic moieties in the same molecule (Shubina et al.,

2015). Some of them have antimicrobial activity, such as lipopeptides (surfactin, iturin, etc.) produced by *Bacillus* and *Pseudomonas* (Lang, 2002), or amphisin compounds which possess strong antifungal activity (Nielsen et al., 2002). These biomolecules are often controlling plant pathogenic germs (zoospores) and creating ducts in the cytoplasmic membrane of the infectious germ (Raaijmakers et al., 2006). Biosurfactants also have the advantage of being efficient and stable (*Bacillus subtilis* (Joshi et al., 2008)) in a wide range of environmental conditions (pH, temperature, salinity). Some of them are able to maintain their surface activity at temperatures up to 90°C (Kretschmer et al., 1982) or for salinity up to five times higher than those tolerated by chemical surfactants (Donaldson and Staub, 1981). The emulsifying properties of surfactants synthesized by *Serratia marcescens* are also preserved at temperatures in the range of 10–120°C and pH values ranging from 2 to 12 (Pruthi and Cameotra, 1997). Moreover, biosurfactants exhibit good biodegradability and lower toxicity (Nitschke and Costa, 2007).

In this study, a lipopeptide biosurfactant (viscosinamide) derived from *Pseudomonas fluorescens* was used. It was produced on a solid medium, as previously described (Meylheuc et al., 2001). Briefly, plates of King's B (KB) agar were densely inoculated with two loops of a suspension of *Pseudomonas fluorescens* 495. The inoculated plates were incubated for 4 days at 22°C. The bacterial lawns were scraped from the agar and the cells were resuspended in sterile, demineralized water and dispersed, using a vortex mixer operated at maximum speed. The supernatant containing the biosurfactant was separated from the cells by centrifuging for 30 minutes. The supernatant was then filtered through a 0.22- μm pore-size filter and stored at 4°C. The surface activity of the biosurfactant and its critical micelle dilution (CMD) were determined by surface tension measurements of the supernatants and dilutions using the Wilhelmy plate method and a tensiometer.

20.4 Corrosion study

Though chloride ion attack and carbonation have been identified as the main mechanisms responsible for the initiation of reinforcing steel corrosion (Cao et al., 1993; Boah et al., 1990; Sagoecretil et al., 1993; Freire et al., 2009; Albani et al., 1990; Moreno et al., 2004; Abd El Haleem et al., 2010a; Tang et al., 2012), sulfate ions have also been reported to actively participate in the corrosion of reinforcing steel (Abd El Haleem et al., 2010b, 2013; Ghods et al., 2009; Haruna and Komete, 2002; Gui and Devine, 1994; Montemor et al., 1998; Altayyib et al., 1988). The sulfate source for concrete can be external (from water or soil) or internal, when sulfate is initially present in the cement or has been added as gypsum to regulate the hydration reactions of the Portland cement. The presence of sulfates has been reported to have two effects: the first one is related to the resistance of the concrete and the second one to the corrosion resistance of the rebars. When the concentration of sulfates is high enough in the concrete pore solution, it is known to react with tri-calcium aluminates of the cement to form ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) which reduces the strength of concrete (Page and Treadaway, 1982). Moreover, according to

Abd El Haleem et al. (2013), the presence of sulfates can significantly influence the composition and the thickness of the oxide layer. Comparing the shift of the open-circuit potential of iron in interstitial solutions containing the same amount of chlorides and sulfates, it was concluded that sulfate ions are even more corrosive than chloride ions toward steel rebars.

To follow the stability or the breakdown of the passive film using electrochemical methods, a convenient way is to perform measurements in simulated concrete pore solutions. Corrosion rates, determined by means of experiments involving steel electrodes immersed in simulated solutions, can hardly be extrapolated to the rates measured in concrete, since the diffusion kinetics of the reactants are very different in aqueous solutions than in the solid material. Nevertheless, experiments performed in aqueous solutions provide useful information on the influence of a specific reactant at different concentrations (anions or cations present in the concrete, as well as different additives and inhibitors). Moreover, the pH value of a solution can be easily adjusted.

This approach was used in the present work to check the influence of the presence of the bioadmixture (BA) described above, on the corrosion rate of carbon steel in interstitial solutions with different sulfate concentrations, and in synthetic solutions with different chloride concentrations. The corrosion resistance was evaluated using electrochemical methods such as linear polarization and impedance spectroscopy.

20.4.1 Material

The material studied is a C15 mild steel, generally used as metal reinforcement in concrete, according to EN 10277-2. The composition of the major elements of C15 steel is presented in the Table 20.1.

20.4.2 Interstitial solutions obtained from different cements

Interstitial solutions were obtained by adding cement powder to deionized water with a water-cement (w/c) ratio of 0.45. Three Portland cements (CEM I 52.5 N, CEM II/B-S 42.5 N, and CEM III/A 42.5 N-LH with 61% by mass of slag) were used and the cement paste was mixed using a IKA Eurostar 20 mixer with a deflocculating blade. After mixing for ~1.5 minutes, the paste was filtered by means of a vane pump, using two filters of 11 and 20 μm , then using a 1.0 and 0.2 μm filter syringe. The elemental concentrations of Ca^{2+} , Na^+ , K^+ , and SO_4^{2-} in the pore so-

Table 20.1 Chemical composition (% weight) of the carbon steel C15 (W.NR.: 1.0401) (in accordance with “EN 10227-2”)

C	Si	Mn	P	S	Fe
0.12–0.18	0–0.40	0.30–0.80	0–0.045	0–0.045	Balance

lutions extracted shortly after mixing were then monitored as follows: concentrations in alkali (sodium and potassium) were assayed by atomic absorption spectrometry, whereas sulfate and calcium concentrations were determined respectively by turbidimetry and by potentiometry using a calcium ion-selective electrode. The pH value and the concentrations obtained for the various cements are shown in Table 20.2. Similar calcium concentrations and similar pH values were observed for the three cements (as expected), since the interstitial solution of the concrete is usually saturated with lime. CEM I cement, which contains higher amount in clinker than CEM II and CEM III cements, also shows the higher sulfate and alkali (Na^+ and K^+) contents. In all solutions used for electrochemical measurements, the pH value was systematically adjusted to a fixed value of 13.0, in order to avoid the effect of small pH differences between the solutions. At the end of each experiment, the pH was measured again and its value was found to be always greater than or equal to 12.5. This small pH variation due to the carbonation of the solution is assumed to have no effect on the corrosion behavior of the steel.

In order to obtain interstitial solutions with BA, 10% by volume of the bioadmixture (BA) was added.

To study the influence of BA on the corrosion behavior of the C15 steel sample in the presence of chlorides, a synthetic solution was prepared, containing 0.1 mol/L (4 g/L) of NaOH (pH=13). Two chloride concentrations were investigated: 0.5 and 1 mol/L (17.75 and 35.50 g/L).

20.4.3 Corrosion inhibition of bio-based admixture in interstitial solutions without chlorides

Anodic polarization curves obtained in the interstitial solutions of CEM I and CEM III are presented in Fig. 20.1, after 60 hours of immersion of the steel sample at the open-circuit potential. The shape of all polarization curves is similar, showing a passivity plateau extended over several hundreds of millivolts. This passive step is followed by an increase in the current, corresponding to the transpassive domain for potentials $E > 0.1$ V/MSE (saturated mercury sulfate electrode $E = +0.645$ V/SHE).

Since the behavior in interstitial solutions obtained with CEM II and CEM III are identical, only the results obtained in the latter case are here reported and discussed.

Table 20.2 Majority ions content in the simulated concrete pore solutions (extracted from concrete mixture with w/c=0.45)

Concrete mixture	Na^+ (g/L)	K^+ (g/L)	Ca^{2+} (g/L)	SO_4^{2-} (g/L)	pH
CEM I	2.02	13.65	0.64	18.24	13.6
CEM II	1.38	8.58	0.60	11.52	13.5
CEM III	0.85	7.41	0.76	7.68	13.2

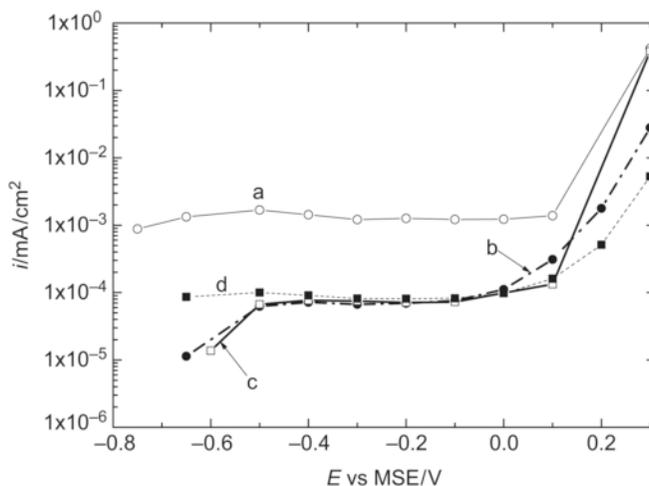


Figure 20.1 Stationary anodic curves of a C15 steel electrode after 60 h of immersion in interstitial solution: (a) CEM I; (b) CEM I with bioadmixture; (c) CEM III; (d) CEM III with bioadmixture.

20.4.3.1 Without bio-based admixture (BA)

In the absence of BA (curves a and c) the amplitude of the stationary passive current density is 15 times higher in the CEM solution I compared with that obtained in the CEM III solution. Since sodium and potassium ions are not likely to influence the corrosion rate, and since the pH of the solution was adjusted to the same value in the two solutions, the difference in the amplitude of the passive plateau was attributed to the difference in sulfate concentration, with a significant increase in the stationary passive current density when the concentration of sulfates increases. A higher sulfate content in the CEM I solution is not surprising since CEM I has a higher clinker content than CEM III.

The results in the present work are in agreement with those obtained by Haruna and Komote (2002), Abd El Haleem et al. (2010a, 2010b), Ghods et al. (2009), and Gui and Devine (1994), who have demonstrated the detrimental effect of sulfate ions on the protective oxide layer of reinforcing steel. Using XPS surface analyses, Montemor et al. (1998) have highlighted the influence of the chemical composition on the interstitial solution on the composition of the passive oxide layer. The presence of sulfates in the interstitial solution has been shown to lead to the formation of a hydrated passive film of mainly oxyhydroxide (FeOOH), in accordance with the results of Al-Tayyib et al. (1988) who concluded that corrosion of steel in concrete in the presence of sulfates is induced by the modification of the protective oxide layer.

20.4.3.2 In the presence of bio-based admixture (BA)

The open-circuit potential of the C15 mild steel sample immersed during 60 hours in the two different interstitial solutions shows roughly the same value in the presence and absence of BA, as shown in Fig. 20.1 (compare curves a and c to curves b and d). The shapes of the anodic curves are similar with and without BA, showing a passive behavior characteristic of the presence of a passive oxide layer on the surface of the C15 mild steel. A clear effect of BA addition was observed in the CEM I solution, for which the amplitude of the passive current density decreased significantly in the presence of BA. Indeed, the passive current density of 1.2×10^{-6} A/cm² in absence of the BA is 17 times larger than that recorded in the presence of the BA (7×10^{-8} A/cm²), thereby evidencing the BA's inhibiting effect towards corrosion. On the contrary, in the CEM III solutions no significant influence of BA addition could be deduced from the anodic curves. The passive currents in these two solutions did not differ significantly and are very low in the two cases (in the range of 0.08 μ A/cm²). Since the current density plateau starts in the vicinity of the open-circuit potential, its value can provide a good estimation of the corrosion current density. This approach was used in Table 20.3 for estimating the corrosion rates from Fig. 20.1. The impedance diagrams obtained at the open-circuit potential in CEM I solutions with and without BA are shown in Fig. 20.2. The low frequency limit of the real part of the diagram (R_p) is inversely proportional to the corrosion current density. In the CEM I solution, the low frequency limit is significantly higher in the presence of BA, thus reflecting the inhibiting effect of the bioadmixture added to the solution CEM I. On the contrary, the modification of the impedance diagrams in the presence of BA is negligible for CEM II and CEM III solutions (results not shown). These results are in agreement with that obtained from the anodic polarization curves where the corrosion current in the presence of BA is 17 times less than without addition of BA for the solution CEM I. In the other solutions, the difference in the electrochemical behavior with and without BA was not very obvious. However, the addition of BA in solution CEM I demonstrated the good inhibition efficiency of the bioadmixture towards corrosion in the presence of sulfates.

Table 20.3 Corrosion rate of C15 in the different interstitial solutions: i_{passive} is the passive current density, Δm the mass loss calculated from Faraday's law, Δe is the loss of thickness

Solution	CEM I	CEM I with BA	CEM III	CEM III with BA
i_{passive} (μ A/cm ²)	1.2	0.07	0.08	0.08
Δm (mg/cm ² per year)	11	0.64	0.73	0.73
Δe (μ m/year)	14	0.82	0.94	0.94

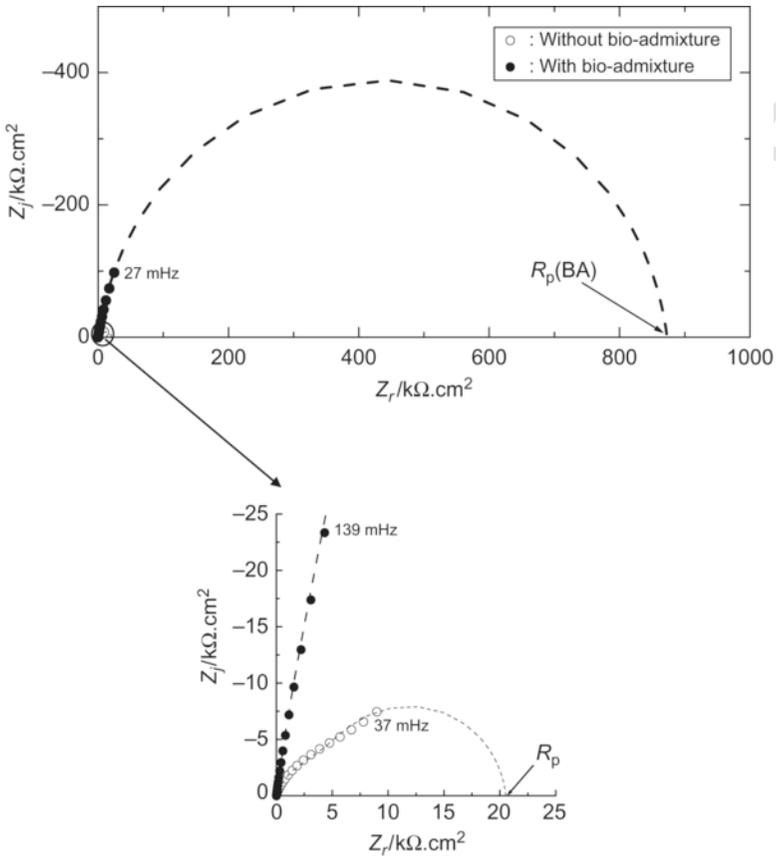


Figure 20.2 Impedance diagrams of C15 steel electrode at corrosion potential E_{corr} after 60 h of immersion in interstitial CEM I solution with and without bioadmixture.

20.4.4 Corrosion inhibition of bio-based admixture (BA) in synthetic solutions containing chlorides

The anodic polarization curves of the C15 mild steel obtained after 60 hours of immersion at the corrosion potential in different solutions are presented in Fig. 20.3.

In the presence of chloride ions, the curves have the same shape, with a passivity plateau extending over few-hundred millivolts, depending on the concentration of chloride ions. The value of the passive current is similar with and without chlorides, with an amplitude of several microampere. The value of the corrosion potential E_{corr} is about -0.9 V/MSE in the presence of chlorides—slightly more negative than the value obtained in the absence of chlorides (-0.7 V/MSE) (Fig. 20.1). This is in agreement with numerous studies reported in the literature, and in particular with the

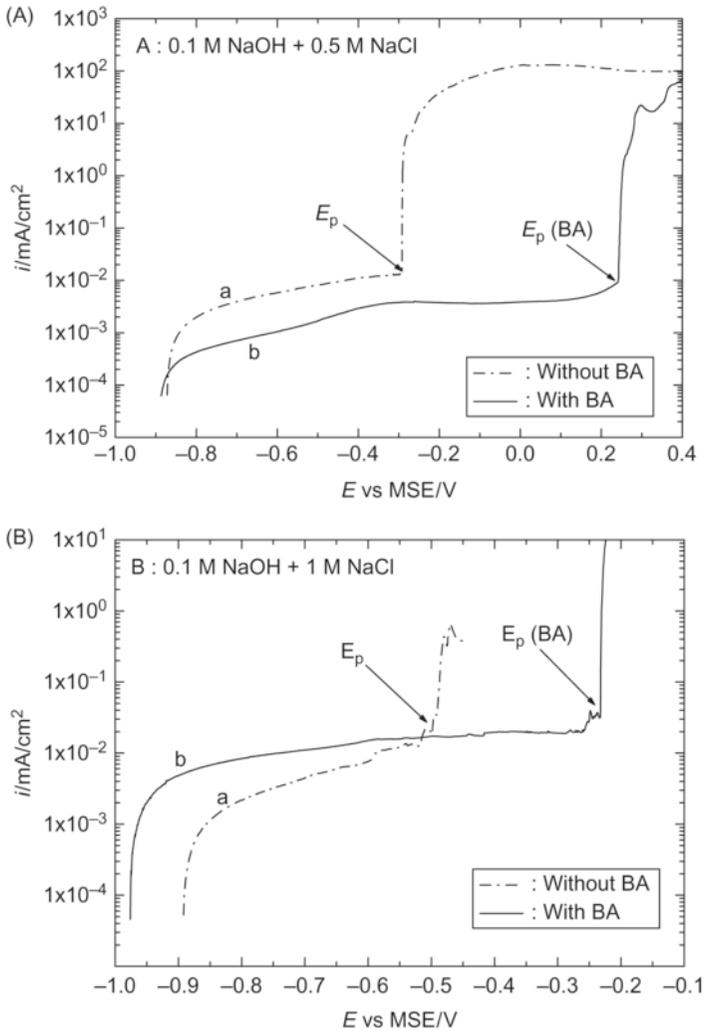


Figure 20.3 Anodic polarization curves ($v=0.5$ mV/s) of a C15 steel electrode after 60 h of immersion in 0.1 M NaOH solution (pH=13) containing 0.5 (A) or 1 M NaCl (B) with and without bioadmixture.

work of Abd El Haleem et al. (2010a, 2010b), for which the corrosion potential becomes less and less noble, when the chloride concentration increases.

20.4.4.1 Effect on pitting potential

An abrupt increase in the current density is observed at $E=-0.3$ V/MSE for the solution with 0.5 mol/L NaCl, and at $E=-0.5$ V/MSE for the solution with 1 mol/L NaCl. This potential corresponds to the pitting potential and its value gets less and

less anodic when the chloride concentration increases. Simultaneously, the passive plateau gets shorter and the susceptibility to pitting is enhanced. This result is in agreement with the literature which reports that the risk of corrosion increases when the ratio $[Cl^-]/[OH^-]$ increases (Page and Treadaway, 1982; Wasime and Hussain, 2015).

The shape of the curves is the same with and without BA. Nevertheless, the influence of the addition of BA clearly modifies the value of the pitting potential which moves ~ 500 mV towards more anodic potentials for 0.5 M NaCl and 300 mV for 1 M NaCl. These results demonstrate the good corrosion-inhibiting effect of the bioadjuvant towards pitting. It is also noted that the efficiency of BA on the current of passivity is comparable in the presence and absence of chloride ions in solution.

Impedance diagrams were plotted at the open-circuit potential with and without addition of BA and are shown in Fig. 20.4.

The diagrams in Nyquist representation show a capacitive loop. The diameter of this capacitive loop increases considerably in the presence of BA, corroborating the protective character of the layer of oxides, which is in agreement with the results obtained from the polarization curves.

20.4.4.2 Corrosion inhibiting mechanism of bioadmixture (BA)

The efficiency of BA as a corrosion inhibitor was studied by Shubina et al. (2016) in chloride containing solutions. The current potential curves in the anodic and the cathodic potential range are presented in Fig. 20.5. It clearly appears that the presence of the biomolecules decrease both the anodic current (metal oxidation through the passive layer) and the cathodic current (oxygen or water reduction). Such a behavior is characteristic of a mixed inhibitor and is in agreement with previous observations (Fig. 20.1) that BA addition into the interstitial solution has no influence on the value of the open-circuit potential.

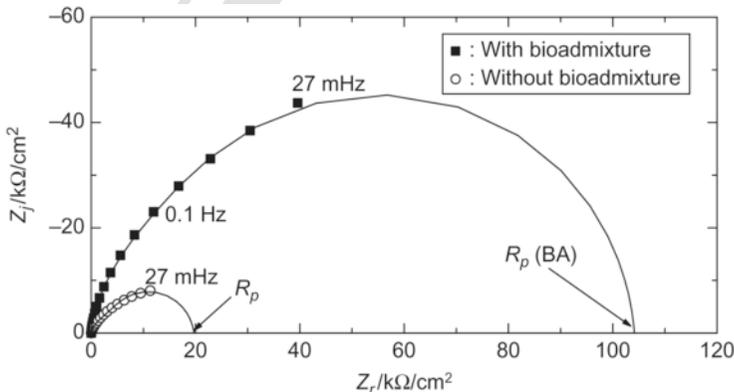


Figure 20.4 Impedance diagrams of C15 steel in representation of Nyquist at E_{corr} after 60 h of immersion in chloride solution with and without addition of BA.

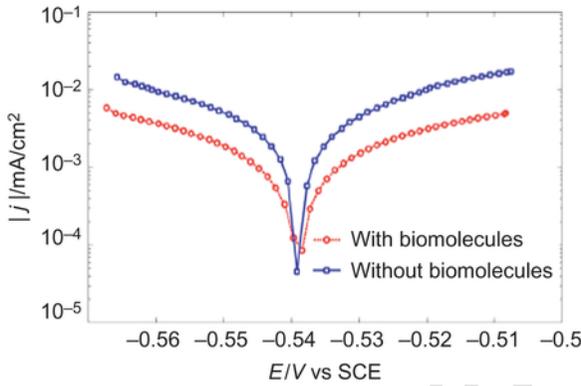


Figure 20.5 Polarization curves of carbon steel in aggressive simulated concrete pore solution with and without biomolecules (Shubina et al., 2016).

In order to get further insights into the corrosion inhibiting mechanism of BA, the authors Shubina et al. (2016) performed XPS analyses of the surface of carbon steel samples immersed in the BA containing alkaline solution (Fig. 20.6). The presence of a nitrogen peak on the survey spectrum is assumed to be the fingerprint of an adsorbed layer of biomolecules at the steel surface.

In the present case, the BA molecules are likely to be adsorbed at the passivated steel surface, via a nitrogen containing group. This behavior is usually observed in the case of organic inhibitors, which possess at least one functional group containing a heteroatom (like N, O, S) able to interact with the metallic substrate.

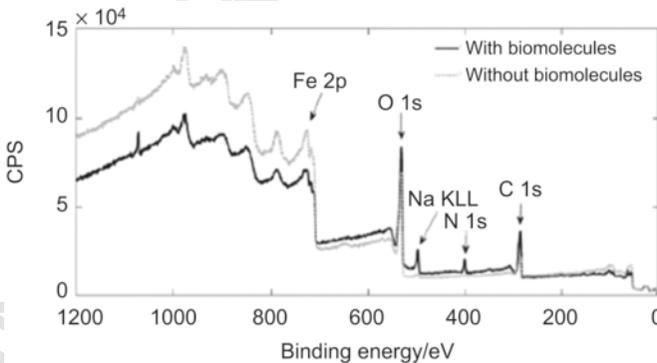


Figure 20.6 XPS survey spectra for the carbon steel specimens after corrosion tests in simulated concrete pore solution: without (dashed line) and with biomolecules (full line) (Shubina et al., 2016).

20.5 Conclusions

Electrochemical measurements clearly showed the beneficial influence of BA addition towards corrosion of a reinforced steel sample in interstitial concrete solutions.

In the absence of chlorides and of any carbonation, the corrosion rate is already very low in solutions with low sulfate addition. In this case, addition of BA has no influence on the corrosion rate. In the presence of higher sulfate concentrations, for instance in the solutions obtained with CEM I cement, the presence of BA is able to compensate the detrimental effect of sulfates on the corrosion rate.

In the case of chloride uptake by the concrete, the chloride-induced depassivation of steel is clearly inhibited in the presence of BA. In summary, biomolecule addition to the interstitial solution has a beneficial effect on the stability of the passive film on mild steel, improving its resistance against damage caused by uniform attack, as well as by pitting process.

The product prepared from bacterial extracellular substances, validated as bioadmixture with composition and dosage determined for the most common concretes (CEM I) proved its effectiveness as a corrosion inhibitor on young concrete (pH 13).

Original experimental procedures have been developed to provide a better understanding of:

- Modifications of the films formed on the steels subjected to different electrolytes representative of the interstitial fluids present in different types of concretes.
- The inhibitory capacities of these films.

The effectiveness of the bioadmixture in real conditions still needs to be tested with respect to the corrosion of reinforcement within different concrete mixtures subjected to different environmental conditions (sea water, alpine environment ...). The bioadmixture developed thus proves to be an eco-friendly and innovative solution with a high potential in the field of the market for agents protecting concrete.

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