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A study on the corrosion of reinforcing bars in alkali-activated fly ash mortars under wet and dry exposures to chloride solutions

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ABSTRACT

This research investigates the corrosion protection afforded to the embedded rebars by room temperature-cured alkali-activated mortars, based on class F fly ash (FA), during wet and dry (w/d) exposures to 0.1 M NaCl solution. The results were compared to those obtained in a traditional cement-based mortar (REF). The rebar corrosion behaviour was characterized by corrosion potentials (E_{cor}) and potentiostatic polarization resistance (R_p) measurements, polarization curve recording and electrochemical impedance spectroscopy (EIS). The information collected suggested that FA mortars afforded a lower corrosion protection to the rebars and the reason was investigated by microstructural, physical–mechanical and chemical analyses of the mortars. FA mortars were found to undergo a fast carbonation, so that depassivation of the rebars occurred concurrently, in spite of a limited total chloride content inside these mortars. REF mortar was much less susceptible to carbonation and rebar corrosion started when a sufficiently high chloride concentration was built up.

1. Introduction

The increasing focus on issues concerning environmental sustainability and the enhancement of recycled materials and industrial wastes is stimulating research into the development of alternative sustainable building materials. With regard to traditional construction materials, the environmental impact of ordinary Portland cement (OPC), which produces nearly one ton of CO_2 per ton of cement, is well-known. 50% of its carbon dioxide emissions are caused by the processing of raw materials, 40% by the fuel consumption required to achieve the high processing temperatures (1450 °C) and the remaining 10% by the use of electricity and transportation [1]. Similar considerations may also apply to traditional ceramic materials (bricks and tiles), for which natural origin raw materials and high processing temperatures are used (between 1000 and 1300 °C).

Alkali-activated materials (AAMs), which include geopolymers as the subset with the higher amount of silica and alumina and the lowest content of calcium oxide, represent a viable alternative to traditional building materials [2,3]. The alkali activation is a chemical process, which induces dissolution/reprecipitation reactions on amorphous alumino-silicate powders giving origins to solid products quite similar to cement paste or ceramics. The consolidation process takes place at moderate temperatures ($20 \leq T \leq 100$ °C) and, thanks to their specific chemical compositions, it is possible to activate various types of industrial wastes such as ground-granulated blast furnace slag (GGBS), coal-derived fly ash (FA) and other types of precursors derived from waste streams such as coal gangue and red mud [4]. These kinds of wastes are today only partially used, and without large opportunities for recycling, so that they are commonly disposed in landfills. The sustainability advantage of the alkali activation process is thus evident, as it allows the realization of materials that can be used as alternatives to OPC pastes or ceramics, with the same forming techniques (casting, extrusion, etc.) and final performances.

In view of exploiting the potentialities of AAMs as construction materials, the scientific community is now concentrated in understanding and optimizing the geopolymerization process and much work is focused on achieving high material durability [5–7]. Concerning reinforced structures, it is very important to understand if alkali-activated binders can guarantee the steel reinforcements a protectiveness comparable to that offered by OPC, also in aggressive environments. In fact, corrosion of reinforced elements is one of the main causes of structural failures, generally connected to carbonation and/or chloride penetration [8].

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The corrosion behaviour of steel rebars in activated fly ash mortars depends on many factors, which still need to be fully investigated. Among these factors, the composition and nature of alkaline activator, the mortar/concrete curing temperature and the exposure conditions play a fundamental role. As far as the activating solution composition is concerned, it was found that the addition of sodium silicate to sodium hydroxide stimulated network formation in geopolymers so leading to improved mechanical strength, lowering chloride ion mobility and slightly improving corrosion performances [9–11]. However, also a high sodium hydroxide content was observed to improve the geopolymer protective properties because of stimulation of the geopolymerization rate [12]. The addition of an alkaline solid activator based on sodium silicate and sodium carbonate induced a descending alkaline pH in mortar specimens and/or a high total porosity [13]. In geopolymers, the presence of high concentrations of inhibiting silicate ions in the pore electrolyte was reputed to contribute to reinforce steel passivity [14,15]. The durability of reinforced geopolymer specimens in high relative humidity atmosphere was proved to be quite high and comparable to that in traditional mortars, in the absence of admixed chlorides or in the presence of a limited chloride contamination. Instead, the addition of 2% chlorides to the mortar mixes impaired the stability of the rebar passive films [10,13,16]. During continuous contact with 3.5% NaCl solution [10] or wet and dry (w/d) exposure to this solution [12], the performances of reinforced geopolymer specimens were slightly better than those in OPC-based reference specimens. The latter alternated immersion tests were carried out on high temperature-cured geopolymer specimens to improve the concrete performances. Actually, high temperature curing is a quite common way to achieve high geopolymer durability [9,12,13,16,17], although this reduces the material environmental sustainability and its use on building sites. Thus, many efforts aim at formulating room temperature (RT) activation of these new construction materials [18–21].

The aim of this paper was to evaluate the performances of reinforced RT-cured geopolymer mortars subjected to w/d cycles in chloride solution. Three different mortar compositions were formulated by modifying the Na_2O/SiO_2 ratio and their performances were compared to those of a traditional cement-based mortar. The corrosion behaviour of the embedded rebars was investigated by electrochemical tests (potentiostatic polarization resistance (R_p) measurements, electrochemical impedance spectroscopy (EIS) and polarization curve recording) and by a concomitant physical–chemical investigation of the mortar microstructures and characteristics, which helped interpretation of electrochemical test results.

2. Materials and methods

2.1. Raw materials

Geopolymers were prepared using class F FA sourced from the Enel Produzione S.p.A Italian power station of Torrevaldaliga, Civitavecchia, Roma and supplied by General Admixtures S.p.A. (Ponzano Veneto, Treviso, Italy). It is a fine ($d_{50} = 22$ μm) and mostly amorphous FA (65 ± 0.8 wt.%) with chemical composition, expressed in main oxide content, as follows: $SiO_2 = 49.0$, $Al_2O_3 = 29.2$, $Fe_2O_3 = 2.7$, $CaO = 6.6$, $MgO = 1.1$, $SO_3 = 0.3$, $Na_2O < 0.05$, $K_2O = 0.6$ wt.%. A detailed characterization of this FA is reported elsewhere [20].

The chosen activator solutions for the studied systems consisted in different mixtures of sodium silicate solution ($SiO_2/Na_2O = 1.99$ as molar ratio, density at 20 °C $= 1.5 \pm 0.2$ g/cm^3, Ingessil, Verona, Italy) and 8 M NaOH solution, which were pre-mixed 24 h before sample preparation and additionally stirred immediately before casting.

CEM II/A-LL 42.5 R was used as reference binder while natural sand with standardized grain size distribution according to EN 196-1 [22] was used as aggregate for FA and cement-based mortar samples.

2.2. Mortar design and characterization

The samples were prepared by keeping constant both the binder amount (FA or cement) and the binder/sand and liquid/binder (L/B) ratios (binder/sand = 1:2.7 and L/B = 0.52). For geopolymers, the liquid part consisted in a fixed amount of alkaline solutions (10.7 wt.%) plus water (1.6 wt.%). Three different mixes of geopolymers were prepared by changing the relative amounts of 8 M NaOH and sodium silicate solutions in order to achieve specific molar ratios of Na_2O/SiO_2, namely equal to 0.12, 0.14 and 0.16 (chosen on the basis of previous works [10,20]). Geopolymer mortars were referred to as G_1, G_2 and G_3 ($Na_2O/SiO_2 = 0.12$, 0.14 and 0.16, respectively), while cement mortar samples were named REF.

Before casting, the mortar consistency was determined in the fresh state by flow-table test. All the slurries exhibited a good consistency showing an average spread diameter of about 200 mm. Geopolymer slurries were denser compared to REF and, among the FA-based formulations, G_3 exhibited the fastest setting time (20 min compared to 40 min, as average) thus meaning that the presence of a higher content of NaOH accelerates consolidation reactions.

The slurries were cast in different types of moulds (cylinders, prisms or cubes), depending on the characterization tests.

Sixteen cylinders (h = 100 mm, φ = 35 mm) were cast for each type of mortar. Ten cylinders were prepared for electrochemical tests with embedded rebars (acting as working electrodes, W) and activated titanium wires (acting as quasi-reference low-impedance electrodes (R)), which were fixed in the proximity of each reinforcement (Fig. 1a).

The rebars were ribbed carbon steel rods (sandblasted surface, φ = 10 mm) with both ends masked by epoxy paint. This surface protection was made more long-lasting by applying a further thermoset band on the paint. The area of the exposed surface was 1000 mm^2. These rebars were positioned along the longitudinal axis of the cylindrical samples, so that the mortar cover was about 13 mm.

Further six unreinforced cylinders were prepared for chloride content and pH measurements (Fig. 1b).

Prismatic samples ($40 \times 40 \times 160$ mm^3) and cubes ($100 \times 100 \times 100$ mm^3) were also cast, for mechanical and microstructural characterization and chloride diffusion test, respectively.

Both geopolymer and REF mortar samples were vibrated on a shaker table to reduce entrained air and cured for 28 days under conditions chosen with the aim to maximize their mechanical properties. In particular, independently from the absence or presence of a reinforcing bar, geopolymers were cured at T = 25 °C and R.H. = 35%, while REF samples were cured at T = 25 °C and R.H. > 95% until testing.

After 28 days of curing, epoxy varnish was applied to screen all reinforced cylinder surfaces, with the exception of the surface surrounding the exposed rebar region (Fig. 1a). The same screening geometry was adopted for unreinforced samples (Fig. 1b) to produce similar chloride penetration paths.

After the same curing time, physical–mechanical properties such as bulk density, compressive strength, dynamic elastic modulus and mortar shrinkage were investigated. In particular, bulk density (ρ in g/cm^3) was determined from mass/apparent volume ratio. Compressive strengths (σ_c) were 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. Dynamic elastic modulus (E_d) was calculated as an average of 3 measurements, according to the formula $E_d = \rho \cdot V^2$, where V is the ultrasonic pulse velocity, measured by a Matest instrument with 55 kHz transducers. The mortar shrinkage was determined according to EN 12617-4 [23].

The mortar microstructure, in terms of pore size distribution, was studied by a mercury intrusion porosimetry (MIP) (Carlo Erba 2000) equipped by a macropore unit (Model 120, Fison Instruments). A mercury surface tension of 0.48 N/m and a contact angle of 141.3° were assumed [24].