Corrosion behaviour of coated steel rebars in carbonated and chloride-contaminated alkali-activated fly ash mortar

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ABSTRACT

The corrosion behaviour of hybrid organic-inorganic coatings applied on carbon steel embedded in carbonated ordinary Portland cement (OPC) and alkali-activated fly ash (AAFA) mortars and immersed in a 3 wt.% NaCl solution was evaluated using electrochemical methods. The sol-gel coatings were prepared by condensation and polymerization of TEOS/MPTS, TEOS/MTES, TMOS/MPTS and TMOS/MTES mixtures with a molar ratio of 1.0 and deposited by dip-coating on the carbon steel substrates. The coated steels embedded in AAFA mortar presented higher corrosion potential and lower corrosion current density values than those embedded in OPC mortar, indicating that the coatings were more efficient in preventing corrosion of the rebars in this environment. Hybrid coatings synthesized with TEOS/MTES and TMOS/MTES mixtures showed the longest permanence of steel in the passive state when covering rebars embedded in carbonated AAFA mortar. This enhancement of protection may be due to the denser and more compact structure of sol-gel coatings and their greater adhesion to the metallic surface. The study also considered uncoated steel specimens embedded in OPC and AAFA mortars for comparative purposes.

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1. Introduction

Concrete is the most widely used construction material in the world with an estimated current consumption of $1\,m^3$ per person per year [1]. The cement industry is regarded to be responsible for up to 6–7% of all greenhouse gases emitted world-wide, producing 0.85–1.0 t of carbon dioxide (CO_2) per ton of cement. This is mainly a consequence of the calcination of limestone, one of the key ingredients of Portland clinker, which involves the formation and release of CO_2 and high energy consumption during the heating of raw materials in a rotating kiln [1]. Thus the construction industry is very interested in the development of new cementitious binders as an alternative to ordinary Portland cement (OPC).

One of the most promising alternatives is the use of clinker-free cements, known as alkali-activated cements, which are based on wastes and industrial by-products and are produced by the chemical reaction of a poorly crystalline precursor with a highly alkaline solution to form a hardened solid [2]. One of the most widely used precursors for production of alkali-activated cements is fly ash

(FA) from the combustion of coal in thermal power stations [3]. Alkali-activated FA (AAFA) has been extensively studied over the past decades [4–7], and its mechanical and durability properties have been seen to be strongly dependent on the type of FA [8] and activating conditions used [9].

Several studies have reported that carbon steel reinforcements are compatible with AAFA mortar [10,11], showing lower corrosion rates than those recorded in OPC mortar. Reinforcing carbon steel embedded in carbonated AAFA mortar specimens partially immersed in a water solution containing 1% (by binder weight) sodium chloride (NaCl) has shown one order of magnitude higher linear polarization resistance (LPR) values than those measured for OPC mortar [10]. The resulting corrosion current density (i_{corr}) was about 0.9 and 0.2–0.5 $\mu A\,cm^{-2}$ for OPC and AAFA mortars, respectively, indicating lower corrosion rates in alternative cementitious materials based solely on AAFA. Consistent results have been found in naturally carbonated AAFA concretes, where long-term electrochemical testing showed that the high alkalinity of these systems promoted passivation of the steel rebar during the first 200 days after casting [12]. In the case of alkali-activated concretes based on low-Ca FA, the corrosion potential (E_{corr}) values were within the range of minimal corrosion risk, while higher-Ca FA-based concretes yielded E_{corr} values within the range of high risk of corrosion of the steel rebars.

Corrosion of reinforcing steel is one of the main causes of the premature failure of reinforced concrete structures (RCS). The passivity of reinforcing steel in concrete is often attributed to the formation on its surface of a thin passive film whose growth and stability is dependent on the high pH of the surrounding concrete [13,14]. The onset of corrosion in RCS can be accelerated by the presence of chloride ions or CO_2. When chloride ions reach the metal/concrete interface they produce pits on the steel surface and localized corrosion takes place [15], while in the presence of CO_2 the passive film may be destroyed when CO_2 reacts with the hydrated cement matrix and lowers the pH (below 9), leading to generalized corrosion attack [16].

Corrosion protection of RCS is often achieved by adding corrosion inhibitors to the concrete, using high performance concrete mixtures, protective coatings, stainless steel rebars, or applying cathodic protection (CP) systems. Of these methods, the use of protective coatings is most attractive because of their low cost compared to other systems such as CP or the use of galvanized steel or stainless steel [17,18].

In recent years the sol-gel process has proven to be a useful method for obtaining protective coatings on a wide variety of materials such as glass [19], ceramics [20], organic materials [21], and metals like copper [22], aluminium and its alloys [23], stainless steel [24] and carbon steel [25]. The sol-gel process is a chemical route based on the hydrolysis of various alkoxides to form the respective silanols [26–28], followed by a condensation reaction between the silanols or the silanols and alkoxides. The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel) [29]. The precursors for the synthesis of such colloids are metal or metalloid elements surrounded by various reactive ligands. Metal alkoxides are often used because of their high reactivity with water. The most widely used alkoxides are alkoxysilanes such as tetraethyl orthosilicate (TEOS). There are also other alkoxysilane precursors modified with a polymerizable group, such as epoxy, methacrylic or acrylic organofunctional species, and a common compound with polymerizable organic groups is 3-methacryloxy-propyl-trimethoxysilane (MPTS). The main advantages of this process are the low production cost, high efficiency, good adherence to the substrate, low processing temperature, high homogeneity of the final product and resistance against corrosion and oxidation, homogeneity of the treated surfaces, and high mechanical and chemical resistance.

Depending on their nature, protective sol-gel coatings can be inorganic (when prepared from metal alkoxide precursors) [30] or hybrid organic-inorganic (obtained by including organic groups in the inorganic network to obtain thicker layers and/or flexible films) [31]. Organic-inorganic hybrid materials have attracted particular interest in the microelectronics and optics industries because of their molecular homogeneity, transparency, flexibility, rigidity and durability [27].

In recent studies [32,33] the authors have evaluated the thickness and composition of four types of hybrid organic-inorganic coatings produced with TEOS, MPTS, methyl-triethoxysilane (MTES) and tetramethyl orthosilicate (TMOS) at various molar ratios and analysed their corrosion behaviour when deposited on steel rebars immersed in a simulated concrete pore (SCP) solution contaminated with chloride or in a carbonated synthetic solution simulating the carbonated concrete pore (SCCP) solution. The results show that all the considered organic-inorganic coatings improve the corrosion resistance of carbon steel when exposed to both aggressive media, though their effectiveness is strongly dependent on the nature of the organic reagents used.

In the present study the protective properties of hybrid organic-inorganic coatings prepared via sol-gel with a molar ratio of 1.0 and deposited on carbon steels are assessed using LPR and

Table 1
Chemical composition (% in mass) and Blaine fineses of the tested ordinary Portland cement (OPC) and fly ash (FA).

	OPC	FA
LOI	3.28	6.76
IR	1.04	1.96
SiO_2	21.13	46.32
Al_2O_3	4.16	31.01
Fe_2O_3	3.80	4.50
CaO	63.94	4.90
MnO	0.01	0.05
Na_2O	0.25	0.34
K_2O	0.74	1.34
MgO	0.13	1.29
SO_3	3.06	0.91
Si_{react}	–	36.4
Free CaO	1.28	–
Blaine ($m^2 \, kg^{-1}$)	386.7	336

LOI = Loss on Ignition, IR = Insoluble Residue.

electrochemical impedance spectroscopy (EIS) methods. The coated rebars were embedded in carbonated OPC and AAFA mortars and immersed in a 3 wt.% NaCl solution for up to 240 days.

2. Experimental methodology

2.1. Preparation of coated steel reinforcing bars

Sol-gel coatings were prepared by condensation and polymerization of TEOS $(Si(OCH_2CH_3)_4)$ and MPTS $(CH_2 = C(CH_3)COO(CH_2)_3Si(OCH_3)_3)$; TEOS and MTES $((CH_3)Si(OCH_2CH_3)_3)$; TMOS $(Si(OCH_3)_4)$ and MPTS; or TMOS and MTES. All the organic reagents used were analytical grade from Sigma-Aldrich. As described in detail elsewhere [34], the sol-gel coatings were prepared by mixing 5 g of MPTS or MTES with TEOS or TMOS at a molar ratio of 1.0. This molar ratio was selected on the basis of previous reported results [32–34], where it was determined that a molar ratio of 0.5 was insufficient to obtain a corrosion protective hybrid organic-inorganic film, and that the use of a molar ratio of 2.0 may increase the cost of coating synthesis without improving on the protective properties achieved with coatings produced with a molar ratio of 1.0.

Carbon steel bars of 10 mm in diameter and 100 mm in height were used for the electrochemical tests. Their chemical composition (% by weight) was: 0.45C, 0.22 Si, 0.72 Mn, <0.010 P, 0.022 S, 0.13Cr, 0.13 Ni, 0.18Cu, and balance Fe. The carbon steel bars were dipped in the hybrid organic-inorganic solutions, withdrawn at a rate of 14 mm min^{-1}, and air-dried for approximately 10 min. This procedure was carried out twice, after which the coated steels were heated at 65 °C for 24 h and cured at 160 °C for 3 h.

2.2. Preparation of prismatic mortar specimens

A type I (42.5 R) commercial Portland cement and a Class F FA obtained from a steam power plant in Córdoba (Spain) were used as binding materials to produce the mortar slabs. The chemical composition and Blaine fineness of the materials (Spanish/European Standard UNE-EN 196-6) are shown in Table 1.

As alkaline activator a solution containing 85 wt.% 10 M NaOH and 15 wt.% sodium silicate was used. The reagents used to prepare this solution were laboratory grade sodium hydroxide (NaOH) pellets (Panreac) and sodium silicate or waterglass containing 27% SiO_2, 8.2% NaOH and 64.8% H_2O (Merk). The sand:OPC and sand:FA ratio used in the mortars was 3.0. A standardized, evenly graded siliceous sand was employed (99% SiO_2 content, with 65% particle size <1 mm and 35% <0.5 mm). In all mortar types the liquid:binder ratio was 0.6 in order to favour the carbonation process.