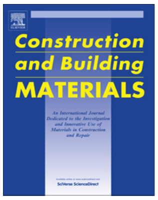
Construction and Building Materials 48 (2013) 734–744

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat



Long-term chloride-induced corrosion monitoring of reinforced concrete coated with commercial polymer-modified mortar and polymeric coatings

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HIGHLIGHTS

- Efficiency of concrete coating was tested on concrete samples under accelerated chloride penetration.
- Organic coatings delay initiation of corrosion since they reduce chloride penetration.
- The coatings greatly increase the chloride apparent diffusion coefficient.
- Coatings reduce concrete water absorption thus reducing rebar corrosion rate.

ARTICLE INFO

Article history:
Received 4 December 2012
Received in revised form 23 July 2013
Accepted 25 July 2013
Available online 24 August 2013

Keywords:
Coating
Concrete
Corrosion
Chloride
Diffusion

ABSTRACT

The efficiency of four commercial concrete coatings (a polymer modified cementitious mortar and three elastomeric coatings) against chloride-induced corrosion is discussed by means of steel corrosion long-term monitoring and by chlorides penetration profiles in concrete. The cement-based coating shows the best effect on delay chlorides penetration in concrete by acting as a physical barrier in addition to concrete cover. Despite its lower polymer content, the higher thickness guarantees a longer time-to-corrosion with respect to organic coatings. Once corrosion has started, corrosion rate is lower in the presence of coatings, due to their ability to reduce water ingress in concrete.

1. Introduction

On ordinary steel reinforcements embedded in alkaline concrete, a thin protective film (the so-called passive film) is thermodynamically stable and is formed spontaneously, as Pourbaix reported in his Atlas [1]. Corrosion of steel reinforcements represents the most widespread form of deterioration of concrete structures and its accurate knowledge is compulsory in order to predict the service life of reinforced concrete structures, which can be divided in two phases [2].

The first is corrosion initiation, during which steel is in passive condition and processes which can lead to steel depassivation (concrete carbonation or chloride penetration in the concrete cover) are taking place. In carbonation, carbon dioxide, diffusing into concrete, it neutralizes its alkalinity by the reaction with calcium hydroxide, so that the pH of the concrete pore solution decreases to a value lower than 9. In this condition, the passive film is not thermodynamically stable. Chloride ions penetrate into concrete in water solution causing a local breakdown of the passive film if their concentration at the metal surface reaches a critical threshold (in atmosphere between 0.4% and 1% by cement weight) [2]. The duration of this phase depends on concrete cover thickness and penetration rate of aggressive species.

The second phase is corrosion propagation, which starts after corrosion initiation and ends when a limit state is achieved, over which corrosion cannot be further accepted. Once the passive layer is destroyed, corrosion occurs only in the presence of water and oxygen on the metal surface.

Prevention of corrosion is firstly assured by casting an high quality concrete (i.e., proper concrete mixture proportion, W/C ratio and cover). If proper concrete cover cannot be assured, when a very long service life is required or in very severe environmental

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http://dx.doi.org/10.1016/j.conbuildmat.2013.07.099

exposure, the durability of the structure could be increased by adopting a specific preventative measure that modifies the characteristics of concrete, reinforcement, external environment or the structure itself. These techniques act by preventing aggressive species penetration in concrete or by controlling the corrosion process through inhibition of the anodic process or of the galvanic flow in the electrolyte. Nowadays, different preventative measures are claimed to prevent, or at least to reduce, steel corrosion in concrete [2]. In this wide context, concrete surface treatments and corrosion inhibitors [3] offer a possible way to improve concrete structures durability. By the way, the efficiency of organic substances as corrosion inhibitors and concrete coatings on chloride-induced corrosion was investigated during a research project started in 1997 and initially granted by an Italian company leader in the production of adhesives and chemical products for building. While the effectiveness of organic substances in preventing chloride-induced corrosion in synthetic alkaline pore solution and in concrete was recently discussed elsewhere [4,5], in this paper results about the effect of polymer-modified mortar and elastomeric coatings on time-to-corrosion and corrosion rate of reinforced concrete are reported.

Commonly, it is possible to distinguish four principal classes of surface treatments for concrete [2]: organic coatings that form a continuous film, hydrophobic treatments that line the surface of the pores, treatments that fill the capillary pores and cementitious layers. Their effect is twofold: to reduce the permeability of aggressive agents in concrete and to decrease the water content of concrete with the resulting decrease of concrete electrical conductivity and corrosion rate [6–13]. In this work, the effect of three organic coatings and a polymer modified cementitious mortar on chloride induced corrosion of reinforced concrete was investigated. Organic coatings are commonly used to block the penetration of carbon dioxide or chloride ions by forming a continuous polymeric film on concrete surface of thickness from 0.1 to 1 mm. They are based on various types of polymers (e.g. acrylate, polyurethane, and epoxy), pigments and additives and their effectiveness is related to the absence of pores or defects. Cementitious coatings form a layer of low permeability and thickness of a few millimetres, typically lower than 10 mm. The mortar is generally fine grained and modified with polymers to decrease its permeability and to increase its bond to concrete. European standardizations [14,15] report several methods to test coating characteristics, as for instance water absorption, water vapour, chlorides and carbon dioxide permeability, adhesion, crack-bridging and self-repairing properties, mainly to short-term tests. There is a lack of data about long-term behaviour of organic and cement-based coatings. This work reports almost seven years corrosion monitoring of reinforced concrete specimens coated with cementitious and organic coatings. Coating efficiency was investigated by means of corrosion potential and corrosion rate monitoring and by chlorides penetration profiles in concrete.

2. Materials and methods

2.1. Concrete coatings

Four commercial concrete coatings were tested:

- Coating A: two-components mortar based on cementitious binders, fine-grained selected aggregates, special additives and synthetic acrylic polymers dispersed in water with polymer-to-cement ratio 0.33.
- Coating B: hydro-dispersed fibrous coating, based on elastomeric acrylic emulsions cement-free.
- Coating C: cement-free and elastomeric acrylic-based fibrous coating mixed with graded sand.
- Coating D: single-component acrylic resin-based paint in water dispersion which forms a flexible film on the concrete surface due to the action of natural light.

Polymeric coatings were applied on concrete after a previous surface treatment with a specific primer which aims to improve coating-to-concrete bonding. While the thickness of organic coatings (Coating B, C and D) is in the range between 0.2 and 1 mm, the mortar (Coating A) has a thickness between 1 and 3 mm.

The tested coatings were commercial products available on the market on 2005; technical data are in conformity with the requirements of international standard tests.

2.2. Concrete mix design

Concrete coatings (Section 2.1) were tested on laboratory concrete specimens prepared with a Portland-limestone cement, type CEM II A/L 42.5R that, according to EN 197-1 [16], indicates a cement containing from 6% to 20% by mass of limestone and with a minimum compressive strength of 20 and 42.5 MPa after 2 and 28 days, respectively. Concrete specimens were prepared with two water-to-cement ratios (W/C), 0.55 and 0.65, in order to study coating efficiency in concretes with different porosity. Limestone aggregates were used with maximum diameter 16 mm. An acrylic plasticizer was mixed to fresh concrete in order to guarantee S5 workability, according to EN 206-1 [17] (slump $\geqslant$220 mm). Concrete mix design is reported in Table 1.

Two prismatic reinforced concrete specimens (Sample A and B, 340 × 250 × 50 mm, Fig. 1) were prepared for each experimental condition. Five carbon steel reinforcements (diameter 10 mm and length 290 mm) with chemical composition and mechanical properties according to EN 10080 [18] were placed in each concrete specimen; the ends (40 mm) of each steel bar were coated with heat shrinkage sleeve, so that only a length of 210 mm was exposed to concrete. Concrete cover was 20 mm. A Ti-MMO reference electrode and two stainless steel wires (diameter 2 mm) were placed next to each rebar for corrosion rate measurements. Specimens were cured for 28 days at 20 °C and 95% relative humidity, before the application of the coating on the top surface. The organic coatings (A, B and C) were applied only on concrete specimens prepared with the highest water-to-cement ratio (0.65). Plain concrete cubic samples (side 150 mm) were also prepared in order to allow concrete cores extraction for chloride concentration profiles determination. Concrete mix design and exposure condition are the same of reinforced specimens.

2.3. Exposure condition

Both plain cubic samples and reinforced specimens were exposed to accelerated chlorides penetration wet–dry cycles, i.e. ponding cycles. A ponding cycle consist of one week wetting with a 5% sodium chloride solution (almost 30,000 mg/L chloride ions), and two weeks drying. The test solution was placed in contact with the upper surface of the specimen by putting the solution in a plastic box fixed on the top of the specimen.

According to EN 206-1 [17], cyclic ponding to chloride solution can be classified as XS3 and XD3 exposure classes, which refer to corrosion induced by chlorides from seawater and other than from seawater, respectively.

It should be pointed out that W/C ratio and concrete cover thickness (Section 2.2) were not adopted in agreement with standards requirements recommendations [17,19], in order to reduce chlorides penetration time into concrete, compatibly with the laboratory research time schedule.

2.4. Corrosion monitoring

Almost seven years long tests were performed. Steel reinforcements corrosion was monitored by open circuit potential (in the following called corrosion potential, E_{CORR}) measurement with respect to a saturated calomel reference electrode (SCE, +0.244 V SHE) placed on the upper surface of the concrete specimen by means of a wet sponge, and by linear polarization resistance (LPR) measurement, which is considered an accurate and rapid way to determine the instantaneous corrosion rate of steel reinforcements [20]. In LPR technique a small potential scan defined with respect to corrosion potential ($\Delta E = E - E_{CORR}$) is applied to the metal and the polarization current (which varies approximately linearly with potential within a few millivolts from E_{CORR}) is recorded. Corrosion current density (i_{CORR}, mA/m^2) is related to the specific LPR (Ω m^2) by Stern–Geary equation [21]:

$$i_{CORR} = B/\mathrm{LRP} \qquad (1)$$

where B is the Stern–Geary coefficient (related to anodic and cathodic Tafel slopes) which assumes approximately a value of 26 mV or 52 mV for steel in active or passive condition, respectively [2,21]. LPR measurement was carried out by means of an

Table 1
Concrete mix design.

		W/C = 0.55	W/C = 0.65
CEM II A/L 42.5 R	kg/m^3	320	310
Water	L/m^3	180	200
Limestone aggregates	kg/m^3	1876	1812
Plasticizer	% by cement weight	0.64%	0.14%