Comportamento a corrosione di armature in acciaio e acciaio zincato in una malta ad attivazione alcalina a base di metacaolino dopo carbonatazione accelerata

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Il lavoro presenta il comportamento a corrosione di armature in acciaio e acciaio zincato immerse in malte ad attivazione alcalina a base di metacaolino e malte tradizionali cementizie appartenenti alla stessa classe di resistenza meccanica (classe R3 con $R_c \geq 25$ MPa, secondo la UNI EN 1504-3). I test sono stati effettuati valutando il potenziale di libera corrosione e la resistenza alla polarizzazione durante il primo mese di stagionatura e durante i successivi cicli settimanali di bagnasciuga in acqua dopo esposizione in camera al 3% di CO_2. Durante la stagionatura, l'elevato pH della malta in metacaolino rallenta il raggiungimento dello stato passivo delle armature zincate che, successivamente, raggiungono resistenze di polarizzazione paragonabili alle barre immerse nella malta cementizia. Durante carbonatazione accelerata, il pH della malta in metacaolino si abbassa più velocemente di quello della malta cementizia. Durante i cicli di bagnasciuga, entrambe le tipologie di armatura mostrano simili resistenze alla polarizzazione in entrambe le matrici studiate.

PAROLE CHIAVE: MALTE AD ATTIVAZIONE ALCALINA, MALTE CEMENTIZIE, ARMATURE ZINCATE, CORROSIONE, CARBONATAZIONE.

INTRODUCTION

Alkali-activated materials (AAMs) are ceramic-like materials with a reduced embedded CO_2 compared to cement-based materials, obtained by the chemical reaction between an alkali metal source with amorphous or vitreous calcium-aluminosilicate precursors [1]. Metakaolin (MK) is a low-calcium aluminosilicate precursor [2] and it can be considered as the model system to study the activation process of AAMs.

Durability of building materials is of utmost importance for civil engineering [3] and one of the major durability problems is the corrosion of steel in reinforced concrete structures. It is promoted by carbonation, which in cement-based materials leads to a reduction of pH controlled by portlandite ($Ca(OH)_2$). In the case of low-calcium AAMs, this phase does not form, and therefore the pH is controlled exclusively by the pore solution [4,5]. It has

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been found that in metakaolin-based AAMs, accelerated carbonation in highly concentrated environment (CO_2 = 50%), leads to the formation of sodium bicarbonates which lower the pH of the pore solution much more than 10.5, resulting in a potential risk of corrosion [6].

In order to mitigate the corrosion of steel rebars, a possible solution is the use of galvanized ones.

In the literature, there are few papers concerning the durability of AAMs in CO_2-rich environments [7–9], mainly related to slag-based compounds [10–13], and limited studies deal with the corrosion of steel embedded in AAMs [4,14,15], especially if galvanized. Therefore, the aim of this paper is to compare the corrosion behavior of bare and galvanized reinforcements embedded in MK-based alkali-activated and in traditional cement-based mortars with the same mechanical strength class (R3 class, with R_c ≥ 25 MPa) just after casting and after exposure to CO_2-rich environment.

MATERIALS AND METHODS

The alkali-activated mortar (R3 MKK) was manufactured with MK as aluminosilicate precursor, and a mix of sodium silicate solution (SiO_2 = 29.86 wt.%, Na_2O = 14.64 wt.%, H_2O = 55.50 wt.%) and potassium hydroxide solution as liquid alkaline activator. The cement-based mortar (R3 CEM) was prepared with Portland Cement CEM II/A-LL 42.5R (CEM). Commercial calcareous sand with maximum grain size of 8 mm was used for both mortars. R3 CEM was manufactured with sand/binder ratio of 3 and water/binder (w/b) ratio of 0.65. R3 MKK was manufactured with sand/precursor equal to 3 and w/b ratio of 0.54. In AAMs, the binder is the sum of precursors and solids dissolved in the alkaline solution. In Tab. 1 the mix design of both mortars is reported. After mixing, mortars were poured into molds and cured at T = 20 ± 1 °C and RH = 95 ± 5% for 2 days and then at T = 20 ± 1 °C and RH = 50 ± 5%.

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

Mortars	CEM (g/L)	WATER (g/L)	SAND (g/L)	MKK (g/L)	Alkaline activators (g/L)			
					Sodium silicate	KOH pellets	Demin. Water	
R3 CEM	450	292	1350	-	-	-	-	0.65
R3 MKK	-	-	1156	428	257	64	193	0.54

A reinforced cylindrical specimen (115 mm diameter and 125 mm height) was manufactured for both types of mortar. Four corrugated steel rebars (Ø = 8 mm), 2 of bare steel (Fe) and 2 of galvanized steel (Zn), were symmetrically embedded in the cylinder with a mortar cover of 15 mm and were separately used as working electrodes. The corrosion behavior of reinforcements was evaluated by free corrosion potential (E_{corr}) measurements, using a Saturated Calomel Electrode (SCE; 241 mV/SHE) as reference, and polarization resistance (R_p) measurements. A centrally positioned AISI 316 stainless steel rod (Ø = 6 mm) was used as counter-electrode during R_p measurements. Measurements have been carried out for a duration of 28 days of curing from the cast (T = 20 ± 1 °C and RH = 50 ± 5%) at set periods of time. Afterwards, the specimens were exposed for 110 days to accelerated carbonation in a chamber at T = 21 ± 1 °C, RH = 60 ± 5% and CO_2 = 3 ± 0.2 vol.%, until complete carbonation of the mortar cover (evaluated by phenolphthalein method according to UNI 9944). Subsequently, the mortars were submitted to 12 weekly wet-dry cycles in tap water (1 day wet and 6 days dry) and both E_{corr} and R_p were measured in wet condition immediately before extraction from water. At the end of the exposure, the zinc coating thickness of galvanized rebars was evaluated by metallographic analysis to check the effects of corrosion.

RESULTS AND DISCUSSIONS

E_{corr} and R_p values measured on bare and galvanized steel rebars during the first 28 days of curing in air and then in the CO_2-rich environment are shown in Fig. 1. Immediately after the cast, E_{corr} values of bare steel in R3 CEM mortar increase (Fig. 1a), whereas in R3 MKK they decrease because of the high alkalinity of the matrix (pH = 13.9), much higher than that of CEM one (pH = 13.2). After 7 days, E_{corr} of bare steel embedded in R3 MKK moves to more positive values and becomes comparable to that of the rebars embedded in R3 CEM mortar, because the alkalinity of MKK matrix decreases (pH = 12.8) [6], and becomes less aggressive for rebars. In the same time period,

R_p values (Fig. 1c) of the steel bars embedded in both mortars follow E_{corr} trends (Fig. 1a): in R3 CEM, the R_p values increase up to 30 kΩ·cm^2, whereas those of R3 MKK remain low until the 7th day and then increase up to 20 kΩ·cm^2 at 28 days of curing. Similar trends are found for galvanized steel rebars, since the active state of reinforcements (corresponding to E_{corr} around -1400 mV/SCE, Fig. 1b) is almost stable for 7 days in R3 MKK (R_p lower than 10 kΩ·cm^2, Fig. 1d). After this period, both E_{corr} and R_p values increase and become even higher than those relative to R3 CEM (Fig. 1b and 1d). After 28 days of air curing, R_p reaches values of about 60-70 kΩ·cm^2 and the pH of mortars becomes equal to 13.1 for R3 CEM and 12.2 for R3 MKK. For galvanized rebars embedded in CEM mortars, the increase of R_p is due to the formation of a crystalline and protective passivation layer of calcium hydroxyzincate (CHZ) [16]. This layer cannot form in R3 MKK because of the little presence of calcium; however, the increase of R_p of galvanized steel embedded in R3 MKK mortar is a consequence of the lowering of the mortar pH. During accelerated carbonation (from 30 to 140 days), bare steel rebars embedded in R3 MKK seem not influenced by the carbonation of the mortar cover (Fig. 1a). Conversely,

those in R3 CEM show a decrease of E_{corr} (Fig. 1a) and an increase of R_p values (Fig. 1c) after the complete carbonation of the mortar cover, which occurs around 120 days of curing (90 days in the carbonation chamber). The carbonation of the mortar cover occurs faster for R3 MKK than R3 CEM mortars owing to the higher total porosity of the matrix (34% for the former and 18% for the latter). However, the pH of R3 MKK matrix remains around 10.1, whereas that of R3 CEM decreases up to 9.2. On the other hand, a slight decrease both of E_{corr} (Fig. 1b) and R_p (Fig. 1d) values can be observed for galvanized steel rebars embedded in R3 MKK, whereas those in R3 CEM gradually increase their R_p values, especially after complete carbonation of the mortar cover (R_p = 350 kΩ·cm^2). Although the carbonation of R3 CEM mortar destroys the CHZ protective layer, typically formed on galvanized steel, this behavior can be explained by considering that CHZ is chemically transformed into hydroxyzincite (HZ) [16], an amorphous product with good passivating properties. Conversely, in R3 MKK mortar, where CHZ cannot form, the carbonation lowers the alkalinity of the matrix, but the pH remains still high, maintaining in any case a significant risk of corrosion.
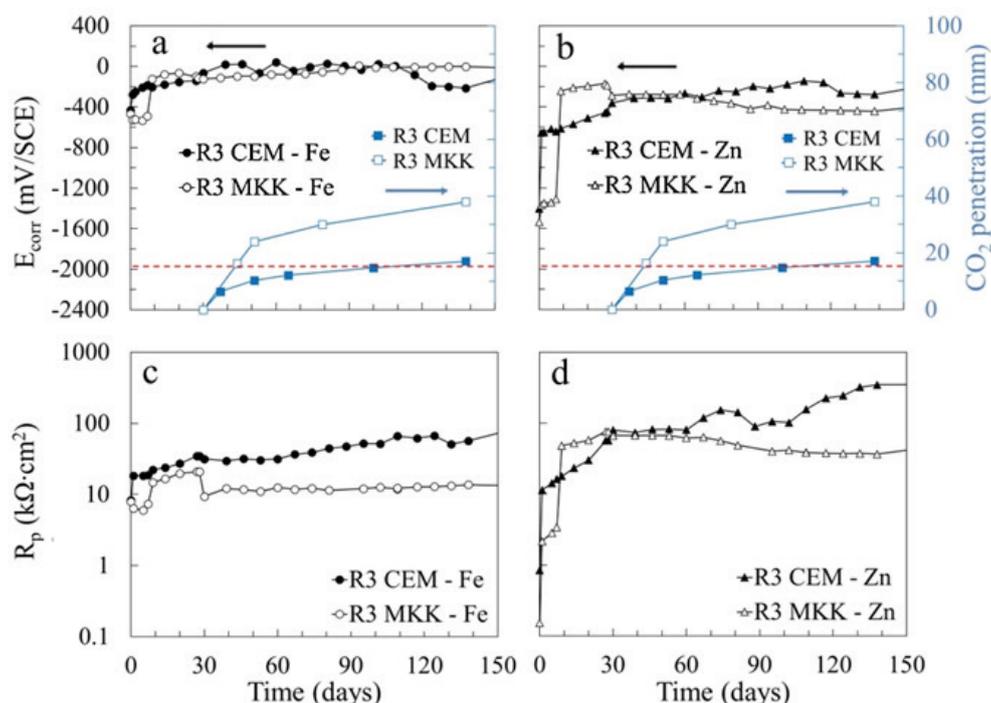

Fig.1 - Andamenti di E_{corr} e R_p delle armature in acciaio (a, c) e acciaio zincato (b, d) durante 28 giorni di stagionatura in aria e 110 giorni di carbonatazione accelerata. L'andamento del fronte di carbonatazione è riportato nelle curve in blu, mentre lo spessore del copriferro è mostrato dalla linea rossa tratteggiata – Trends of E_{corr} and R_p of bare steel (a, c) and galvanized steel (b, d) rebars during 28 days of air curing and 110 days of accelerated carbonation. The trend of carbonation depth is reported by blue curves, whereas the dashed red line shows the mortar cover depth.

After complete carbonation of the mortar cover, during the following wet-dry cycles in tap water, the probability of corrosion increases instantaneously for bare steel rebars embedded in R3 CEM mortar (Fig. 2). In fact, just after the first immersion in water, they show an immediate decrease of E_{corr} from -70 to -420 mV/SCE and R_p values drop from 90 kΩ·cm² to 15 kΩ·cm² (Figs. 2a and 2c, respectively) compared to those of rebars embedded in R3 MKK which remain unchanged for the whole exposure (around -10 mV/SCE for E_{corr} and 8 kΩ·cm² for Rp, Figs. 2a and 2c). On

the contrary, galvanized rebars show an immediate drop of E_{corr} to -800 mV/SCE and R_p values reach 10-20 kΩ·cm² in both mortars (Figs. 2b and 2d). Anyhow, for galvanized reinforcements, the probability of corrosion remains low because the zinc coating thickness measured after the exposure (Figs. 2e and 2f) maintains around 160 μm in both mortars and shows the slight persistence of the pure zinc layer (η phase), which is similar to that of galvanized steel reinforcements before the exposure to aggressive environment, which is around 170 μm.
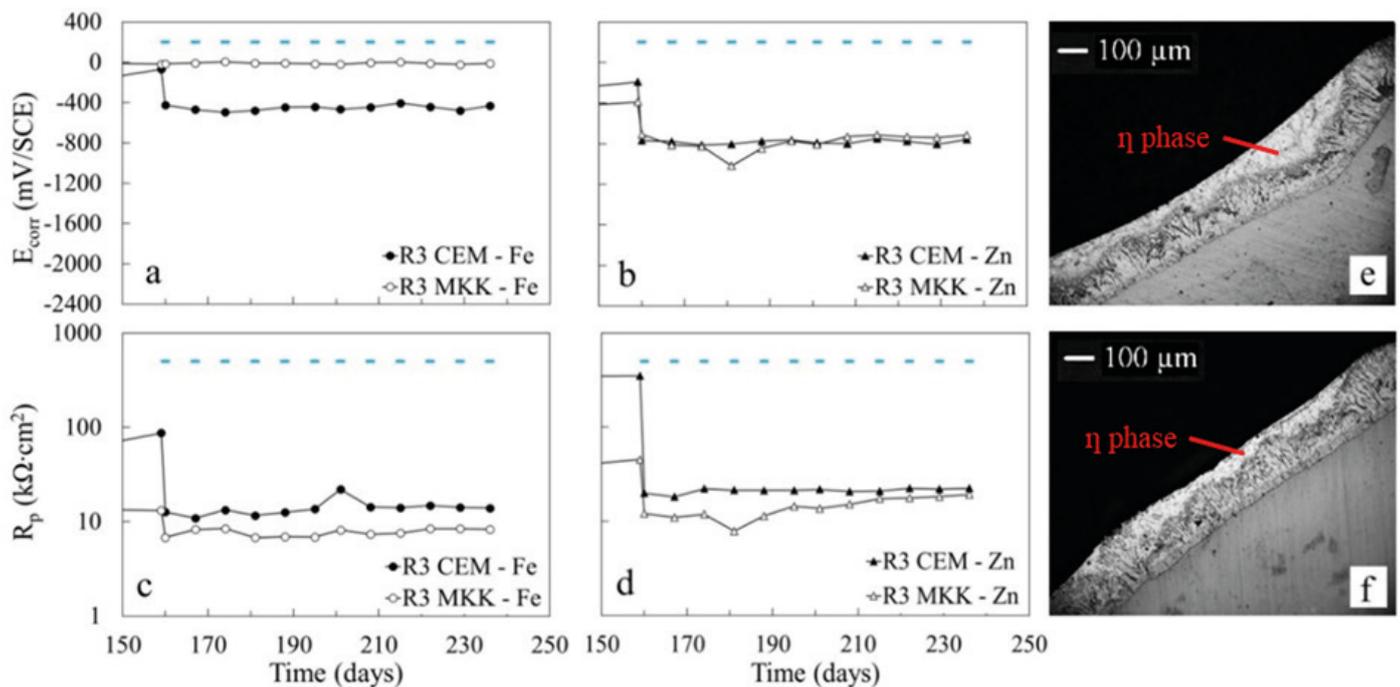

Fig.2 - Andamenti di E_{corr} e R_p delle armature in acciaio (a, c) e acciaio zincato (b, d) durante i cicli di bagnasciuga in acqua dopo carbonatazione accelerata. In blu sono riportati i periodi in bagnato. Microstruttura del rivestimento di zinco a fine prova delle armature in R3 CEM (e) e R3 MKK (f) – Trends of R_p and E_{corr} of bare steel (a,c) and galvanized steel (b,d) rebars during the exposure to wet/dry cycles in tap water after accelerated carbonation. The wet periods are reported in blue. Microstructure of the zinc coating of rebars at the end of tests in R3 CEM (e) and R3 MKK (f).

CONCLUSIONS

During 28 days of exposure in air, the high alkalinity of alkali-activated mortar delays the achievement of the passive state for bare and galvanized steel rebars. However, after few days, reinforcements reach the same R_p values of those embedded in the traditional cement mortar with the

same strength class. The carbonation of the mortar cover occurs faster for alkali-activated mortar owing to its higher total porosity. During exposure to wet-dry cycles in water, after accelerated carbonation, R_p values are similar in both matrices for both type of rebars.

References

[1] A. MOBILI et al., Environments, 4(3), 64 (2017).

[2] C. GIOSUÈ et al., Construction and Building Materials, 220, 565–576 (2019).

[3] A. BELLI et al., Sustainability, 10(11), 4013 (2018).

[4] M. SUFIAN BADAR et al., Construction and Building Materials, 61, 79–89 (2014).

[5] S. A. BERNAL et al., Cement and Concrete Research, 42(10), 1317–1326 (2012).

[6] R. POUHET, M. CYR, Cement and Concrete Research, 88, 227–235 (2016).

[7] M. NEDELJKOVIĆ et al., Ceramics International, 44(16), 19646–19660 (2018).

[8] A. M. RASHAD, Green Materials, 7(3), 118–136 (2019).

[9] Z. LI, S. LI, Construction and Building Materials, 163, 668–680 (2018).

[10] S. A. BERNAL et al., Cement and Concrete Research, 41(1), 1–8 (2011).

[11] O. A. MOHAMED, Materials, 12(8), 1198 (2019).

[12] D. E. CADORE et al., Construction and Building Materials, 226, 117–125 (2019).

[13] D. E. ANGULO-RAMIREZ et al., Materiales de Construcción, 69(333), 182 (2019).

[14] M. BABAEE et al., Cement and Concrete Composites, 85, 32–43 (2018).

[15] C. MONTICELLI et al., Cement and Concrete Research, 80, 60–68 (2016).

[16] G. ROVENTI et al., Materials and Corrosion, 64(11), 1007-1014 (2013).

Corrosion behavior of galvanized and bare steel reinforcements embedded in carbonated alkali-activated metakaolin mortar

The work presents the corrosion behavior of bare and galvanized steel rebars embedded in metakaolin alkali-activated and traditional cement-based mortars belonging to the same mechanical strength class (R3 class with $R_c \geq 25$ MPa, according to UNI EN 1504-3). Tests were conducted evaluating both the corrosion potential and the polarization resistance throughout the first month of curing and during the subsequent weekly wet/dry cycles in tap water after exposure to a chamber with 3% of CO_2. During the first month, the high alkalinity of alkali-activated mortar delays the achievement of the passive state in particular for galvanized steel rebars, even though, after that period, they reach the same polarization resistance of those embedded in the cement-based mortar. During accelerated carbonation, the neutralization of alkalinity in alkali-activated mortar occurs more quickly than in cement-based mortar. During exposure to wet/dry cycles in tap water, both bare and galvanized steel rebars show comparable polarization resistance values in both studied mortars.

KEYWORDS: ALKALI-ACTIVATED MATERIALS, CEMENT-BASED MORTARS, GALVANIZED REINFORCEMENTS, CORROSION, CARBONATION.