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Corrosion behavior of steel in alkali-activated fly ash mortars in the light of their microstructural, mechanical and chemical characterization

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ABSTRACT

This study concerns the corrosion behavior of steel in different room temperature cured alkali-activated fly ash mortars exposed to chloride solution. The corrosion process was monitored by polarization resistance and corrosion potential measurements and the results were interpreted in the light of a complete microstructural, mechanical and chemical characterization of the mortars. The most compact alkali-activated mortars have higher porosity and lower mechanical properties than a cement-based mortar (CEM), but the protectiveness afforded to the rebars is slightly higher than that obtained in CEM. The reason for this discrepancy is connected to a lower chloride content accumulated in the former mortar type and to a specific inhibition of the rebar corrosion afforded by the pore electrolyte in alkali-activated mortars.

1. Introduction

Reinforced concrete (RC) is the most commonly used construction material worldwide, but several problems can affect its matrix, in terms of durability and even sustainability.

As far as durability is concerned, the main factors that cause deterioration of RC are mostly linked to corrosion of the reinforcements, with consequent fatal decrease in terms of construction service life, loading capacities and seismic resistance, so that preventing corrosion is one of the most important goals to avoid RC deterioration. Normally, pH of the pore electrolyte in Ordinary Portland Cement (OPC) is strongly alkaline (around 13 or even higher), aiding the formation of a passive film which can prevent corrosion. This film can be damaged due to chloride attack [1–3] or due to carbonation, which causes a reduction of the pH of the pore electrolyte and undermines the stability of the passive film [4]. The binder plays a fundamental role in preventing or accelerating chloride penetration and concrete carbonation, because it affects the nature of the binder hydration products and the concrete porous microstructure.

Nowadays, worldwide commitments aim at achieving a more sustainable development by promoting a gradual replacement of Ordinary Portland Cement by binders with production systems at low-CO_2 emission [5]. In these terms, various studies have highlighted alkali-activated materials (AAM) as a potential competitive alternative to OPC [6,7]. This class of inorganic amorphous materials derives from the alkali-activation of aluminosilicate powders with suitable amorphous content. The final products have binding properties and engineering performances very similar to cement-based products and even superior in case of high temperature applications [8,9]. Many aluminosilicate precursors are suitable for activation and when the raw material has a high content of $SiO_2 + Al_2O_3$ (generally >80%) and a low CaO content, like class F fly ash (FA), the final product is referred to as geopolymer [10]. The chance to use industrial by-products as precursors, such as FA or slags [11–13], along with a room or slightly higher curing temperature, makes AAM low-polluting products and, consequently, promising green building materials.

Many features of geopolymers obtained with different types of precursors have already been investigated, such as chemistry activation processes [14], gel-phase analysis [15], microstructure and mechanical properties [16,17]. As far as geopolymer durability is concerned, encouraging results have been obtained about their resistance to sulfate attack and alkali–silica reactions and about the high stability in the presence of fire or freeze–thaw cycles, besides an excellent adhesion to steel reinforcement [18]. Only a few studies focus on room temperature (RT) activation [13,19,20], long-term performances and corrosion resistance of reinforcing bars in the presence of these alternative binding materials [18,21–25], which are key factors to permit the industrial application of these new mortar and/or concrete systems.

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Early studies in this field show that, during 1-year exposure to a 95% R.H. atmosphere in the presence of 0 or 0.4% admixed chlorides, alkali activated FA mortar (cured at 85 °C) and a RT cured mortar with an alkali activated 70 FA/30 OPC binder mix afforded an excellent corrosion protection to the reinforcing bars. Protection was comparable to that obtained by traditional OPC mortar. On the contrary, with a 2% admixed chlorides, passive conditions were maintained for 200 days only in the mortar with the alkali-activated 70 FA/30 OPC binder mix, due to its lowest porosity [26]. After accelerated carbonation, FA mortars partially immersed in 0.2 M NaCl solutions afforded a higher corrosion protection to steel rebars than traditional mortar exposed to the same aggressive environment [27,28]. The reason was connected to the higher concentration of carbonate/bicarbonate ions in Na-containing pore electrolyte of FA mortars than in Ca-containing pore electrolyte of traditional OPC mortar. A high concentration of these ions is the consequence of the higher solubility of sodium carbonate/bicarbonate salts in comparison to calcium salts. Therefore, an effective pH buffer forms in carbonated FA mortars capable to hinder local pH variations induced by electrochemical activity of the rebars, connected to corrosion. This would hinder the formation of local galvanic cells and would inhibit corrosion [27].

Even the type of FA activator is expected to affect the corrosion behavior of reinforcing bars. In fact, the addition of sodium silicate to sodium hydroxide in the binder activating solution was found to induce lower porosity and higher mechanical properties in geopolymers [13,16,29–33]. As a consequence, an improvement of the corrosion resistance of the embedded rebars was measured [34].

The aim of this paper was to study the corrosion behavior of RT-cured steel-reinforced class F fly ash geopolymer mortars by an integrated approach based on mechanical, physical, microstructural and electrochemical tests. In particular, different formulations were prepared by changing the relative amounts of the activators in order to evaluate their effect on mechanical strength, porosity distribution and rebar corrosion behavior in a chloride-rich environment (NaCl 3.5 wt%). During the exposure, the chloride content in close proximity of the rebars and the initial and final pH values were also assessed. A comparison was made between geopolymer performances and those characterizing a cement-based mortar and the different behavior observed was justified on the basis of tests carried out in leachate solutions obtained from the different mortar types in contact with water.

2. Experimental

2.1. Raw materials

Class F FA used as raw material for the geopolymer matrices was sourced from Enel Produzione S.p.A., Torrevaldaliga Nord power station (Civitavecchia, Roma, Italy), and was supplied by General Admixtures S.p.A. (Ponzano Veneto, Treviso, Italy). It exhibited a $d_{50} = 22$ μm, while its mineralogical composition was found to have 65 ± 0.8 wt% amorphous phase and crystalline phases of quartz, mullite and maghemite. The main oxide composition of FA is reported in Table 1. Detailed particle size distribution and mineralogical phase analysis are reported elsewhere [13]. Sodium silicate ($SiO_2/Na_2O = 1.99$, density at 20 °C = 1.5 ± 0.2 g/cm^3, Ingessil, Verona, Italy) and 8 M NaOH were used as activating solutions and were mixed together and stirred 24 h before samples casting. Reference mortar was prepared using CEM II/A-LL 42.5 R. For both geopolymer and cement-based mortars, natural calcareous sand ($d_{max} = 4$ mm) was used as fine aggregate.

Table 1
Main oxide composition of FA and LOI (loss on ignition).

Components (wt% as oxides)								
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
49.37	29.23	2.71	6.63	1.05	0.33	0.05	0.60	3.28

2.2. Preparation of mortar specimens

Three different geopolymer mortar mixes and a reference cement-based one were prepared. Their mix design is shown in Table 2. All geopolymers were activated by adjusting the relative amount of 8 M NaOH and sodium silicate solutions in order to achieve Na_2O/SiO_2 molar ratios of 0.12, 0.14 and 0.16. The liquid/binder weight ratio (L/B) was fixed at 0.52.

The selected Na_2O/SiO_2 ratios were chosen on the basis of the results of a previous research [13] where Na_2O/SiO_2 ratios ranging from 0.12 to 0.20 were investigated. Lower molar ratios were not used as the determined loss of workability was found to critically affect mortar samples preparation.

The geopolymer acronyms (FA12, FA14 and FA16) refer to the precursor name (FA) and the Na_2O/SiO_2 molar ratio (e.g., FA16 indicates the FA-based mortar with a Na_2O/SiO_2 molar ratio of 0.16). The reference mortar (CEM) was prepared with the same sand/binder and L/B ratios adopted for geopolymer mortars (Table 2).

Microstructural and mechanical characterizations were performed on prismatic samples ($40 \times 40 \times 160$ mm^3), mechanically compacted and de-molded after 1 day curing at T = 25 °C and R.H. = 35%. Then, the specimens were kept at the laboratory atmosphere (R.H. ≈ 35%) and tests were performed in due time. These exposure conditions aim at reproducing those often adopted at the construction sites.

Electrochemical tests and analyses of penetrated chloride content were carried out on slabs with dimensions $200 \times 250 \times 50$ mm^3. Three manually compacted slabs were prepared for each formulation: two reinforced slabs with embedded steel bars (Fig. 1a) and one unreinforced slab for chloride concentration analysis (Fig. 1b). Each reinforced slab contained two sandblasted degreased ribbed carbon steel rods acting as working electrodes (W, $\phi = 10$ mm), with ends masked with epoxy resin and isolated by thermo-shrinking adhesive tape to leave an exposed surface area of 7400 mm^2. In close proximity to these bars, two activated titanium wires and three symmetrically arranged stainless steel bars acted as reference (R) and counter (C) electrodes, respectively, during the electrochemical tests.

Slabs were cured in the molds at T = 25 °C and R.H. = 35% for a week, then they were de-molded and cured at the laboratory atmosphere (R.H. ≈ 35%) for further 3 weeks, again to simulate practices often adopted in field applications. Finally, the lower side of each slab was ground so reducing the slab thickness by 2 mm, in order to avoid the skin effect and accelerate the ingress of chlorides. The ground side was finally exposed to the aqueous chloride solution, without slab pre-saturation (Fig. 2).

2.3. Characterization

2.3.1. Microstructure and mechanical characterization

Compressive strength (σ_c) was measured by an Amsler-Wolpert machine (maximum load: 100 kN) at a constant displacement rate of 50 mm/min. The results are reported as average values of 5 measurements, respectively. Flexural strength measurements were also carried out and the results are reported in [25].

Two different tests were performed to determine water absorption properties by capillarity. The first test was accomplished with a procedure similar to the one described in UNI EN 1015-18 [35] on prismatic samples after flexural test. The capillary coefficient was determined according to the formula $C = 0.1 \times (W_2 - W_1)$ kg/m^2 min$^{0.5}$ and the height of water capillary penetration was measured at the end of the test by longitudinally splitting the samples. The second test was performed according to UNI EN 15801 [36]: the weight gain of pre-dried regular form samples, partially immersed in a constant 5 mm water head, was monitored over 8 days. The amount of water absorbed per