

Article

Inhibition Effect of Tartrate Ions on the Localized Corrosion of Steel in Pore Solution at Different Chloride Concentrations

Marina Cabrini ^{1,2,3}, Sergio Lorenzi ^{1,2,3,*}, Denny Coffetti ^{1,2,3}, Luigi Coppola ^{1,2,3} and Tommaso Pastore ^{1,2,3}

¹ Department of Engineering and Applied Sciences, School of Engineering, University of Bergamo, 24044 Dalmine (BG), Italy; marina.cabrini@unibg.it (M.C.); denny.coffetti@unibg.it (D.C.); luigi.coppola@unibg.it (L.C.); tommaso.pastore@unibg.it (T.P.)

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Research Unit of Bergamo, 24044 Dalmine (BG), Italy

³ Center for Colloid and Surface Science (CSGI), Research Unit of Bergamo, 24044 Dalmine (BG), Italy

* Correspondence: sergio.lorenzi@unibg.it

Received: 23 April 2020; Accepted: 28 May 2020; Published: 1 June 2020

Abstract: The aim of this work is the evaluation of the inhibition effect of tartrate ions with respect to the localized corrosion of steel reinforcements in alkaline solution as a function of the concentration of chlorides ions. Weight loss tests and electrochemical tests were carried out in saturated $\text{Ca}(\text{OH})_2$ solution with NaOH at pH 12.7 and 13.2. The results only evidence a slight inhibition effect at pH 12.7, whereas at pH 13.2 the pitting onset is inhibited also for chloride concentration up to 3 M. Tartaric acid is a dicarboxylic acid with nucleophile substituents, which can act as a chelating agent both adsorbing on the surface of the passive film and forming a soluble complex with ferrous and ferric ions. Tartrate causes an increase in the passive current density but it prevents the depassivation of carbon steel due to the action of chlorides, thus preventing pitting initiation due to the competitive adsorption on metal surface.

Keywords: tartrate ions; corrosion inhibitor; chloride corrosion rebar; cyclic voltammetry

1. Introduction

The aging of concrete structures is nowadays still actual, and the theme of concrete durability is now increasing its importance also from the point of view of eco-sustainability, in terms of raw materials quarrying savings. One of the most important issues that is far from being solved is surely carbon steel reinforcements' corrosion [1–6]. Well compacted and low porosity concretes manufactured with ordinary Portland cement protect carbon steel reinforcement against general corrosion due to the formation of the passive film on the steel surface that occurs naturally in alkaline environments. However, the reaction with the atmospheric CO_2 reduces the pH of concrete, thus causing the occurrence of general corrosion [7–9]. Carbonation can be conveniently delayed by considering suitable concrete design strategies, i.e., by increasing the cover thickness and decreasing the water/cement ratio [10]. However, in structures in contact with seawater—i.e., port installations, bridges and coastal buildings—or exposed to the action of de-icing salts—i.e., viaducts, bridge decks and garages [11,12]—more severe corrosion issues can arise due to chloride ions' diffusion inside concrete. Chloride corrosion is more dangerous than carbonation because the attack is more localized, thus leading to a severe reduction of the cross section of the rebar and increasing the risk of collapse [13–15]. In high-strength steels typically used for prestressed and post-tensioned

structures, localized corrosion attacks can also give rise to the insurgence of hydrogen embrittlement phenomena [16–20].

Suitable mix design strategies as well as the proper placing and curing of concrete can reduce the risk of chlorides penetration, but, when very prolonged service life is required in severe environments, additional protection or prevention methods must be considered. Such methods include—but are not limited to—the application of concrete coatings [21], coated reinforcing bars [22], galvanized or stainless steels [23,24] and cathodic protection or prevention [25,26]. In addition, corrosion issues can be also mitigated using corrosion inhibitors which are chemical admixtures added during concrete mixing. They can be considered a cost-effective and easy solution for common concrete practices [27,28]. Many studies were carried out on nitrite ions [29–33], alcohol amine [31], and inorganic and organic compounds [34–37]. Several studies have shown that the ions of organic acids with nucleophilic substituents are able to act as corrosion inhibitors; the greatest efficiency is represented by dicarboxylic acids, such as tartaric acid, which can coordinate on the metal surface with a chelating effect [38–41]. The properties of tartaric acid as a corrosion inhibitor were underlined by several authors [42,43]. However, it is a strong set retarder and its dosage must be well determined to achieve chlorides corrosion protection thus avoiding excessive retardation. Vice versa, it could be evaluated for the new binders characterized by very fast setting times [44,45]. In fact, the global warming problem has directed research towards the use of new binders with a lower environmental impact than Portland cement [46–48]. These new binders require the use of retarders [49], such as tartaric acid [50,51].

The aim of this work is to analyze the effect of the tartrate ions on the localized corrosion of carbon steel in alkaline solutions at a different concentration of chloride ions in order to promote the combined use of tartaric acid as set retarding admixture and corrosion inhibitors for concrete manufactured with alternative binders to Portland cement. Due to the stochastic nature of pitting initiation and propagation [52–58] and the number of environmental parameter involved, electrochemical cyclic voltammetry tests have been performed as a rapid and reliable technique for the screening of the behavior of different inhibitors in solution [59,60].

2. Experimental

Weight loss tests were carried out on an aerated alkaline saturated solution of $\text{Ca}(\text{OH})_2$ added with NaOH in order to obtain pH 12.7 at room temperature. The tests were performed with a constant molar ratio between tartrate and chloride ions of 0.28 M. In addition, weight loss tests were also conducted with sodium nitrite as the most effective commercial chlorides corrosion inhibitor for concrete, by considering the same concentration of the tartrate. The specimens were taken from steel rebar, grounded, and finally polished with emery paper. Before the tests, the specimens were cleaned by means of sonication in acetone and weighted using an analytical scale (± 0.00001 g accuracy). Three weightings were carried out for each specimen and the average weight value was considered. Two specimens for each condition were passivated in the alkaline solution for more than 72 h. The tests were conducted both adding the substances before or after the chloride ions addition in the solution. The total time of exposure was 790 h. At the end of the tests, the specimens were cleaned according to ASTM G1-90, by using solution C.3.5 (inhibited HCl with hexamethylenetetramine) and then weighted again. The mass loss was calculated as a percentage of the initial weight of the specimens. All the specimens were observed at the optical microscope in order to evaluate the corrosion morphologies.

Cyclic voltammetry tests were performed by using Ivium CompactStat potentiostat in a glass cell of about one liter of volume with a stainless-steel counter electrode designed to grant uniform current distribution over the specimen surface. A saturated calomel electrode (SCE) was used; the potential of the electrode is +0.242 V vs. SHE. A Huber–Luggin capillary was adopted to minimize the ohmic drop into the electrolyte. Before the tests, the specimens were passivated in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12.7 or in aerated saturated $\text{Ca}(\text{OH})_2$ solution added with NaOH at pH 13.2 for 72 h. The specimen was removed from the passivation solution just before the cyclic voltammetry test. The cyclic voltammetry tests were carried out in solutions with the same composition of the

passivation one, increasing the chlorides concentration from zero to 3.5 M. The tests were at least repeated twice. The specimen was replaced after each test. The cyclic voltammetry tests procedure was as follows: specimen conditioning at -1 V vs. SCE for 60 s in order to clean the surface avoiding relevant damage of the passive film, followed by 15 s of equilibration at open circuit potential and two consecutive voltammetry cycles from -1.7 to $+0.8$ V vs. SCE at a 50 mV/s scan rate. This procedure was already applied in a previous work devoted to the study of corrosion inhibitors in alkaline solutions and in concrete slabs after long-term exposure [60].

For cylindrical specimens with a diameter equal to 10 mm, a 20 mm height was considered. All samples were ground with silicon carbide emery paper up to 1200 grit and then ultrasonically cleaned in acetone. Rotating electrode at 2550 rpm was used to avoid diffusion effects. Localized corrosion occurrence was confirmed by optical microscopy after all the tests.

3. Results and Discussion

The weight loss tests of the specimens after 790 h of immersion in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12.7 and 0.28 M of tartrate ions and chloride ions are significantly lower than the values obtained in absence of inhibitors (Figure 1). A one order of magnitude weight loss decrease was noticed once the inhibitor was added to the solution 72 h before the chlorides (TR + Cl⁻). Slight increases were observed if the inhibitor was added after the chlorides (Cl⁻ + TR), thus indicating a tartrate ion's ability to affect the pitting propagation. Shallow pits were always noticed at the end of the tests (Figure 2). The efficiency of the tartrate is comparable with the nitrite added before the chloride. The nitrite ions are anodic passivating inhibitors and their action is beneficial only if they are added to the solution before the pitting initiation. On the contrary, they act cathodically, thus leading to an increase in the corrosion rate. The tartrate does not have an oxidant effect, and it does not have a stimulating effect on the pitting propagation.

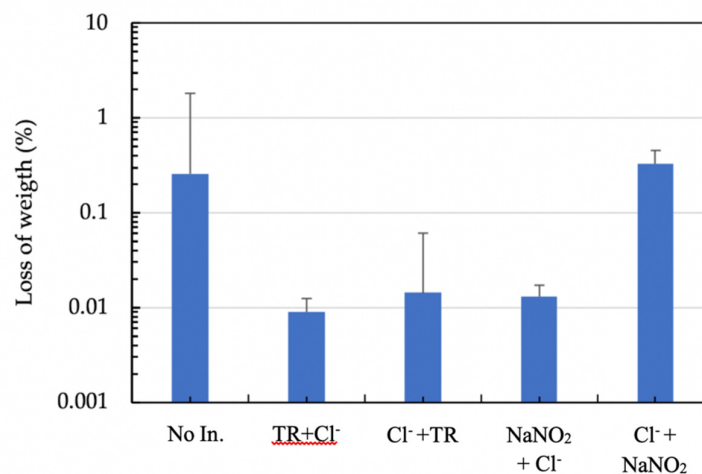


Figure 1. Results of the loss of weight tests in $\text{Ca}(\text{OH})_2$ solution at pH 12.7 and 0.28 M of tartrate ions and nitrite.

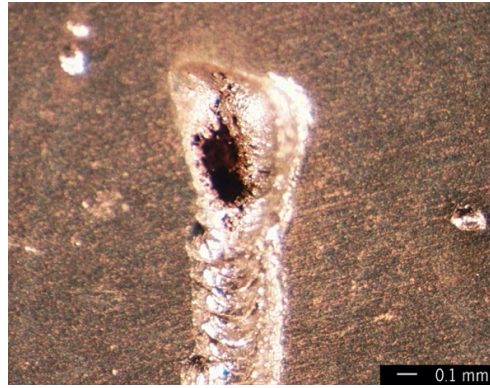


Figure 2. Shallow localized attack on the specimen after 790 h of exposition in saturated $\text{Ca}(\text{OH})_2$ solution added with 0.23 M tartrate and 0.23 M chloride ions. Chlorides were added 72 h after the inhibitor.

The effect of chloride concentration and pH on the inhibition efficiency of tartrate was electrochemical evaluated, according to a precedent work [59].

Figure 3 shows the typical voltammogram of carbon steel in alkaline solutions. The peaks can be interpreted as described in literature [36,61–64].

The peaks in zone I of the curve are connected to the first oxidation of Fe to $\text{Fe}(\text{OH})_2$, the peaks II are related to the transformation of the $\text{Fe}(\text{II})$ hydroxide in $\text{Fe}(\text{III})$ hydroxide. The oxide film has a thin and protective inner layer and an outer layer generally thick, hydrate porous and less protective. This film growth with the time of immersion until a stable state. The equilibrium composition of the outer layer is strictly dependent upon the composition of solution and applied potential. Typically, the film thickness increases during each voltammetry cycle and, in the concrete pore solutions, Ca^{++} ions can be absorbed into the film as calcium oxide gel [64–66]. $\text{Fe}(\text{III})$ oxide layer is an n-type semiconductor, the predominant donors inside it are either oxygen vacancies [67] and $\text{Fe}(\text{II})$ ions [68,69]. The electrical conductivity of the film permits the growth of the localized attacks by means of the mechanism of the occluded cell. The peaks IV and V indicate partial reaction reversibility. The part of the curve between the peak III and the potential of the oxygen electrochemical discharge (E_{ox}) represents the passive range. At least, at E_{H} , the hydrogen electrochemical evolution takes place.

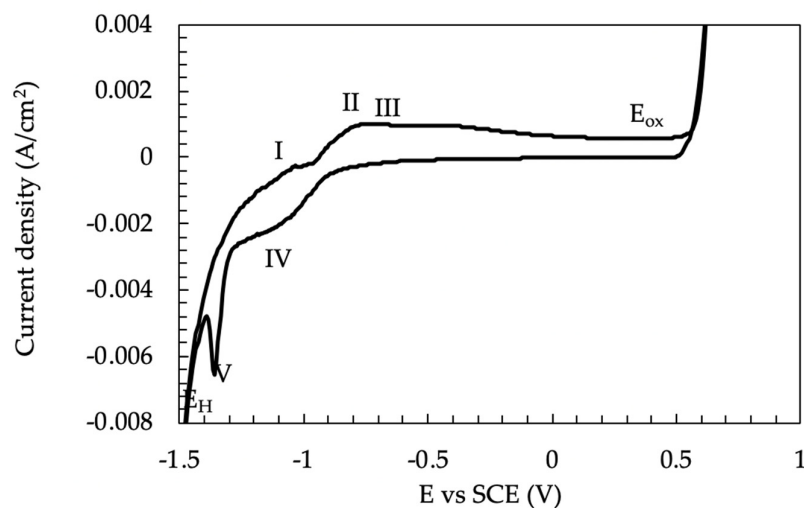


Figure 3. Cyclic voltammetry curve of carbon steel in $\text{Ca}(\text{OH})_2$ saturated solution at pH 12.7.

The presence of chlorides modifies the passive range of the voltammetric curve as shown in Figure 4. The initiation of localized attack causes a sharp increase in the current density at a potential

named $E_{1,1st}$, before E_{ox} , with a very pronounced hysteresis during the subsequent return of scanning [59]. The hysteresis is associated with the low repassivation potential of the inner zones of pit. In the second cycle of voltammetry, localized corrosion was observed above a potential, named $E_{1,2nd}$, analogous to the $E_{1,1st}$ but less noble. At very high chloride contents, repassivation does not occur and a monotonic increase of current during anodic scan of the second cycle denotes an active electrochemical behavior (red curve in Figures 5 and 6).

According to [59], the potentials $E_{1,1st}$ and $E_{1,2nd}$ were defined as the values at which current rapidly increases during the first and second voltammetry cycle, respectively, exceeding the 10% of the mean current over the passive range, from 0 to 0.5 V vs. SCE. They substantially differ from pitting potential because they are obtained in non-stationary conditions.

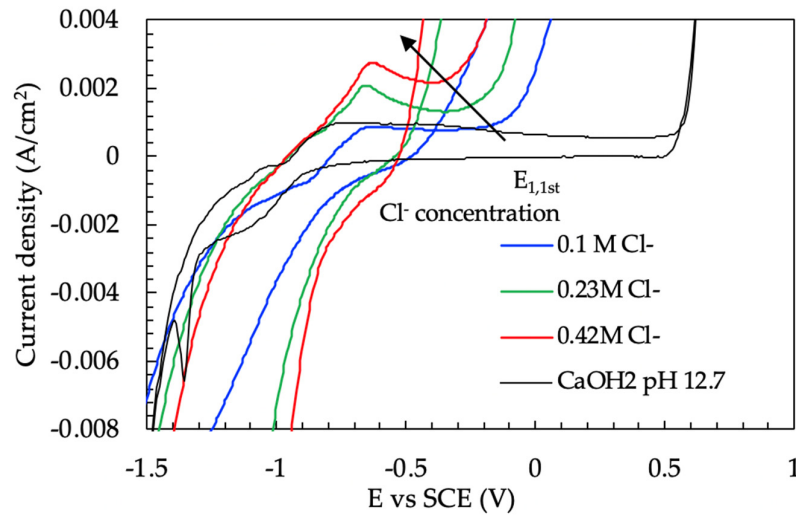


Figure 4. Effect of chloride ions on the first cycle of the voltammetric curves of steel in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12.7.

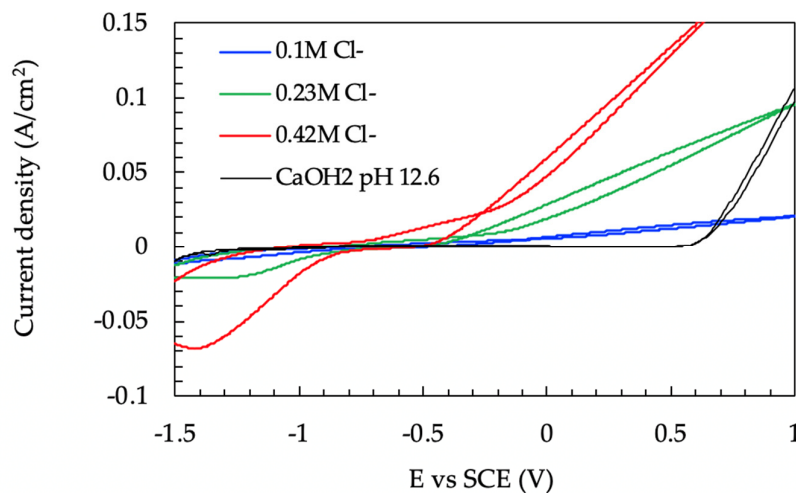


Figure 5. Effect of chloride ions on the second cycle of the voltammetric curves of steel in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12.7.

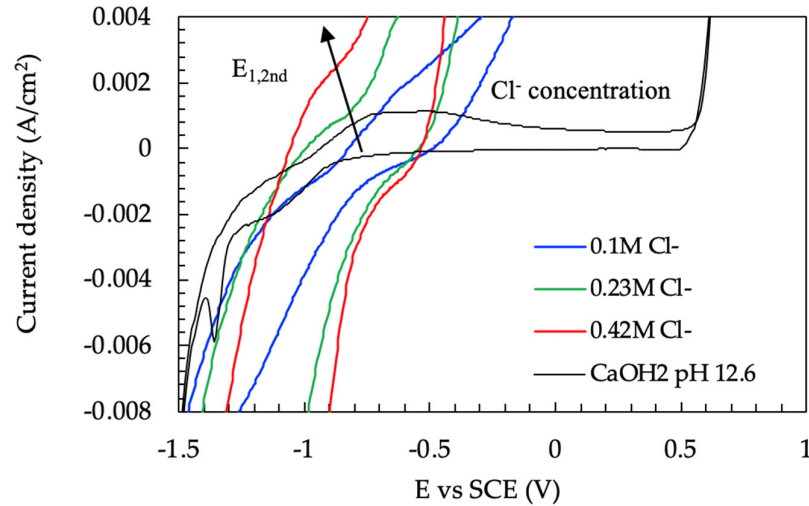


Figure 6. Close-up of Figure 5 in the zone of the increases in the anodic current that evidenced the potential $E_{1,2nd}$.

The tartrate ions are able to inhibit the localized attack in saturated solution of $\text{Ca}(\text{OH})_2$ at pH 12.7 only at a very low chloride ion concentration. In the presence of 0.23 M of Cl^- , there is an increment of the potential $E_{1,1st}$ with respect to the reference tests without any inhibitor (Figure 7). The second cycle of the voltammetry tests [59] demonstrated the possibility to repassivate the steel only in the presence of the lower concentration of chlorides ions; as the Cl^- concentration is increased at 0.23 M or higher, the second cycle of the voltammetry curve is practically active (Figure 8).

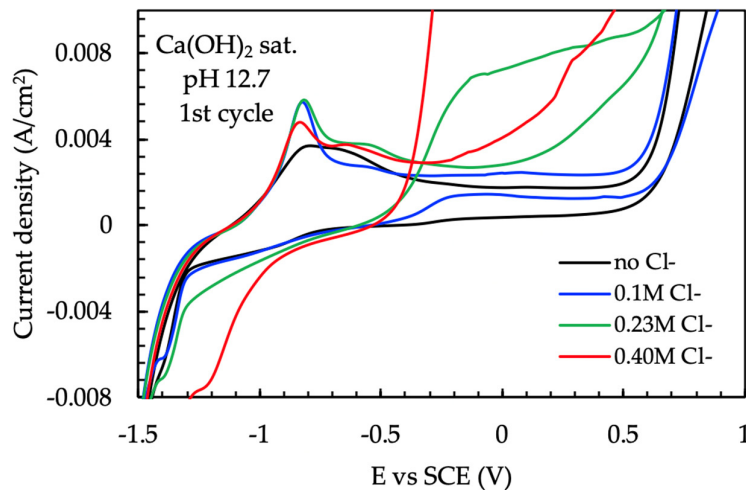


Figure 7. Effect of chloride ion concentration on the first cycle of the voltammetric curves of steel in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12.7 and tartrate ions in a concentration of 1 M.

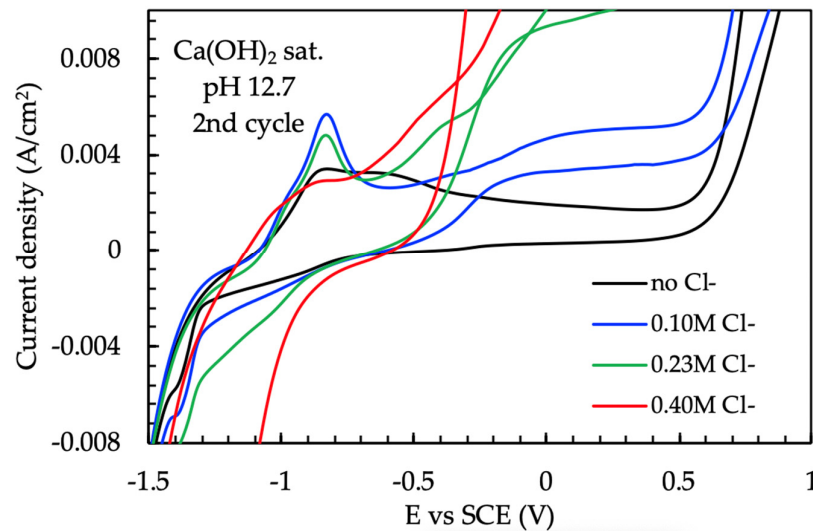


Figure 8. Effect of chloride ion concentration on the second cycle of the voltammetric curves of steel in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12.7 and tartrate ions in a concentration of 1 M.

Increasing the pH of the solution at 13.2, the inhibition effect of the tartrate ions is more pronounced: the $E_{i,1st}$ remains over the potential E_{ox} for all the chloride concentrations used, until a chloride ion concentration of 3 M is reached (Figure 9). In the presence of a chloride ion concentration of 3.5 M, the value of $E_{i,1st}$ reached the E_{ox} , but the presence of hysteresis in the return scan of potential evidenced the initiation of localized attack during the oxygen evolution. Oxygen evolution causes the acidification of the electrode surface favoring the pitting initiation [70]. The second cycle of the voltammetric curves confirms the absence of localized attack initiation for chloride concentration lower than 3 M (Figure 10).

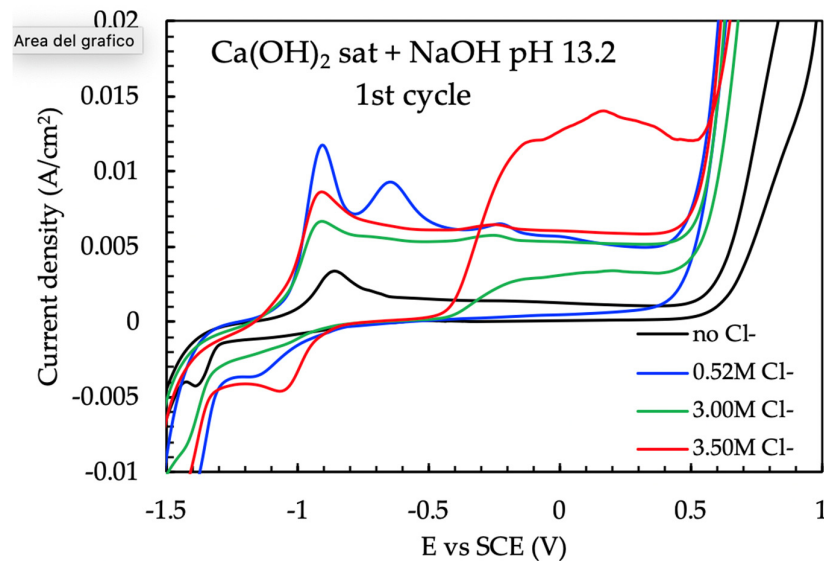


Figure 9. Effect of chloride ions concentration on the first cycle of the voltammetric curves of steel in saturated $\text{Ca}(\text{OH})_2$ solution at pH 13.2 and tartrate ions in a concentration of 1 M.

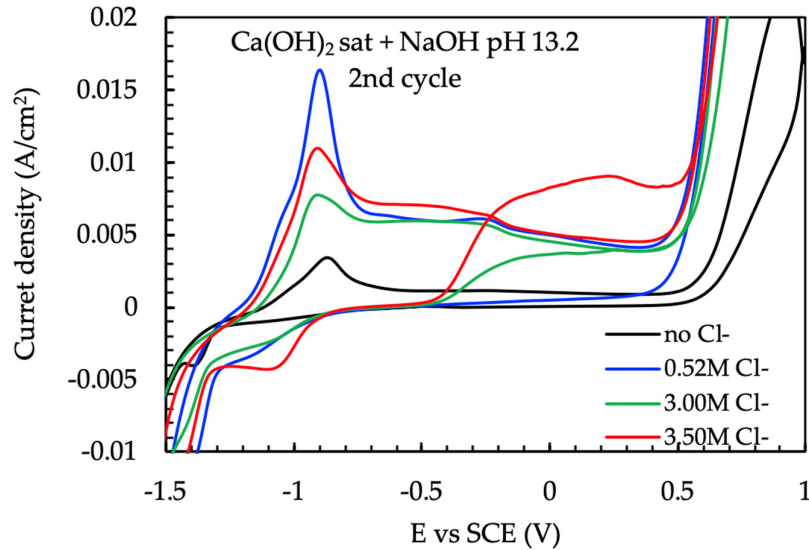


Figure 10. Effect of chloride ions concentration on the second cycle of the voltammetric curves of steel in saturated $\text{Ca}(\text{OH})_2$ solution at pH 13.2 and tartrate ions in a concentration of 1 M.

The analysis of the cyclic voltammetry curves in order to detect a parameter for describing the corrosion susceptibility of carbon steel in simulated poor solution added with chlorides and corrosion inhibitors was previously proposed by the authors [59]. The difference ΔE_n was defined, according to the following relationship (Equation 1):

$$\Delta E_n = E_{1,nth} - E_{ox} \quad (1)$$

where ΔE_n is referred to as n -cycle. The subtraction of potential E_{ox} from $E_{1,nth}$ is necessary to consider the correlation between oxygen evolution potential and pH. If ΔE_n is equal to zero, no localized corrosion occurred before the E_{ox} value is reached. Otherwise, it assumes negative values, approaching a very negative asymptote for very high chloride content because $E_{1,1st}$ and $E_{1,2nd}$ reach the potentials of the active peak. The interpolation of the experimental data of carbon steel in solution at different pH without inhibitors permitted to obtain the following empirical relationships, valid for $\Delta E_n \leq 0$ in the range of pH of 12.6 ÷ 13.87:

$$\Delta E_{1,1st} = 1.2 \cdot \left(0.6 \cdot \frac{[\text{OH}^-]}{[\text{Cl}^-]} - 1 \right) \quad (2)$$

and

$$\Delta E_{1,2nd} = 1.5 \cdot \left(0.5 \cdot \frac{[\text{OH}^-]}{[\text{Cl}^-]} - 1 \right) \quad (3)$$

The curves obtained by Equations (2) and (3) are compared with the values of $\Delta E_{1,1st}$ (Figure 11) and $\Delta E_{1,2nd}$ (Figure 12) measured in the presence of tartrate ions at pH 12.7 and 13.2. At pH 12.7, the tartrate ions are able to improve the carbon steel resistance to localized corrosion, because the values of $\Delta E_{1,1st}$ are shifted on the right of the curve representing the behavior in the absence of an inhibitor, but, at this value of pH, the inhibitor is not able to fully stop the pitting initiation.

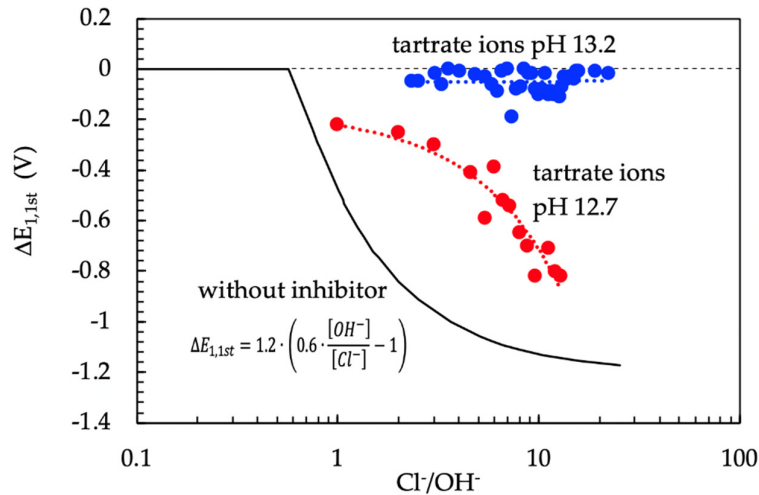


Figure 11. $\Delta E_{1,1st}$ as a function of Cl^-/OH^- ratio in simulating pore solutions at pH 12.6–13.87 without inhibitors [59] and in $Ca(OH)_2$ saturated at pH 12.7 and $Ca(OH)_2$ sat. + NaOH at pH 13.2 solutions, added with 1 M of tartrate ions.

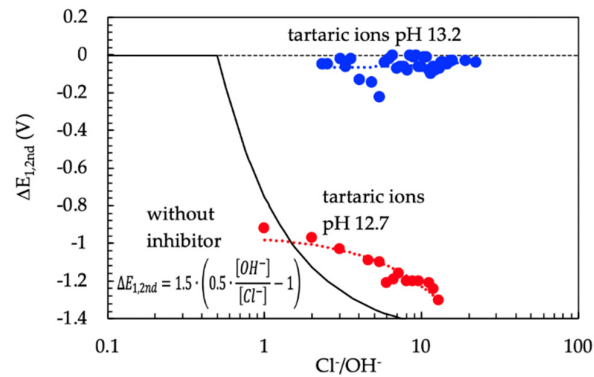


Figure 12. $\Delta E_{1,2nd}$ as a function of Cl^-/OH^- ratio in simulating pore solutions at pH 12.6–13.87 without inhibitors [59] and in $Ca(OH)_2$ saturated at pH 12.7 and $Ca(OH)_2$ sat. + NaOH at pH 13.2 solutions, added with 1 M of tartrate ions.

Once the pitting has initiated, the tartrate is not able to promote carbon steel repassivation, as evidenced by the practically overlapped points of $\Delta E_{1,2nd}$ with the reference curve in Figure 12. Conversely, increasing the pH at 13.2, the effect of tartrate ions is very pronounced: the pitting was also not initiated for a very high concentration of chlorides (Figures 11 and 12).

The mechanism commonly assumed for pitting initiation is the competitive chemisorption of chloride and hydroxyl ions on passive film [71]; higher chloride content results in a higher probability of the substitution of Cl^- by OH^- ions in the outer layer of the passive film. If chlorides substitute hydroxyls in enough adjacent sites, the rupture of the passive film can occur with the formation of pit embryos. However, in these areas, hydroxyl ions and dissolved oxygen can again restore the protective film on the inner surface of the primitive pit that thus does not reach stable propagation. On the contrary, the pit propagates by an occluded-cell mechanism; consequently, repassivation gradually becomes less probable due to acidification and the high concentration of chloride [59].

Cornell and Schindler reported the adsorption of tartaric acid on the surface of both $FeOOH$ and amorphous $Fe^{(III)}$ hydroxide, based on the partial replacement of the surface hydroxyl groups by carboxylate groups. The surface concentration of the tartrate acid decreases with the increasing of pH

due to the increasing of the stability of complexes in solution [72]. The formation of a complex between tartrate ions and Fe^(III) that influences the Fe^(II)/Fe^(III) redox potential at a pH below 4 is reported by [73], while Toropova reported a complex of tartrate ions and Fe^(III) ions, stable in the range of pH 3.4 and 7.0 [74]. In the literature, the inhibition effect of the tartrate acid on carbon steel that is enhanced in the presence of Fe²⁺ ions is reported. Gomma attributes the inhibition effect to a film of the tartrate-Fe²⁺ complexes existing on the electrode surface. The diffusion of the proton through this film would be the most likely rate-determining step of both the hydrogen electrochemical reduction and the overall corrosion process [75]. An inhibiting effect by means of mixed anodic and cathodic mechanism was also reported by Qiang et al., based on corrosion tests in 0.5M HCl, XPS, atomic force microscope and theoretical quantum calculations, due to the adsorption of the carboxylate on the metal surface. All these tests were carried out in acidic solution [76]. In alkaline solution, Valek Žulj et al. proposed a competitive adsorption of tartrate ions and chlorides as a mechanism of corrosion inhibition of rebar in pore solution [42]. Bazzaoui et al. reported the formation of a passive layer on iron in 0.2M sodium tartrate at pH 6.8, at a potential of -0.35 V versus Ag/AgCl, according to the reaction:



This passive film is stable until the transpassive breakdown that occurs near the oxygen evolution potential [77].

By the analysis of the cyclic voltammetry curves, an increase in the height of peaks II and III and of the current density in the passive state is evident (Figures 7–10); this effect is more pronounced as the chloride ions concentration or pH increases, but are present also in absence of chloride ions (Figure 13). A voltammetric test, carried out on platinum in the same Ca(OH)₂ saturated solution added with NaOH at pH 13.2 excluded the direct oxidation of the tartrate ions (Figure 13). In fact, the voltammetric curve of platinum did not present any peaks in the anodic scan, but only a small cathodic peak of the reduction of the platinum oxide formed during the oxygen evolution. It could be said that the peaks in the voltammograms are due to the enhanced dissolution of the steel to Fe^(II) by means of the soluble complex formed with the tartrate ions and its successive oxidation to Fe^(III)oxide. The competitive formation of soluble complexes of Fe^(III) and the adsorption of the tartrate ions on the electrode surface to substitute the hydroxyl in the passive film, increases the current density in the passive range of potential, but, at the same time, inhibits the adsorption of chloride ions, and, as a consequence, the pitting initiation. In the inhibition mechanism proposed by Valek Žulj et al., the tartaric acid stabilized the Fe^(III) in the passive film; as a consequence of this, the concentration of Fe^(II) ions in the film decreases, and, in this way, the conductivity of the n-type semiconductor passive film is reduced, for the decreasing of the concentration of the donors, reducing the efficiency of the occluded cell in the propagation of the localized attack [42]. At the same time, the presence of the negative carboxylate group of the tartrate on the film surface counteracts the adsorption of the chloride ions, favoring the re-passivation. The same authors also reported that increasing the concentration of tartrate above 2.5×10^{-3} M results in the deterioration of passive film due to the dissolution of the surface complex induced by the lowering metal/ligand ratio [42]. For this reason, the overall effect of tartrate ions on carbon steel could be to enhance the generalized dissolution of the passive film, but, at the same time, its carboxylate groups counteract the adsorption of the chlorides on the film surface, inhibiting the localized corrosion onset and propagation. Unfortunately, this effect is efficient in order to increase the critical chloride concentration for localized corrosion only in solution with pH higher than that of saturated Ca(OH)₂ solution. In traditional Portland cement, high values of pH can be reached for the presence of Na₂O and K₂O. On the contrary, innovative co-sustainable binders, i.e., calcium-sulfoaluminate-based binders, are characterized by the lower pH values of the cement matrix and a very low alkalinity reservoir compared to traditional ordinary Portland cement [47,48]. In this way, the efficiency of tartrate as a corrosion inhibitor can be strongly affected. More in depth studies are needed to assess the inhibition efficiency of tartrate in concretes manufactured with innovative eco-sustainable binders.

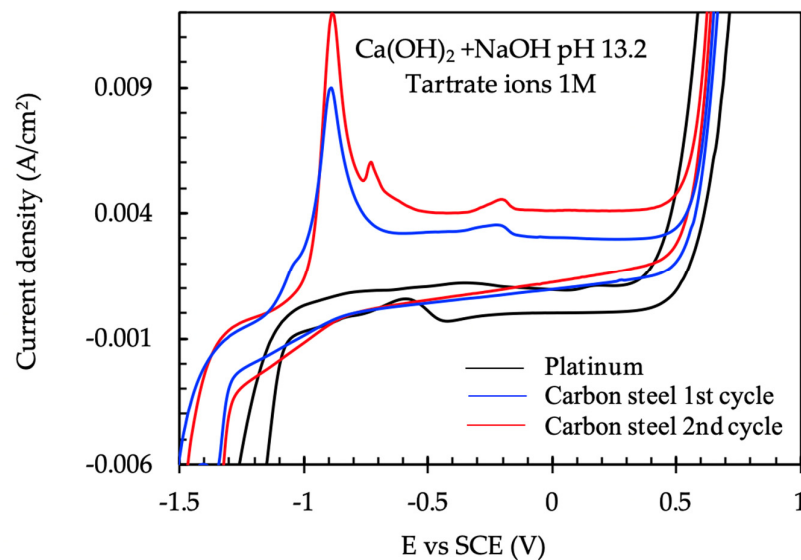


Figure 13. Cyclic voltammetry curves of carbon steel and platinum in saturated $\text{Ca}(\text{OH})_2$ solution + NaOH at pH 13.2 and tartrate ions 1 M.

4. Conclusions

The inhibition efficiency of tartrate ions to counteract chlorides' corrosion of reinforcements was evaluated in saturated calcium hydroxide alkaline solutions at pH 12.7 and 13.2.

Weight loss tests and electrochemical tests were carried out at the same concentration of chlorides and tartrate, equal to 0.28 M. The results were compared to those obtained by considering sodium nitrite as a well-established commercial rebar corrosion inhibitor for concrete. The effect of pH and chloride concentration was studied by means of cyclic voltammetry tests.

According to the experimental results, the following conclusions can be drawn:

- In presence of tartrate, a decrease in the corrosion rate in terms of weight loss was noticed at pH 12.7 with respect to the solution without inhibitor. However, it is not able prevent the localized attack initiation and propagation.
- Weight loss tests evidenced a similar effectiveness between tartrate and sodium nitrate at equal concentration only if they are added to the solution before the pitting initiation. On the contrary, if tartrate was used after the pitting initiation, it performs better than sodium nitrate.
- The pitting onset was inhibited in the presence of tartrate until very high chloride concentration at pH 13.2. When pH is 12.7, the tartrate ions' capability to inhibit the localized attack is limited only at very low chloride ions concentration.
- The tartrate ions are adsorbed on the passive film of iron, favoring the oxidation of $\text{Fe}(\text{II})$ to $\text{Fe}(\text{III})$ by means of the formation of slightly soluble salt and stable chelating complexes. In this way, there is an enhanced general dissolution of the passive film, but, at the same time, the carboxylate group of the tartaric acid counteracts the adsorption of the chlorides on the film surface.

Author Contributions: Methodology, S.L., M.C.; Investigation, S.L., D.C.; Data Curation, M.C.; All the authors contributed to writing the original draft of the paper. Writing—Review & Editing T.P., L.C., M.C. Supervision, T.P.; Project Administration, T.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hansson, C.M. An introduction to corrosion of engineering materials. In *Corrosion of Steel in Concrete Structures*; Poursaeed, A., Ed.; Woodhead Publishing: Oxford, UK, 2016; pp. 3–18. ISBN 978-1-78242-381-2.
2. Bertolini, L.; Elsener, B.; Pedferri, P.; Redaelli, E.; Polder, R.B. *Corrosion of Steel in Concrete: Prevention, Diagnosis, Repair*; Wiley WCH: Weinheim, Germany, 2013; ISBN 978-3-527-33146-8.
3. Angst, U.M.; Hooton, R.D.; Marchand, J.; Page, C.L.; Flatt, R.J.; Elsener, B.; Gehlen, C.; Gulikers, J. Present and future durability challenges for reinforced concrete structures. *Mater. Corros.* **2012**, *63*, 1047–1051, doi:10.1002/maco.201206898.
4. Yu, X.-H.; Quian, K.; Lu, D.; Li, B. Progressive collapse behavior of aging reinforced concrete structures considering corrosion effects. *J. Perform. Constr. Facil.* **2017**, *31*, 04017009.
5. Yalciner, H.; Sensoy, S.; Eren, O. Seismic performance assessment of a corroded 50-year-old reinforced concrete building. *J. Struct. Eng.* **2015**, *14*, 05015001.
6. El Maaddawy, T.; Soudki, K.; Topper, T. Long-Term Performance of Corrosion-Damaged Reinforced Concrete Beams. *ACI Struct. J.* **2005**, *102*, doi:10.14359/14660.
7. Page, C.L. Degradation of reinforced concrete: Some lessons from research and practice. *Mater. Corros.* **2012**, *63*, 1052–1058, doi:10.1002/maco.201206716.
8. Lollini, F.; Redaelli, E.; Bertolini, L. Analysis of the parameters affecting probabilistic predictions of initiation time for carbonation-induced corrosion of reinforced concrete structures. *Mater. Corros.* **2012**, *63*, 1059–1068, doi:10.1002/maco.201206720.
9. Andrade, C. Evaluation of the degree of carbonation of concretes in three environments. *Constr. Build. Mater.* **2020**, *230*, 116804, doi:10.1016/j.conbuildmat.2019.116804.
10. Page, C.L. Corrosion and protection of reinforcing steel in concrete. In *Durability of Concrete and Cement Composites*; Woodhead Publishing: Oxford, UK, 2007; pp. 136–186.
11. Pradhan, B.; Bhattacharjee, B. Rebar corrosion in chloride environment. *Constr. Build. Mater.* **2011**, *25*, 2565–2575, doi:10.1016/j.conbuildmat.2010.11.099.
12. Manera, M.; Vennesland, Ø.; Bertolini, L. Chloride threshold for rebar corrosion in concrete with addition of silica fume. *Corros. Sci.* **2008**, *50*, 554–560, doi:10.1016/j.corsci.2007.07.007.
13. Montemor, M.F.; Simões, A.M.P.; Ferreira, M.G.S. Chloride-induced corrosion on reinforcing steel: From the fundamentals to the monitoring techniques. *Cem. Concr. Compos.* **2003**, *25*, 491–502, doi:10.1016/S0958-9465(02)00089-6.
14. Li, L.; Sagüés, A.A. Chloride Corrosion Threshold of Reinforcing Steel in Alkaline Solutions—Open-Circuit Immersion Tests. *Corrosion* **2001**, *57*, 19–28, doi:10.5006/1.3290325.
15. Cady, P.; Weyers, R. Chloride Penetration and the Deterioration of Concrete Bridge Decks. *Cem. Concr. Aggreg.* **1983**, *5*, 81–87, doi:10.1520/CCA10258J.
16. Sanchez, J.; Fullea, J.; Andrade, C. Corrosion-induced brittle failure in reinforcing steel. *Theor. Appl. Fract. Mech.* **2017**, *92*, 229–232, doi:10.1016/j.tafmec.2017.08.006.
17. Sanchez, J.; Lee, S.F.; Martin-Rengel, M.A.; Fullea, J.; Andrade, C.; Ruiz-Hervías, J. Measurement of hydrogen and embrittlement of high strength steels. *Eng. Fail. Anal.* **2016**, *59*, 467–477, doi:10.1016/j.engfailanal.2015.11.001.
18. Morales, J.A.; Torres, J.; Rebolledo, N.; Sánchez, J. Experimental and Statistical Analysis of the Corrosion in Tendons in Contact with Water. *Front. Mater.* **2019**, *6*, 167, doi:10.3389/fmats.2019.00167.
19. Belletti, B.; Vecchi, F.; Bandini, C.; Andrade, C.; Montero, J.S. Numerical evaluation of the corrosion effects in prestressed concrete beams without shear reinforcement. *Struct. Concr.* **2020**, doi:10.1002/suco.201900283.
20. Cabrini, M.; Lorenzi, S.; Pastore, T.; Bucella, D.P. Effect of hot mill scale on hydrogen embrittlement of high strength steels for pre-stressed concrete structures. *Metals* **2018**, *8*, 158, doi:10.3390/met8030158.
21. Kumar, V. Protection of Steel Reinforcement for Concrete—A Review. *Corros. Rev.* **1998**, *16*, doi:10.1515/CORRREV.1998.16.4.317
22. Bolzoni, F.; Brenna, A.; Beretta, S.; Ormellese, M.; Diamanti, M.V.; Pedferri, M.P. Progresses in prevention of corrosion in concrete. *IOP Conf. Ser. Earth Environ. Sci.* **2019**, *296*, 12016, doi:10.1088/1755-1315/296/1/012016.
23. Hurley, M.; Scully, J.R. Threshold Chloride Concentrations of Selected Corrosion Resistant Rebar Materials Compared to Carbon Steel. *Corrosion* **2006**, *62*, 892–904.
24. Bertolini, L.; Pedferri, P. Laboratory and field experience on the use of stainless steel to improve durability of reinforced concrete. *Corros. Rev.* **2002**, *20*, 129–152.

25. Bertolini, L.; Bolzoni, F.; Gastaldi, M.; Pastore, T.; Pedferri, P.; Redaelli, E. Effects of cathodic prevention on the chloride threshold for steel corrosion in concrete. *Electrochim. Acta* **2009**, *54*, 1452–1463, doi:10.1016/j.electacta.2008.09.033.
26. Pedferri, P. Cathodic protection and cathodic prevention. *Constr. Build. Mater.* **1996**, *10*, 391–402, doi:10.1016/0950-0618(95)00017-8.
27. Elsener, B.; Angst, U. Corrosion inhibitors for reinforced concrete. In *Science and Technology of Concrete Admixtures*; Aïtcin, P.-C., Flatt, R.J., Eds.; Woodhead Publishing: Oxford, UK, 2016; pp. 321–339. ISBN 978-0-08-100693-1.
28. Coppola, L.; Coffetti, D.; Crotti, E.; Gazzaniga, G.; Pastore, T. Chloride Diffusion in Concrete Protected with a Silane—Based Corrosion Inhibitor. *Materials* **2020**, *13*, 2001, doi:10.3390/ma13082001.
29. Elsener, B. *Corrosion Inhibitors for Steel in Concrete*; State of the Art Report; EFC Publications; Maney Publishing: Leeds, UK, 2001.
30. Söylev, T.A.; Richardson, M.G. Corrosion inhibitors for steel in concrete: State-of-the-art report. *Constr. Build. Mater.* **2008**, *22*, 609–622, doi:10.1016/J.CONBUILDMAT.2006.10.013.
31. Ormellese, M.; Berra, M.; Bolzoni, F.; Pastore, T. Corrosion inhibitors for chlorides induced corrosion in reinforced concrete structures. *Cem. Concr. Res.* **2006**, *36*, 536–547, doi:10.1016/j.cemconres.2005.11.007.
32. Collepardi, M.; Fratesi, R.; Moriconi, G.; Corradetti, V.; Coppola, L. Use of nitrite salt as corrosion inhibitor admixtures in reinforced concrete structures immersed in sea-water. In *Proceedings of the International RILEM Symposium on Admixtures for Concrete*; Barcelona, Spain, 14–17 May, 1990; pp. 279–288.
33. Garcés, P.; Saura, P.; Zomoza, E.; Andrade, C. Influence of pH on the nitrite corrosion inhibition of reinforcing steel in simulated concrete pore solution. *Corros. Sci.* **2011**, *53*, 3991–4000, doi:10.1016/j.corsci.2011.08.002.
34. Morris, W.; Vázquez, M. A migrating corrosion inhibitor evaluated in concrete containing various contents of admixed chlorides. *Cem. Concr. Res.* **2002**, *32*, 259–267, doi:10.1016/S0008-8846(01)00669-X.
35. Ben Mansour, H.; Dhouibi, L.; Idrissi, H. Effect of Phosphate-based inhibitor on prestressing tendons corrosion in simulated concrete pore solution contaminated by chloride ions. *Constr. Build. Mater.* **2018**, *171*, 250–260, doi:10.1016/j.conbuildmat.2018.03.118.
36. Troconis de Rincón, O.; Pérez, O.; Paredes, E.; Caldera, Y.; Urdaneta, C.; Sandoval, I. Long-term performance of ZnO as a rebar corrosion inhibitor. *Cem. Concr. Compos.* **2002**, *24*, 79–87, doi:10.1016/S0958-9465(01)00029-4.
37. Cabrini, M.; Lorenzi, S.; Pastore, T. Study of localized corrosion of steel reinforcement in inhibited alkaline solutions [Studio della corrosione localizzata degli acciai per armature in soluzioni alcaline inibite]. *Metall. Ital.* **2013**, *105*, 21–31.
38. Zecher, D. Corrosion inhibition by surface-active chelants. *Mater. Perform.* **1976**, *15*, 33–37.
39. Ormellese, M.; Lazzari, L.; Goidanich, S.; Fumagalli, G.; Brenna, A. A study of organic substances as inhibitors for chloride-induced corrosion in concrete. *Corros. Sci.* **2009**, *51*, 2959–2968, doi:10.1016/j.corsci.2009.08.018.
40. Nmai, C.K. Multi-functional organic corrosion inhibitor. *Cem. Concr. Compos.* **2004**, *26*, 199–207, doi:10.1016/S0958-9465(03)00039-8.
41. Li, J.-H.; Zhao, B.; Hu, J.; Zhang, H.; Dong, S.-G.; Du, R.-G.; Lin, C.-J. Corrosion inhibition effect of D-sodium gluconate on reinforcing steel in chloride-contaminated simulated concrete pore solution. *Int. J. Electrochem. Sci.* **2015**, *10*, 956–968.
42. Valek Žulj, L.; Serdar, M.; Martinez, S. Effect of tartrate on the electrochemical behaviour and semiconductive properties of passive film on steel in saturated calcium hydroxide. *Mater. Corros.* **2015**, *66*, 1344–1353, doi:10.1002/maco.201408203.
43. Nithya Devi, P.; Rajendran, S.; Sathiyabam, J.; Pandiarajan, M.; Joseph Rathish, R.; Santhana Prabha, S. Corrosion resistance of mild steel in simulated concrete pore solution in presence of simulated urine, tartaric acid and lactic acid. *Eur. Chem. Bull.* **2016**, *5*, 163–166.
44. Tang, S.W.; Zhu, H.G.; Li, Z.J.; Chen, E.; Shao, H.Y. Hydration stage identification and phase transformation of calcium sulfoaluminate cement at early age. *Constr. Build. Mater.* **2015**, *75*, 11–18, doi:10.1016/j.conbuildmat.2014.11.006.
45. Winnefeld, F.; Lothenbach, B. Hydration of calcium sulfoaluminate cements—Experimental findings and thermodynamic modelling. *Cem. Concr. Res.* **2010**, *40*, 1239–1247, doi:10.1016/j.cemconres.2009.08.014.

46. Provis, J.L.; Palomo, A. Advances in understanding alkali-activated materials. *Cem. Concr. Res.* **2015**, *78*, 110–125, doi:10.1016/j.cemconres.2015.04.013.
47. Coppola, L.; Bellezze, T.; Belli, A.; Bignozzi, M.C.; Bolzoni, F.; Brenna, A.; Carsana, M. *et al.*, Binders alternative to Portland cement and waste management for sustainable construction—Part 2. *J. Appl. Biomater. Funct. Mater.* **2018**, *16*, 207–221, doi:10.1177/2280800018782852.
48. Coppola, L.; Bellezze, T.; Belli, A.; Bignozzi, M.C.; Bolzoni, F.; Brenna, A.; Carsana, M. *et al.*, Binders alternative to Portland cement and waste management for sustainable construction—Part 1. *J. Appl. Biomater. Funct. Mater.* **2018**, *16*, 186–202, doi:10.1177/2280800018782845.
49. Sugama, T. Citric acid as a set retarder for calcium aluminate phosphate cements. *Adv. Cem. Res.* **2006**, *47*–57, doi:10.1680/adcr.2006.18.2.47.
50. Bishop, M.; Bott, S.G.; Barron, A.R. A New Mechanism for Cement Hydration Inhibition: Solid-State Chemistry of Calcium Nitrilotris(methylene)triphosphonate. *Chem. Mater.* **2003**, *15*, 3074–3088, doi:10.1021/cm0302431.
51. Coppola, L.; Coffetti, D.; Crotti, E. Use of tartaric acid for the production of sustainable Portland-free CSA-based mortars. *Constr. Build. Mater.* **2018**, *171*, 243–249, doi:10.1016/j.conbuildmat.2018.03.137.
52. Stewart, M.G.; Al-Harthy, A. Pitting corrosion and structural reliability of corroding RC structures: Experimental data and probabilistic analysis. *Reliab. Eng. Syst. Saf.* **2008**, *93*, 373–382, doi:10.1016/j.res.2006.12.013.
53. Andrade, C. 2013 W.R. Whitney Award Lecture: Probabilistic Treatment of the Reinforcement Corrosion. *Corrosion* **2014**, *70*, 643–651, doi:10.5006/1049.
54. Cabrini, M.; Fontana, F.; Lorenzi, S.; Pastore, T.; Pellegrini, S. Effect of Organic Inhibitors on Chloride Corrosion of Steel Rebars in Alkaline Pore Solution. *J. Chem.* **2015**, *2015*, 521507, doi:10.1155/2015/521507.
55. Li, L.; Sagues, A.A. *Effect of Chloride Concentration on the Pitting and Repassivation Potentials of Reinforcing Steel in Alkaline Solutions*; NACE International, Houston, TX, USA, 1999.
56. Ghods, P.; Isgor, O.B.; McRae, G.A.; Gu, G.P. Electrochemical investigation of chloride-induced depassivation of black steel rebar under simulated service conditions. *Corros. Sci.* **2010**, *52*, 1649–1659, doi:10.1016/j.corsci.2010.02.016.
57. Cabrini, M.; Lorenzi, S.; Testa, C.; Pastore, T.; Manfredi, D.; Lorusso, M.; Calignano, F.; Fino, P. Statistical approach for electrochemical evaluation of the effect of heat treatments on the corrosion resistance of AlSi10Mg alloy by laser powder bed fusion. *Electrochim. Acta* **2019**, *305*, 459–466, doi:10.1016/j.electacta.2019.03.103.
58. Angst, U.; Rønquist, A.; Elsener, B.; Larsen, C.K.; Vennesland, Ø. Probabilistic considerations on the effect of specimen size on the critical chloride content in reinforced concrete. *Corros. Sci.* **2011**, *53*, 177–187, doi:10.1016/j.corsci.2010.09.017.
59. Cabrini, M.; Lorenzi, S.; Pastore, T. Cyclic voltammetry evaluation of inhibitors for localised corrosion in alkaline solutions. *Electrochim. Acta* **2014**, *124*, 156–164.
60. Pastore, T.; Cabrini, M.; Coppola, L.; Lorenzi, S.; Marcassoli, P.; Buoso, A. Evaluation of the corrosion inhibition of salts of organic acids in alkaline solutions and chloride contaminated concrete. *Mater. Corros.* **2011**, *62*, 187–195, doi:10.1002/maco.201005789.
61. Schrebler Guzman, R.S.; Vilche, J.R.; Arvia, A.J. The voltammetric detection of intermediate electrochemical processes related to iron in alkaline aqueous solutions. *J. Appl. Electrochem.* **1981**, *11*, 551–561, doi:10.1007/BF00616674.
62. Page, C.L.; Ngala, V.T.; Page, M.M. Corrosion inhibitors in concrete repair systems. *Mag. Concr. Res.* **2000**, *52*, 25–37, doi:10.1680/mac.2000.52.1.25.
63. Page, C.L. Aspect of the performance of corrosion inhibitors applied to reinforced concrete. In Proceedings of the 9th European Symposium on Corrosion Inhibitors; Ferrara, Italy, 4–8 September 2000.
64. Garcés, P.; Saura, P.; Méndez, A.; Zornoza, E.; Andrade, C. Effect of nitrite in corrosion of reinforcing steel in neutral and acid solutions simulating the electrolytic environments of micropores of concrete in the propagation period. *Corros. Sci.* **2008**, *50*, 498–509, doi:10.1016/j.corsci.2007.08.016.
65. Ngala, V.T.; Page, C.L.; Page, M.M. Corrosion inhibitor systems for remedial treatment of reinforced concrete. Part 1: Calcium nitrite. *Corros. Sci.* **2002**, *44*, 2073–2087, doi:10.1016/S0010-938X(02)00012-4.
66. Yamaguchi, M.; Nishihara, H.; Aramaki, K. The inhibition of pit growth on an iron surface in a borate buffer solution containing chloride ion by inhibitors classified as soft bases in the HSAB principle. *Corros. Sci.* **1995**, *37*, 571–585, doi:10.1016/0010-938X(94)00151-U.

67. Macdonald, D.D. Passivity—the key to our metals-based civilization. *Pure Appl. Chem.* **1999**, *71*, 951–978.
68. Stimming, U. Properties of passive film on iron electrodes by capacity and photocurrent measurements. In *Proceedings of the Passivity of Metals and Semiconductors: 5th International Symposium on Passivity*; Bombannes, Paris, France, 30 May–3 June 1983; pp. 477–483.
69. Li, W.; Luo, J. Electric properties and pitting susceptibility of passive films formed on iron in chromate solution. *Electrochem. Commun.* **1999**, *1*, 349–353, doi:10.1016/S1388-2481(99)00070-3.
70. Trasatti, S. Oxygen evolution. In *Encyclopedia of Electrochemical Power Sources*; Garce, J., Dyer, C., Moseley, P., Ogumi, Z., Rand, D., Scrosati, B., Eds.; Elsevier: Amsterdam, The Netherlands, 2009; pp. 49–55.
71. Valcarce, M.B.; Vázquez, M. Carbon steel passivity examined in alkaline solutions: The effect of chloride and nitrite ions. *Electrochim. Acta* **2008**, *53*, 5007–5015, doi:10.1016/j.electacta.2008.01.091.
72. Cornell, R.M.; Schindler, P.W. Infrared study of the adsorption of hydroxycarboxylic acids on α -FeOOH and amorphous Fe (III)hydroxide. *Colloid Polym. Sci.* **1980**, *258*, 1171–1175, doi:10.1007/BF01382462.
73. Green, R.W.; Parkins, G.M. Complexes of iron with d-tartaric and meso-tartaric acids. *J. Phys. Chem.* **1961**, *65*, 1658–1659, doi:10.1021/j100905a523.
74. Toropova, V. Polarographic study of stability of the complexes of iron with tartaric acid. *J. Gen Chem.* **1945**, *15*, 603.
75. Gomma, G.K. Mechanism of corrosion behaviour of carbon steel in tartaric and malic acid in the presence of Fe²⁺ ion. *Mater. Chem. Phys.* **1998**, *52*, 200–206, doi:10.1016/S0254-0584(97)02046-4.
76. Qiang, Y.; Guo, L.; Zhang, S.; Li, W.; Yu, S.; Tan, J. Synergistic effect of tartaric acid with 2,6-diaminopyridine on the corrosion inhibition of mild steel in 0.5 M HCl. *Sci. Rep.* **2016**, *6*, 33305, doi:10.1038/srep33305.
77. Bazzaoui, M.; Martins, L.; Bazzaoui, E.A.; Martins, J.I. New single-step electrosynthesis process of homogeneous and strongly adherent polypyrrole films on iron electrodes in aqueous medium. *Electrochim. Acta* **2002**, *47*, 2953–2962, doi:10.1016/S0013-4686(02)00188-3.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).