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A comparative study of mild steel passivation embedded in Belite-Ye'elimite-Ferrite and Porland cement mortars

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ABSTRACT

An extensive experimental program was designed to investigate the passivation of reinforced low carbon-release Belite-Ye'elimite-Ferrite (BYF) cement mortars compared to the passivation of reinforced conventional Portland equivalents (OPC). The influence of formulation parameters such as the water-to-cement ratio and the presence of fly ash on the steel rebar passivation was evaluated by conventional corrosion measurements such as corrosion potential readings and linear polarization resistance. Visual observations were carried out as a complement. A negligible corrosion rate was reached after 28 days with BYF cement against 14 days with OPC equivalent. This difference is attributed to the pH of the medium in the BYF mortars, which is lower than in the OPC mortars at a very early age, before becoming strongly basic. The exploitation of the Tafel slopes showed that the corrosion current can be evaluated by the Stern and Geary equation with an identical B coefficient for the samples of BYF and OPC basis. Despite some differences compared to the passivation in Portland mortars, the present study clearly points to the BYF mortars intrinsically passivating nature regarding mild steel reinforcing bars.

1. Introduction

Belite-Ye'elimite-Ferrite cements, referred to as BYF, are a promising lower carbon-release alternative to ordinary Portland cements (OPC) [1–4]. The base component is a clinker composed of ye'elimite ($Ca_4Al_6O_{12}(SO_4)$), belite (Ca_2SiO_4), and calcium aluminoferrite solid solution ($Ca_2(Al,Fe)_2O_5$), stated here in decreasing order of content [2]. The clinker production of BYF requires less limestone in the raw materials, a lower clinkering temperature, and less energy to be ground compared to Portland clinker manufacturing [4,5]. Industrial feasibility was checked and in-situ measurements confirmed overall CO_2 savings between 25% and 30% [6]. The partial substitution of BYF cement by supplementary cementitious materials (SCMs) brings an additional reduction of the amount of CO_2 through the clinker substitution and by the valorization of waste by-products such as fly ash. Moreover, the addition of fly ash to cement may improve the engineering properties of fresh (e.g. workability) and hardened concretes (e.g. mechanical and barrier resistances) [7,8]. However, if BYF is to replace OPC binders in a wide range of concrete applications, it must likewise be able to passivate ordinary black steel reinforcements. Once embedded in OPC-based concrete, the steel is spontaneously passivated. The transposition to BYF-based concretes is questionable.

The available literature on the investigation of the corrosion behaviour of steel embedded in sulfoaluminate cement matrices (to which BYF family belongs) are scarce and not conclusive [9–11]. Based on visual inspection of the steel reinforcement embedded in calcium sulfoaluminate (CSA) mortars after 14 years of service, Glasser and Zhang [9] concluded that steel remains passivated within the matrix. However, Kalogridis et al. [10] reported that the lower pH values and the higher average pore diameters of BYF matrix, compared to Portland one, expose the steel rebar to a higher corrosion risk, as suggested by corrosion potential readings and weight loss measurements. Janotka et al. [11] have performed potentiodynamic polarization measurements using steel bars as working electrodes immersed in sulfoaluminate-belite mortar extracts (pH~10.5). In line with Kalogridis et al. [10] results, it was observed that the steel did not exhibit passivation plateau upon

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anodic polarization. The available data are insufficient to an unambiguous conclusion to be drawn upon this issue and an extensive electrochemical survey is lacking to ascertain whether mild steel spontaneously passivates or not when embedded in BYF matrices in normal service conditions.

For a new family of binder arises also the question of the method of evaluation of the steel corrosion. The suitability of the standards (e.g. ASTM C876 [12]) and recommendations (e.g. RILEM TC 154-EMC [13]) to the study the corrosion behaviour of reinforced BYF structures should be experimentally verified since most of them have been established for reinforced Portland structures. For instance, the American Standard ASTM C 876-09 provides a criterion to correlate the risk of corrosion and the potential reading values. However, this criterion was empirically derived from chloride-induced corrosion of mild steel embedded in bridges decks in the USA for specific conditions of Portland concrete type, layer, and exposition [14–16]. The RILEM TC 154-EMC [13], in turn, provides recommendations to evaluate the corrosion rate of steel reinforcement in concrete by means of the linear polarization resistance method (LPR). In this case, an issue of major concern is that the conversion of polarization resistance values, R, into corrosion current densities, i_{corr}, requires the previous knowledge of the coefficient B of the Stern-Geary relationship ($i_{corr} = B/R$), which is related to the Tafel slopes β_a and β_c [17]. For Portland-based reinforced structures, B values of 26 and 52 mV for steel in the active and passive state, respectively, have been recommended [13], but no reliable information about the B values for reinforced BYF structures is available.

In this paper, the intrinsic ability of the BYF mortar to effectively induce mild steel reinforcement passivation was investigated. The study was conducted at different hydration conditions (water-to-cement ratio, w/c, of 0.40, 0.50 and 0.67) and in the presence or not of fly ash (FA), in normal curing and service conditions, that is, in the absence of chloride or carbonation using OPC equivalents as reference. Different electrochemical techniques such as corrosion potential measurements, LPR, and potentiodynamic polarization curves were used to evaluate the corrosion risk and the corrosion rate. Coupling different electrochemical techniques provided a better understanding of the differences and similarities between the passivation of the steel reinforcement embedded in BYF and OPC mortars. Also, the suitability of the current recommendations and standards to assess the corrosion risk and corrosion rate of the steel embedded in BYF mortars was discussed.

A last important introductory remark is that, while in the present study we focused on the inherent passivating properties of BYF matrix compared to OPC one, it is, of course, necessary to extend this study to include the presence of aggressive agents such as chloride ions and their impact on the BYF matrix performance in terms of reinforcement corrosion. This is an issue of major concern and will be a matter of another specific paper.

2. Experimental

2.1. Materials

2.1.1. Steel reinforcement

Thermo-mechanically-treated (TMT) steel ribbed rebars measuring 14 mm in nominal diameter and 130 mm long were used as mortar reinforcement, Fig. 1. The chemical composition of the mild steel used in this study is detailed in Table 1. The values are the average of four analyses, three at the edge and one at the centre of cross-section samples, which gave the same chemical composition considering the precision of the equipment.

Fig. 2a and b show the microstructure of the steel reinforcement, which is composed of a ductile and tough ferrite (brighter phase) and pearlite (darker compound) matrix with a high resistant surface rim of tempered martensite. This resulting composite microstructure is characteristic of the thermomechanical processing in which hot steel bars coming out of last rolling mill stands are quenched through a series of water jets. During such slow cooling, the heat released from the core tempers the hardened surface while the core itself turns into ferrite-pearlite aggregates, providing an optimum combination of high strength, ductility, and bendability.

2.1.2. Cements

An ordinary Portland cement (OPC), designation CEM I 52.5 CE

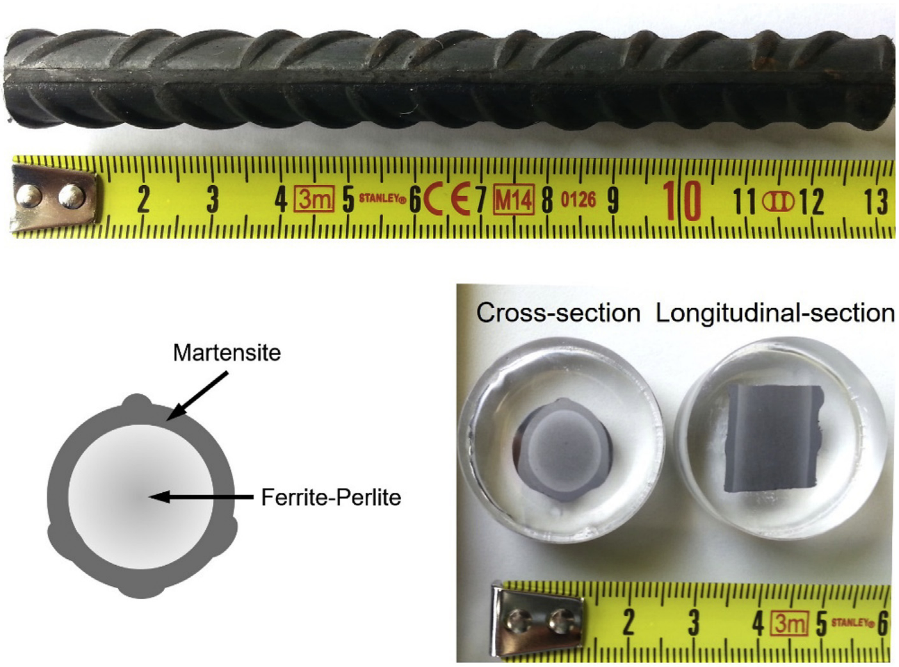

Fig. 1. Steel ribbed rebar used to reinforce mortar samples. Ruler in cm.