

# Corrosion behavior of steel reinforcements in sustainable low-resistive cement mortars

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This work was carried out within the H2020 EnDurCrete project (GA n° 760639). In this study, innovative cement mortars with low electrical impedance were manufactured with sustainable carbon-based additions, such as biochar (BCH) at 0.5 vol% and recycled carbon fibers (RCF) at 0.05 vol% on the total mix. Electrical impedance ( $Z_{Re}$ ) of mortar of cement mortars and corrosion behavior ( $E_{corr}$  and  $R_p$ ) of embedded steel reinforcements were evaluated during both the curing period (i.e., 28 days) and weekly wet/dry cycles in a 3.5% NaCl solution. Results show that the combination of BCH and RCF reduces by approximately 60% the  $Z_{Re}$  value compared to the plain mortar. However, the lower electrical impedance of mortars with carbon-based additions with respect to the plain mortar does not impair negatively the corrosion behavior of embedded rebars, both during the curing and the exposure to wet/dry cycles in the chloride-rich solution, since they seem to be even more protective for reinforcements during the whole experimentation.

**KEYWORDS:** STEEL; BIOCHAR; CORROSION; RECYCLED CARBON FIBERS;

## INTRODUCTION

Carbon-based materials in the form of particles and fibers are often added in cement-based composites to reduce electrical resistivity and enhance mechanical properties, making them suitable for technologically advanced products [1]. Several types of carbonaceous materials have been studied in technical and scientific literature like carbon fibers [2], carbon black [3], graphite [4] and graphene [5] particles, carbon nanotubes [6], gasification char [7], etc. Recently, the present authors have studied the properties of cement-based mortars and concretes prepared with sustainable carbon-based materials, proving that an optimized combination of biochar (BCH) and recycled carbon fibers (RCF) addition enhances both electrical and mechanical performance [8]. Including BCH in concrete at approximately 2% by mass enhances mechanical strength [9], and replacing part of cement with BCH contributes to reduce CO<sub>2</sub> emissions [10] thanks also to the biochar capability of absorbing CO<sub>2</sub> [11]. On the other hand, carbon fibers (CF) have been extensively used in self-sensing and low-resistive cement-based materials, enabling the monitoring of the compressive strain of concrete elements thanks to their physical and chemical properties [12].

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The durability of reinforced cement-based materials governs the service life of structures and it is well known that, the longer is the time between the first sign of degradation to the intervention, the higher the costs needed to repair a concrete structure [13]. Although in recent years many studies have been published on the use of carbon-based additions to enhance physical, mechanical, and electrical properties of cement-based materials, still there are very few works regarding the effect of these materials on the corrosion of embedded steel reinforcements. Previous studies highlighted that CF addition increases corrosion current density ( $I_{corr}$ ) of steel reinforcements, probably due to the decreasing of electrical resistivity [14], and the higher the CF content, the higher is the  $I_{corr}$  value [15]. Del Carmen Camacho et al. [16] added carbon nanotubes (CNT) in reinforced cement paste specimens exposed to carbonation and chloride attacks. Results obtained showed that the increase in CNT content does not modify significantly the mechanical properties but increases steel corrosion rates. On the other hand, other authors added graphene nanoplatelets (GNP) to mortars at 0, 0.05, and 1% by cement mass and concluded that at low level GNP addition may enhance the passivity and resistance to chloride-induced corrosion of carbon steel rebars [17]. Therefore, given the few papers reported by literature on the effect of carbon based addition in cement based materials on corrosion of embedded steel reinforcements and even with contradictory results, in this study innovative cement mortars containing BCH and RCF were studied in terms of electrical impedance ( $Z_{re}$ ) and corrosion behavior of embedded steel rebars during both

the curing period and weekly wet/dry cycles in a 3.5% NaCl solution.

## MATERIALS AND METHODS

Mortars were prepared with a limestone cement CEM II A-LL 42.5R and calcareous sand (0/8 mm) in saturated surface dry (s.s.d.) condition (water absorption of 2% by mass). Recycled carbon fibers (RCF) with 6 mm length and 7  $\mu\text{m}$  diameter supplied by Procotex Belgium SA were used as fibrous addition. RCF have a specific surface area of 0.132  $\text{m}^2/\text{g}$ , a density of 1.85  $\text{g}/\text{cm}^3$  and a carbon content of 94% by mass. BCH supplied by RES Italia was used in filler form (diameter lower than 75  $\mu\text{m}$ ). BCH has a specific surface area of 46.2  $\text{m}^2/\text{g}$ , a density of 2.0  $\text{g}/\text{cm}^3$  and it is composed by 100% amorphous carbon. BCH and RCF were added to mortars at 0.5 vol% and 0.05 vol% on the total, respectively. As superplasticizer (SP), an acrylic one (Dynamon SP1, Mapei S.p.A.) was used to manufacture mortars with plastic consistency (flow value between 140 and 210 mm according to the EN 1015:3 standard). In table 1, the mix design of mortars is reported. After mixing, mortars were poured into molds and placed inside a climatic chamber. Specimens were cured at temperature ( $T$ ) =  $20 \pm 1$   $^{\circ}\text{C}$  and relative humidity (RH) > 95% for 7 days inside molds covered by plastic sheets, then they were demolded, the plastic sheets were removed, and specimens were cured at  $T = 20 \pm 1$   $^{\circ}\text{C}$  and RH =  $50 \pm 5\%$  for 56 days. Then, specimens were exposed to 6 weekly wet/dry cycles in a 3.5% NaCl solution in water (5 days dry and 2 days wet). During the drying period, specimens were left at room conditions.

**Tab.1** - Mix design delle malte (g/L) / *Mix design of mortars (g/L).*

Mortars	CEM (g/L)	Water (g/L)	Sand (g/L)	SP (g/L)	RCF (g/L)	BCH (g/L)
REF	510	255	1530	3	-	-
RCF	510	255	1529	3	1	-
BCH	508	254	1523	3	-	10
RCF+BCH	508	254	1522	3	1	10

The mechanical performance of mortars was studied after 1, 7, and 28 days of curing in terms of compressive strength ( $R_c$ ) with a Galdabini hydraulic press (400 kN full scale and 1% precision). Three specimens (40 mm x 40 mm x 160 mm) per composition were tested and the average strength was calculated.

The electrical properties of mortars were studied in terms of electrical impedance ( $Z_{Re}$ ) with a 4-electrode configuration according to the Wenner's method [18] in alternating current at 10 kHz with a Gamry Reference 600 in galvanostatic mode. This configuration was chosen in order to avoid the polarization of both electrodes and the material itself [19]. Electrical impedance was studied on three prismatic specimens (40 mm x 40 mm x 160 mm) equipped with 4 stainless-steel rods ( $\varnothing$  3 mm and 40 mm length) embedded for 20 mm inside the mortar with a spacing of 20 mm, as reported in [8]. The corrosion behavior of embedded rebars was studied in terms of  $E_{corr}$  and  $R_p$  with an Autolab PGSTAT 204 potentiostat/galvanostat. The  $R_p$  was measured with the potentiodynamic polarization method (scan rate = 0.167 mV/s;  $\Delta V = \pm 10$  mV) by calculating the slope of the anodic branch, which can be indicated as  $R_{anod}$ . For corrosion measurements, cylindrical mortar specimens equipped with 4 corrugated carbon steel rebars ( $\varnothing$  8 mm) acting as working electrode and a stainless-steel rebar ( $\varnothing$  6 mm)

acting as counter-electrode partially embedded inside the specimen were used. The corrugated carbon steel rebars were embedded in the mortar specimens leaving an exposed surface area ( $A_s$ ) of 16 cm<sup>2</sup>. The configuration of the cylindrical specimens is reported in [20]. As reference electrode, a Saturated Calomel Electrode (SCE, +0.241 V vs SHE) was used. The  $Z_{Re}$  and corrosion behavior of embedded reinforcements was studied on mortar specimens during the curing period (i.e. up to 56 days) and during 6 weekly wet/dry cycles in a 3.5% NaCl solution in water (5 days dry and 2 days wet). In order to deurate the corrosion measurements from the mortar resistance, an additional measurement on the cylindrical specimens was performed. An electrochemical impedance spectroscopy measurement has been done in the frequency (f) range between 100 kHz and 10 Hz, then the value of impedance modulus in terms of  $\log |Z|$  and the phase  $\theta$  were reported as a function of  $\log f$  (Bode plot). The minimum value of  $\theta$  (very close to 0°) was found and a range around it was suitably selected. The values of  $\log |Z|$  found in this range were used to calculate an average value that corresponds to the resistance of the mortar ( $R_m$ ). This value was subtracted from the  $R_{anod}$  to find a resistance that becomes  $R_p$  after multiplying it by the exposed area  $A_s$  of the sample:

$$R_p = (R_{anod} - R_m) \cdot A_s \quad (1)$$

## RESULTS AND DISCUSSION

The results of compressive strength tests of mortars during the first 28 days of curing are given in figure 1. During the first week, mortars show approximately the same  $R_c$  values. With the progressive hydration of the matrix, the differences between the studied mixes increase. The REF mortar reaches a  $R_c$  of 78 MPa; the highest obtained  $R_c$  value. When RCF or BCH are added to the mix alone, the  $R_c$  slightly diminishes, reaching 71 and 72 MPa for the two mixes, respectively. The combination of RCF and BCH further decreases the  $R_c$  of the mortar, which obtains 68 MPa (13% less than the plain mortar). As previously found by the authors [8,21], the addition of RCF

or BCH can slightly decrease the mechanical properties of cement-based materials due to an increased porosity. In any case, all mortars reach very high  $R_c$  values, suitable for reinforced structural applications.

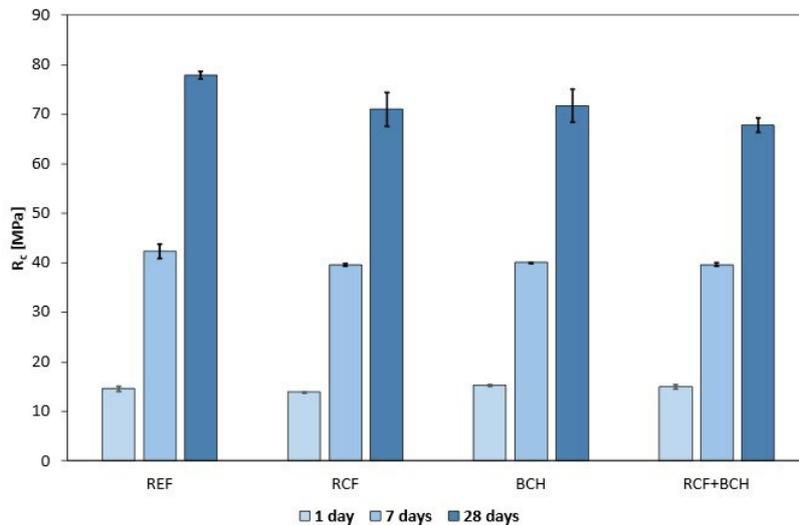


Fig.1 -  $R_c$  durante stagionatura /  $R_c$  during curing.

The calculated values of electrical impedance of mortars during 56 days of curing are given in figure 2. As expected, electrical impedance increases in time [22]; this is due to water consumptions due both to cement hydration and evaporation [23]. The results obtained show that the plain mortar has the highest electrical impedance values during the whole testing period. Conversely, the inclusion of carbonaceous additions contributes to the reduction of the electrical impedance of mortars. With more details, when

RCF is used the  $Z_{re}$  values decrease from 8250 to 4570  $\Omega$  after 56 days, thus become 45% lower than the reference mixture. When BCH is added,  $Z_{re}$  lowers to 6692  $\Omega$ , which is 19% lower than REF mortar. After 56 days of curing, the highest reduction of electrical impedance was registered by the mortar containing the combined addition of RCF and BCH, with a  $Z_{re}$  value of 3700  $\Omega$ , which is 55% lower than that of plain mortar, confirming the results obtained by the same authors in a previous study [8].

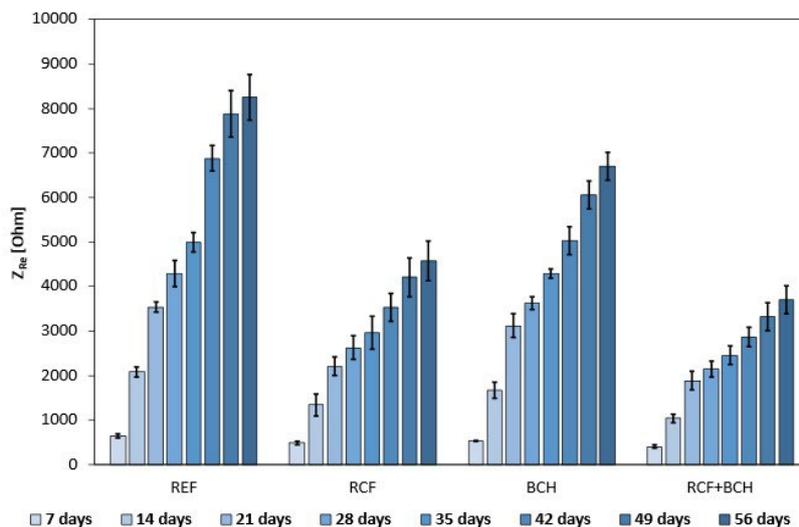


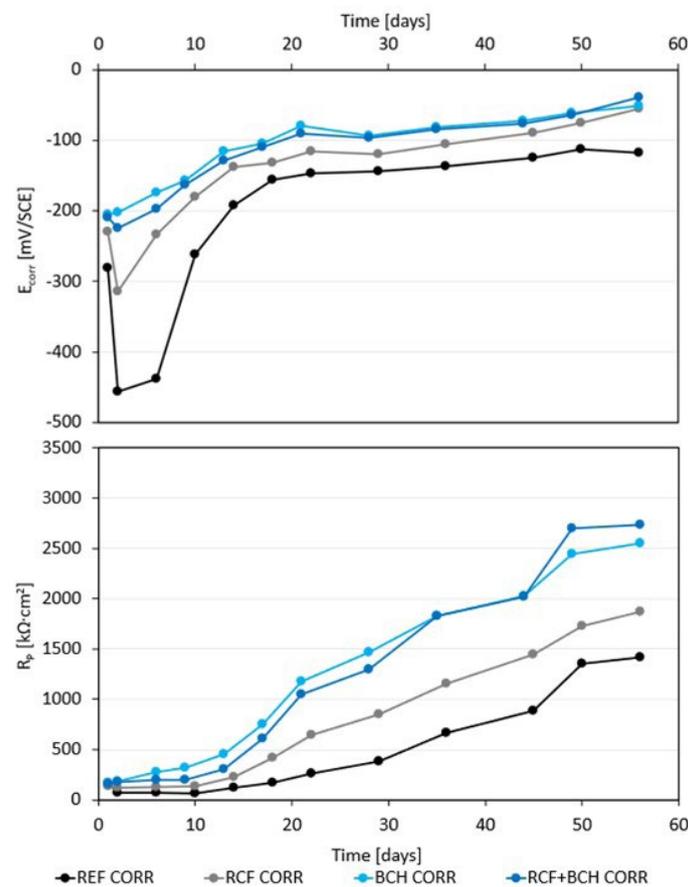
Fig.2 -  $Z_{re}$  delle malte durante stagionatura /  $Z_{re}$  of mortar during curing.

In figure 3  $E_{corr}$  and  $R_p$  values of steel reinforcements embedded in mortars during the curing period (56 days) are reported.  $E_{corr}$  results highlighted that only steel

reinforcements embedded in REF and RCF mortars reached a high probability of corrosion during the first days immediately after casting. However, the higher probability

of corrosion is found for rebars embedded in the reference mortar. After 10 days of curing all reinforcements seem to have reached passivation, given the increasing trend of  $E_{corr}$  values.  $R_p$  values are in agreement with corrosion potential trend, given that all rebars embedded in mortars manufactured with carbon-based additions show  $R_p$  values higher than those embedded in the reference one. With more detail, steel reinforcements embedded in the RCF mix show slightly higher  $R_p$  values compared to the rebars embedded in REF mortar, with a  $R_p$  reaching 2012  $k\Omega \cdot cm^2$  at the end of the test (+8% than REF). On the other hand, steel reinforcements contained in mortars

manufactured with BCH alone and together with RCF recorded 56% and 70% higher  $R_p$  than those in the REF mortar, respectively. This means that when mortars are not exposed to aggressive environments, the addition of carbon-based additions in the form of filler and fibers seems to be beneficial to protect reinforcements from corrosion, confirming the preliminary results found by Shakouri and Abraham [17] when GNP is added to mortars up to 1% by cement mass. Indeed, they concluded that GNP contributed to form a denser passive layer structure.



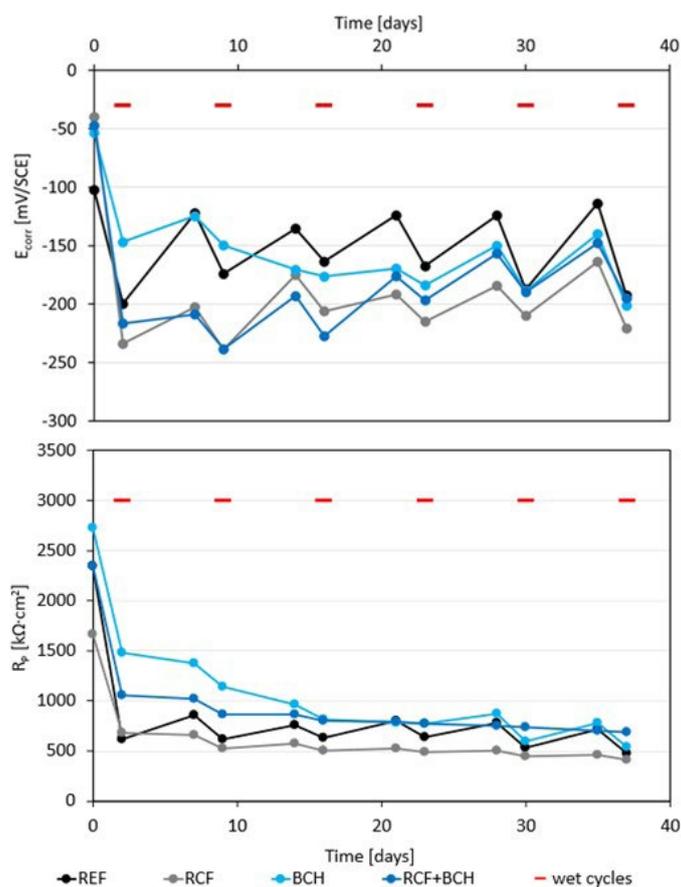
**Fig.3** -  $E_{corr}$  (sopra) e  $R_p$  (sotto) durante stagionatura /  $E_{corr}$  (up) and  $R_p$  (down) during curing.

In figure 4  $E_{corr}$  and  $R_p$  values of steel reinforcements embedded in mortars during wet/dry cycles in 3.5% NaCl solution are given. During the wet/dry cycles in the chloride-rich solution, steel rebars show an immediate drop of both  $E_{corr}$  and  $R_p$  due to the passage from air to a water-based solution. However, as for the curing period, steel reinforcements embedded in the matrix loaded with

BCH alone or coupled to RCF maintain their  $R_p$  higher than those in the REF mortars. Conversely, the addition of the sole RCF seems to be ineffective for corrosion resistance. In any case, all the studied steel reinforcements do not show a high probability of corrosion. Indeed, for carbon steel the probability of corrosion is high when  $E_{corr} < -275$  mV/SCE (as reported in the ASTM C876). Some authors

[24] have found that the addition of graphite powder (GP) to concrete can decrease the corrosion current density of steel rebars immersed in a 0.5 M NaCl solution only when GP is equal to 3% and 5% by cement mass, whereas lower contents seem to be less effective. A decrease of  $R_p$  is expected with the additions of carbonaceous materials in contact with steel reinforcements, due to a coupling effect among them. On the contrary, in this work the  $R_p$  values increased in agreement with other authors [24]. Probably, oxygen binds to carbon particles, reducing its availability in the pore solution and therefore increasing the  $R_p$  values after immersion [24]. On the other hand, the contact between steel rebars and CF causes a more pronounced shift towards more positive  $E_{corr}$  values, thus lower corrosion current density levels, only when the amount

of CF exceeds 1% by cement mass. Indeed, carbon has a more positive potential than steel, so a higher CF content implies a higher  $E_{corr}$  shift [24]. Considering the present experimentation, BCH acts as GP, giving that the amount of BCH in the studied mixes is equal to 2% by cement mass. Probably, this percentage is enough to reduce the steel rebars corrosion exposed to chlorides. In the same way, the RCF content is not sufficient to determine the same corrosion reduction, given that RCF mortar contains only 0.2% of fibers by cement mass. Therefore, the combination of BCH and RCF slightly enhances the corrosion resistance of embedded steels in the 3.5% NaCl solution, given the increased quantity of carbon-based materials.



**Fig.4** -  $E_{corr}$  (sopra) e  $R_p$  (sotto) durante cicli di bagnasciuga. Le linee rosse rappresentano il periodo in bagnato (2 giorni) /  $E_{corr}$  (up) and  $R_p$  (down) during wet/dry cycles. Red lines represent the wet period (2 days).

Although, a decrease of  $E_{corr}$  and  $R_p$  values is registered during the wet/dry cycles, all the reinforcements can be considered in a passive state. Indeed, an estimation of

the corrosion current density ( $i_{corr}$ ) has been performed, according to the following equation:

$$i_{\text{corr}} = \frac{B}{R_p} \quad (2)$$

and considering the coefficient B value equal to 52 mV, characteristic of rebars in a passive state (while B = 26 mV refers to steel in active state) [25]. Results demonstrate that before exposure (after 56 days of curing) the  $i_{\text{corr}}$  ranges around  $0.02 \mu\text{A}/\text{cm}^2$  for reinforcements embedded in all mixes. At the end of curing, the  $i_{\text{corr}}$  slightly increases reaching values close to  $0.1 \mu\text{A}/\text{cm}^2$ . As reported in [25], these values represent a negligible corrosion, therefore all reinforcements remain passive also during accelerated exposure to wet/dry cycles in a 3.5% NaCl solution. Indeed, it should be noted that all  $R_p$  values have been calculated after removing the mortar resistance ( $R_m$ ) which negligibly affects the polarization curve of steel rebars.

## CONCLUSIONS

This research was carried out to evaluate the mechanical and electrical behavior of cement mortars containing sustainable carbon-based additions, i.e., biochar (BCH) and recycled carbon fibers (RCF). Moreover, the corrosion behavior of embedded carbon steel rebars during the curing period and accelerated chloride contamination was investigated in terms of polarization resistance ( $R_p$ ). It was found that the addition of BCH and RCF both alone and coupled together does not negatively impair the mechanical strength of mortars, since the highest  $R_c$  reduction is only 13% for the BCH+RCF mixture, which

reaches a final compressive strength of 68 MPa after 28 days of curing. The obtained results demonstrate that the mortar with the lowest electrical impedance is the one manufactured with the combination of BCH and RCF, which shows a decreased electrical impedance of 55% compared to the reference one. Mortars containing BCH alone and coupled to RCF, despite being more conductive than the reference mixture, do not worsen the corrosion behavior of the embedded reinforcements since they seem to be even more protective for reinforcements both during curing and during exposure to the chloride-rich solution.

## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] D. D. L. Chung, *Composites Part B: Engineering*, 31, 511–526 (2000).
- [2] N. Banthia et al., *Cement and Concrete Research*, 22, 804–814 (1992).
- [3] S. Gwon et al., *Cement and Concrete Composites*, 137, 104942 (2023).
- [4] S. Sun et al., *Construction and Building Materials*, 136, 314–328 (2017).
- [5] W. Li et al., *Construction and Building Materials*, 331, 127284 (2022).
- [6] G. Xing et al., *Journal of Building Engineering*, 95, 110364 (2024).
- [7] A. Mobili et al., *Journal of Building Engineering*, 50, 104237 (2022).
- [8] A. Mobili et al., *Construction and Building Materials*, 376, 131051 (2023).
- [9] H. Maljaee et al., *Construction and Building Materials*, 283, 122757 (2021).
- [10] R. A. Mensah et al., *Sustainability*, 13(16), 9336 (2021).
- [11] D. Winters et al., *Sustainability*, 14(8), 4633 (2022).
- [12] B. Han et al., *Self-Sensing Concr. Smart Struct.*, Ed. Butterworth-Heinemann, (2014).

- [13] W. R. De Sitter, CEB-RILEM Workshop on Durability of Concrete Structures, Ed. Comité Euro-International du Béton, Copenhagen (1984).
- [14] P. W. Chen, D. D. L. Chung, *Journal of Electronic Materials*, 24, 47–51 (1995).
- [15] P. Garcés et al., *Cement and Concrete Research*, 35, 324–331 (2005).
- [16] M. Del Carmen Camacho et al., *Materials*, 7(3), 1640–1651 (2014).
- [17] M. Shakouri, O.F. Abraham, *Construction and Building Materials*, 452, 138948 (2024).
- [18] F. Wenner, *Journal of the Washington Academy of Sciences*, 5, 561–563 (1915).
- [19] G. Cosoli et al., *Construction and Building Materials*, 271, 121546 (2021).
- [20] F. Tittarelli et al., *Corrosion Science*, 134, 64–77 (2018).
- [21] A. Belli et al., *Journal of Building Engineering*, 73 106836, (2023).
- [22] P. Azarsa, R. Gupta, *Advances in Materials Science and Engineering*, 2017, 8453095 (2017).
- [23] A. Mobili et al., *Sustainability*, 14(3), 1775 (2022).
- [24] P. Garcés et al., *Corrosion Science*, 49, 2557–2566 (2007).
- [25] A. M. Aguirre-Guerrero et al., *Applied Clay Science*, 135, 437–446 (2017).

## Comportamento a corrosione di rinforzi in acciaio immersi in malte cementizie sostenibili a bassa resistività elettrica

Questo lavoro è stato realizzato nell'ambito del progetto H2020 EnDurCrete (GA n° 760639). In questo studio, sono state create malte cementizie innovative a bassa impedenza elettrica contenenti aggiunte sostenibili a base di carbonio come biochar (BCH) allo 0.5% e fibre di carbonio riciclate (RCF) allo 0.05% sul volume totale. L'impedenza elettrica ( $Z_{Re}$ ) delle malte cementizie e il comportamento a corrosione ( $E_{corr}$  e  $R_p$ ) di rinforzi in acciaio sono stati valutati sia durante il periodo di stagionatura (28 giorni) sia durante cicli di bagnato/asciutto in una soluzione al 3.5% di NaCl. I risultati mostrano che l'aggiunta combinata di BCH e RCF riduce di circa il 60% il valore di  $Z_{Re}$  della malta. Inoltre, le malte con aggiunte carboniose, nonostante più elettricamente conduttive della miscela di riferimento, non peggiorano il comportamento a corrosione delle armature inglobate sia durante la stagionatura sia durante l'esposizione ai cicli di bagnasciuga nella soluzione ricca di cloruri; anzi, sembrano addirittura essere più protettive per le armature durante l'intera sperimentazione.

**PAROLE CHIAVE:** ACCIAIO; BIOCHAR; CORROSIONE; FIBRE DI CARBONIO RICICLATE;