On the intrinsic passivating ability of Belite-Ye'elimite-Ferrite towards carbon steel: a straightforward comparison with ordinary Portland cement

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Abstract

The quest for low-CO₂ emission alternatives to Portland cement is pushing the cement industry to develop new types of binders. Besides the need of equivalent mechanical properties, a major issue concerns the passivating ability of these new materials. Belite-Ye'elimite-Ferrite binders (BYF) are attracting increasing interest of cement developers, but there are still doubts about their intrinsic protectiveness. Carbon steel passivation in BYF leachates was studied and compared to OPC leachates through electrochemical techniques and X-ray photoelectron spectroscopy. In both media, steel was highly passivated in less than 24 hours, protected by a ca 5 nm thickness film.

Keywords: Steel; Passivity; Sulfoaluminate cement; Portland cement; EIS; XPS.

1. Introduction

Belite-Ye'elimite-Ferrite (BYF) cement family has been proposed as a lower-carbon alternative to the highly polluting ordinary Portland cement (OPC) [1]. Large fraction of the cement production is used to make concrete, which requires reinforcements in applications such as bridges, tunnels, sewer systems, dams, etc. To date, reinforced concrete based on OPC cement are the most used structural material in buildings and infrastructures worldwide. If BYF cements are intended for wide reinforced concrete use while remaining economically competitive, it is mandatory for BYF pore solutions to induce spontaneous passivation of inexpensive carbon steel rebars as the OPC pore solution does.

Pore solution chemistry of cementitious matrices is crucial for the understanding of the corrosion phenomena of steel in concrete. This solution is in equilibrium with the solid phases resulting from the cement hydration process, therefore, its composition is strongly dependent on the cement type. Studies have shown that the composition of the concrete pore solution affects the time to passivation [2], how passive film is formed [3], and its protectiveness against corrosion [4,5]. This means that realistic results for the behavior of steel in concrete are straightforwardly dependent on the testing solution to be effectively representative of the concrete pore solution.

To date, few results have been reported with respect to carbon steel passivation in electrolytes representative of BYF pore solution. Electrochemical studies on reinforcing steel bars in aqueous media have been traditionally conducted in synthetic electrolytes saturated with calcium hydroxide, $\text{Ca}(\text{OH})_2$ [6–11], with addition of ions such as Na^+ , K^+ , $(\text{SO}_4)^{2-}$, Al^{3+} , Si^{2+} , and Fe^{2+} that, in a lower or higher level, contribute to the complex interactions between the metallic surface and the cement's liquid phase. However, BYF systems are not saturated with calcium hydroxide but with ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ [12], which makes the

current approach of using saturated calcium hydroxide solutions no longer representative. In addition, there is no synthetic model solution for hydrated BYF cement matrices.

Because BYF cements have a different composition than OPC ones and due to the novelty of the BYF binders [13], a consistent literature on the passivation of carbon steel in BYF pore solution is still missing. It is, however, worth citing the Janotka's et al. work [14], which indicated that, due to their low pH, carbon steel should not passivate in BYF cement extracts. Similarly, Kalogridis et al. [15], using reinforced mortars, concluded that the low pH and the higher average pores of BYF matrix compared to OPC equivalent exposed the reinforcing steel to a higher corrosion risk. Those results are in line with the Koga's et al. work [16], which proposed that, unlikely to the OPC matrices pore solution that is highly passivating since the first minutes, the pore solution of BYF matrices should be less protective and could even be corrosive at early-age of hydration. However, as the hydration progresses, the pore solution of BYF matrices could become as protective as the OPC pore solution but the passivation in these conditions has not been thoroughly evaluated.

The objective of this study was to evaluate the passivation of carbon steel in BYF compared to OPC mature solutions, i.e., obtained from cement pastes cured for 28 days, a curing period generally used to characterize the concrete characteristics and properties. It is worth noticing that, to unambiguously assess the intrinsic passivating ability of BYF binders, this study has been carried out in the absence of aggressive agents as chlorides or carbon dioxide. Indeed, as mentioned before, there is a lack of knowledge about the interaction between BYF pore solutions and carbon steel so that their inherent protectiveness is still matter of doubt. This paper aimed to go deeper into this issue by evaluating the intrinsic passivating ability of BYF binders – once the effective protectiveness of BYF is unambiguously established, the effect of aggressive agents will be matter of a specific separate paper. Electrochemical measurements such as open-circuit potential (OCP) surveys,

linear polarization resistance (LPR), and electrochemical impedance spectroscopy (EIS) were performed over 7 days to track the corrosion/passivation behavior of carbon steel. X-ray photoelectron spectroscopy (XPS) was performed as a complement, focusing on the characterization of the passive films at their first stages of formation, which were assimilated to corrosion current density values dropping to values below $0.1 \mu\text{A}.\text{cm}^{-2}$. Results were discussed in terms of the straightforward comparison between the protectiveness of 28-day cured OPC and BYF matrices leachate regarding steel passivation.

2. Materials and Methods

2.1. Tested solutions

Realistic concrete pore solution can, in principle, be obtained by pressing bulk specimens of concrete, mortar or cement paste against a steel die (steel die method [17]), resulting in small volume of aqueous phase for aged samples. However, electrochemical and surface analyses often require significant amount of electrolyte (hundreds of millimeters) so the use of the steel die method is not practical, especially for BYF matrices because of the high-water consumption during the hydration of ye'elimite, $\text{Ca}_4\text{Al}_6\text{O}_{12}(\text{SO}_4)$. To replicate the complexity of the electrolyte occurring in concrete, ex-situ leaching (ESL) procedure was used to obtain aqueous solutions from OPC and BYF cement pastes. Even if some dilution effect may occur during the ESL procedure, the resulting electrolytes (the leachates) are a reasonable approximation of the actual BYF pore solution inasmuch as no synthetic pore solution for this system has been proposed.

For the ESL procedure, the different pastes produced with a water to cement ratio (w/c) of 0.5 cured for 28 days were coarsely crushed ($< 5 \text{ mm}$), placed in HDPE bottles, and mixed with distilled water in a 1:1 mass ratio. The mineralogy and the density of the BYF and OPC cements are detailed in **Table 1**, and the phase assemblage of the OPC and BYF cement paste at 28 days shown in **Figure 1**. Leaching was sustained during 24 h under agitation, and 18 h

of rest for decantation, being the solution double filtered to remove particulates using a < 45 μm Millipore membrane filter and a mechanical vacuum pumping system. The pH of the pore solutions was measured with a PH2010 STANDARD pHmeter MaterLab® from Radiometer Analytical and the chemical composition identified by ICP-AES by using a Varian 720-ES ICP Optical Emission Spectrometer. **Table 2** shows the composition of the electrolytes.

2.2. Electrochemical measurements

Mild steel ribbed rebars, 0.21 wt.%C, were used to produce the working electrode (WE). The ribs of the reinforcement were removed by using a lathe and a copper wire coated with insulating polymer was attached to a $\varnothing$ 1.13 cm WE disc (area ≈ 1 cm²). Electrical contact between the copper wire and WE was assured by silver paint. Cross-sections were mounted in cold-curing resin (Araldite® 2020 epoxy) previously degassed under mechanic vacuum to avoid air bubbles at the steel/resin interface. The mounted WE was sequentially ground by SiC papers in decreasing grid size from 240 to 1200 using anhydrous ethanol (ethanol absolute AnalaR NORMAPUR) to reduce heating and oxidation. The initial heterogeneous microstructure of the as-received ribbed steel rebar and the resulting homogeneous ferrite and pearlite microstructure of WE after lathing are presented in **Fig. 2**.

After polishing, the samples were dried with a delicate task wipe, immediately immersed in the electrolyte, and the electrochemical measurements launched. A lid-protected 250-mL electrochemical cell was used to perform open-circuit potential readings (E_{ocp}), linear polarization resistance tests (LPR), and electrochemical impedance spectroscopy measurements (EIS). The counter-electrode was a platinum grid and a mercury/mercury oxide electrode filled with NaOH 1 M solution (XR400, Radiometer Analytical) was used as reference instead of saturated calomel electrode (SCE). This choice was taken to avoid chloride contamination from reference electrode into the solution, which could impair the

passivation. Electrochemical measurements were performed periodically at open-circuit conditions for 7 days. Potential value readings, LPR ($E = \pm 10 \text{ mV vs. } E_{ocp}$; scan rate of $10 \text{ mV} \cdot \text{min}^{-1}$), and EIS ($\Delta E = 10 \text{ mV}_{\text{rms}}$ sine wave signals vs. E_{ocp} ; 10^4 Hz to 10^{-2} Hz , 13 points per decade) were carried out by using a BioLogic potentiostat SP-300. EC-Lab software was used to treat the experimental electrochemical data. All measurements were carried out at $20 \pm 1 \text{ }^\circ\text{C}$ without stirring, conditions commonly observed for steel embedded in concrete. A small hole on the lid of the electrochemical cell ensured the oxygen renewal. Both the pH and the total volume of the electrolyte prior and at the end of 7-day testing period were measured for all the experiments. Results did not show any significant difference through the test duration indicating that both evaporation and carbonation were negligible. Each test was repeated once to ensure reproducibility of the results. After the electrochemical measurements, the interface between the resin and the WE was inspected using an optical microscope and no signs of crevice corrosion was detected.

2.3. X-ray photoelectron spectroscopy (XPS)

Cross-section discs measuring $\varnothing 10 \text{ mm} \times 5 \text{ mm}$ extracted from steel rebars were used in XPS analyses. The face of the substrates were polished from #240 up to #1200 SiC under anhydrous ethanol to reduce heating and air oxidation. After polishing, the samples were put in a beaker with a large volume of anhydrous ethanol for 5 min under ultrasonic agitation, dried with a delicate task wipe, and then immediately immersed in the appropriate leached aqueous solution in sealed containers to avoid carbonation and evaporation. Here again, the pH and the total volume of the electrolyte into the container prior and at the end of 1 and 2 days of the carbon steel immersion did not show any significant evolution, indicating that negligible evaporation and carbonation occurred. Specimens were taken out after 1 and 2 days of immersion, rinsed with anhydrous ethanol and dried with an inert gas. This protocol was used to wash out the elements, which do not compose the passive layer. The samples were

then transferred directly to the fore-chamber of an XPS spectrometer and purged with argon gas before being transferred to the analytical chamber for examination.

A Vacuum Generator XR3E2 apparatus with a Mg-K α X-ray source (characteristic energy $h\nu = 1273.6$ V) at 15 kV and 20 mA operating conditions was used to perform the XPS measurement. In this case, a hemispherical condenser Alpha 110 of Thermo Scientific was used as electron analyzer, being the pressure in the analytical chamber less than 10^{-10} mbar and the analyzed area about 4 mm².

A constant pass of 40 eV, 0.5 eV of resolution, was used to record the survey spectra in a binding energy range from 0 to 1100 eV. Specific spectra were obtained with 0.1 eV of resolution for Fe_{2p} and C_{1s} orbitals with acquisition angles of 30° and 90°. All results were calibrated with respect to the position of the C_{1s} peak, set as 285.0 eV.

Curve fitting of Fe_{2p} spectra was performed to quantify and to decompose the contribution of each compound under interest. In this case, the criteria to select Fe-compounds were based on the binding energies of Fe-based compounds reported in the literature [18–21], and considering what have been reported for mild steel passivation in alkaline solutions [22–24]. Also, because the ambiguity related to the identification of adjacent peaks with energy difference inferior to 1 eV, only the peaks reported in **Table 3** were considered for fitting using Shirley baseline where mild steel substrate was assimilated to metallic iron (Fe⁰) and the passive film composed of both lower (Fe₃O₄, FeO) and higher oxidation-rich (Fe₂O₃, FeOOH) compounds.

3. Results and Discussion

3.1. Open circuit potential and LPR results

Fig. 3 shows the open-circuit potential (E_{ocp}) evolution of steel immersed in naturally aerated OPC and BYF solutions. All the recorded potential values are presented *versus* the

commonly used saturated calomel electrode reference (SCE) instead of the mercury/mercury oxide in 1 M NaOH electrode. The change in E_{ocp} was consistent in repeated tests.

For both OPC and BYF electrolytes, the E_{ocp} tends towards more noble values with the progress of the immersion time. The initial steep increase of the steel potential indicates oxide film formation and thickening following an asymptotical-like tendency to the steady-state value after about 2 to 3 days in BYF electrolyte and 5 to 6 days in OPC electrolyte. These two stages of the potential evolution with an exponential decay function are often verified for steel passivation in alkaline solutions [25,26], and the recorded values of potential are consistent with other works performed on carbon steel in alkaline solution where the typical potential values are ranged between -200 and -300 mV_{SCE} [27,28].

Although the curves exhibit similar trends, the steel immersed in OPC solution shows potential values shifted to more negative values compared with those for steel in BYF medium. This difference can be ascribed to the OPC and BYF chemical compositions (**Table 2**). The effect of the calcium hydroxide, sulfate, and hydroxyl concentrations on the E_{ocp} evolution of steel immersed in synthetic pore solutions during the first hours has been studied by Haleem et al. [29,30]. It has been shown that higher calcium hydroxide, sulfate, and hydroxyl concentrations induce lower E_{ocp} values as it was the case in the present study. Moreover, the corrosion potential corresponds to the intersection of the cathodic curve for the reduction of oxygen and the anodic curve for iron oxidation [31]. Higher oxygen availability tends to intersect the anodic curve at higher potential values while a decrease of oxygen availability results in lower potential values. In this sense, it is worth noticing that there is a correlation between the oxygen solubility and the ionic strength (I_s), where the oxygen solubility in high ionic strength solutions is lower [32,33]. OPC solution presents a higher I_s than the BYF solution (0.122 mol/L against 0.072 mol/L, respectively), therefore, the lower

oxygen availability of OPC solution may explain why the potential evolution of the steel immersed on it is lower than the evolution of steel in BYF solution.

The evolution of the polarization resistance, R_p , and of the calculated corrosion current density, i_{corr} , of the steel immersed in OPC and BYF solutions are shown in **Fig. 4a** and **b**, respectively. i_{corr} values have been determined using the Stern-Geary equation, $i_{corr} = B/R_p$, with $B = 52$ mV. This value, previously proposed in the literature for OPC cement matrices [34], has been held in the present paper after an intensive study confirmed its suitability also for BYF systems [16].

The first measurement was performed after 5 h of immersion. At this time, the R_p values of the steel in both OPC and BYF electrolytes were about 200 k Ω .cm², resulting in low but non-negligible i_{corr} values. R_p values continuously increased during the first days and the i_{corr} exhibited negligible values (< 0.1 μ A.cm⁻²) in less than 24 h, suggesting spontaneous and rapid steel passivation. For steel immersed in the BYF solution, there was a rapid increase of the R_p values during the first 24 h, then a slower increase. With the OPC solution, the increase of R_p was more gradual over the first 5 days of immersion. After stabilization, the R_p values were finally similar regardless of the electrolyte (between 1200 and 1350 k Ω .cm²).

The high alkalinity of the concrete pore solution is an essential prerequisite to ensure passivation of steel rebars as predicted by Pourbaix diagram, being the protectiveness of the passive film affected by the pH [35]. Above pH = 10.5, an increase in alkalinity decreases the corrosion rate because iron becomes increasingly passive in presence of dissolved oxygen [36,37]. The OPC solution has higher pH than that of BYF solution (13.2 against 12.9, **Table 2**). From the pH values, the OPC solution should be more passivating and the carbon steel immersed on it was expected to present a higher increase of R_p over time than the carbon steel passivation in BYF solution. However, an opposite behavior was observed. Besides the pH,

different studies demonstrated the impact of the pore solution chemistry on the electrochemical responses of steel in alkaline media[2–5]. Mancio et al. [38,39] evaluated the passive film formation on carbon steel in alkaline solution with different alkalinity and I_s . As expected, for a fixed I_s , a decrease of the pH yields to a decrease of the R_p . However, the study also found that the effect of pH on the passivation is dependent on the I_s : a decrease of the pH in a range of 13 to 11 with a decrease of the I_s between 10^{-1} to 10^{-5} mol/L may result in the increase of the R_p values. Thus, the fact that BYF solution has lower pH and I_s values than OPC solution may explain why the carbon steel immersed in BYF solution passivates faster than the carbon steel immersed in OPC solution. Moreover, since electrolytes with lower I_s exhibit superior oxygen solubility [32,33], the higher oxygen availability in the BYF solution is an important advantage for the passive film nucleation and thickening compared to the passivation in OPC solution.

3.2. EIS measurements

Fig. 5 shows the evolution of the Nyquist plots and the Bode diagrams with immersion time in BYF and OPC solutions; replicate specimens show similar results and they were not plotted for a better visualization of the diagrams.

Similar trends are observed regardless of the media, i.e., the extrapolated diameter of the capacitive loop increases continuously (a continuous increase of $|Z|$) suggesting that the immersion time enhances the corrosion resistance. This is consistent with the OCP and LPR measurements that show a progressive increase of E_{ocp} and R_p over time. A deeper analysis of the EIS spectra is performed with the help of electrochemical equivalent circuits (EEC).

Engelhardt et al. [40] have shown that, in case of passive iron, the simplest equivalent circuit, i.e., a parallel arrangement of a resistance and a capacitor (or a constant phase element, CPE), adequately describes the EIS behavior of passivated metals. Consequently, the

properties of the overall interface can be represented by this simple parallel arrangement in series with a pure resistor, the modified Randle's circuit, **Fig. 6**, where R_e is the electrolyte resistance, R_p is the polarization resistance, and Q is the non-ideal overall CPE, which reflects the capacitance-like response from the whole interface (passive film, double-layer relaxation, faradaic reactions, etc). As this single Q element represents the overall apparent non-ideal capacitive behavior, the characteristic values of Q related to the passive film only cannot be obtained separately. It is worth noticing that a hierarchically-arranged two-time constant EEC has also been evaluated for the fitting of the experimental results. However, the obtained parameters and the quality of the fitting itself — represented by the ratio $\chi^2 / |Z|$, see below — were poorer than for the modified Randle's one that was then held for the EIS analysis.

A deeper insight of the CPE behavior comes from the plot of the imaginary part of the electrochemical impedance with frequency, as displayed in **Fig. 7a** and **b** [41,42]. The wide frequency range of linear decay seems actually to be related to a single CPE behavior, in other words, a single-time constant. This is confirmed by the analysis of effective α (α_{eff}), which is an alternative representation of CPE behavior to highlight the presence of relaxations processes for a given frequency range [43] and is calculated according to **Eq. 1**:

$$\alpha_{eff}(f) = \left| \frac{d \log |Z_i(f)|}{d \log f} \right| \quad (\text{Eq. 1})$$

Fig. 7c and **d** clearly show the presence of a single time constant (α_{eff} constant value for approximately 3 decades) related to a constant phase element, Q , which appears since the first day and is present up to 7 days of steel immersion in OPC and BYF solutions. The slopes at low frequencies are similar regardless of the media (OPC and BYF) and constant with the immersion time. Values of α of about 0.92 for all cases indicate a clear capacitive-like behavior throughout the EIS survey.

The proposed model in **Fig. 6** seems to be able to afford a coherent interpretation of the EIS results and was thus held for the fitting of the EIS data in **Fig. 5**. Results are listed in **Table 4**. Normalized chi-square of the data fitting ($\chi^2 / |Z|$), which represents the convergence level of the fitted results with the experimental data, was calculated by the software BioLogic EC-Lab V11.01. $\chi^2 / |Z|$ values inferior to 10^{-3} were found during EIS data treatment, indicating satisfactory fitting level.

In the different tests performed in OPC and BYF electrolytes, the R_e did not evolve considerably and its values were negligible compared to the R_p ones due to the high conductivity of ions between the reference and working electrodes. R_p values, in turn, increased rapidly as immersion time elapsed, demonstrating that a protective layer forms and grows since the first moments thanks to the intrinsic passivating nature of both OPC and BYF solutions from cement paste cured for 28 days. As early as 3 days of immersion, R_p reached values around $10^6 \text{ k}\Omega\cdot\text{cm}^2$, which means corrosion rates well below $0.1 \mu\text{A}\cdot\text{cm}^{-2}$. Simultaneously, the Q values decreased and approached the steady-state value of $41 \mu\Omega\cdot\text{cm}^{-2}\text{s}^{-0.94}$ for steel in OPC and $41 \mu\Omega\cdot\text{cm}^{-2}\text{s}^{-0.95}$ for steel in BYF.

Using the constant phase element values (Q and α), R_e , and R_p , the effective capacitance (C_{eff}) can be calculated according to the following equation [44]:

$$C_{eff} = \left[\frac{Q}{(R_e^{-1} + R_p^{-1})^{\{\alpha-1\}}} \right]^{\frac{1}{\alpha}} \quad (\text{Eq. 2})$$

The effective capacitances calculated from the values listed in **Table 4** are ranged from 31 to $25 \mu\text{F}\cdot\text{cm}^{-2}$ for steel in OPC solution and from 45 to $28 \mu\text{F}\cdot\text{cm}^{-2}$ for steel in BYF solution. Assuming that these overall apparent capacitance values include the contribution of the passive layer space-charge capacitance (C_{ox}) and the double-layer capacitance (C_{dl}) in a

series arrangement, if the capacitance of the passive film is small compared to the double-layer capacitance, as expected, the overall capacitances obtained from EIS data are dominated by the response of the passive film [45]. In this case, the passive film thickness can be calculated from **Eq. 3**, which is valid for the parallel-plate capacitor model of a homogeneous oxide layer, assimilating the overall effective capacitance to the capacitance of the protective oxide layer (C_{ox}):

$$d_{ox} = \frac{\varepsilon_0 \varepsilon_r}{C_{ox}} \quad (\text{Eq. 3})$$

where ε_0 is the vacuum permittivity ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m) and ε_r is the relative dielectric constant (taken as $\varepsilon_r = 12$, the dielectric constant of Fe_2O_3 [46]). The calculated thickness of steel immersed in OPC solution ranges from 3.4 to 4.2 Å and from 2.4 to 3.8 Å for steel passivated in BYF solution. Even if these values are qualitatively consistent (thickening of the film with time), they are up to one order of magnitude inferior to the values of the passive layer reported in the literature obtained by *in-situ* techniques [22–24].

This discrepancy can be related to the fact that the double-layer capacitance may not be negligible, or that the dielectric constant of the actual passivating film composed of iron oxyhydroxides and oxides is not well established. Besides the capacitive contribution of the passive film, studies reported the formation of particles on the steel surface due to the local heterogeneous nucleation and growth of minerals (e.g. $\text{Ca}(\text{OH})_2$ and other Ca-rich compounds) [22,23], which may contribute to the overall capacitive response of the system. In addition, the air exposure of the steel surface during the electrochemical cell assemblage may introduce a thin carbon layer on the steel surface.

Calculation of the thickness of the passive layer by **Eq. 3** from the EIS data is an indirect method and, therefore, susceptible to the accumulation of the errors mentioned before. It is worth noticing, however, that the evolution of the polarization resistance and the capacitive

response of the samples during immersion gave a comparative view of steel immersed in OPC and BYF solutions. Indeed, despite a mostly qualitative analysis of EIS, due to the system response collapsed to a single apparent time constant and to the restrictions to a more quantitative analysis of the film thickness, it was possible to unambiguously demonstrate that, unlikely to previous studies, BYF, as well as OPC cement-based matrices, do have an intrinsic passivating ability regarding mild steel.

A final remark concerns the fact that these results illustrate the difficulty of extracting reliable parameters from the fitting of EIS through EEC. This is a widely used procedure that must be carried out very carefully. EEC must be seen as what they actually are: a simple data-handling tool with which we try to make the interface's response to a perturbation signal match the expected behavior of elements of a linear electrical circuit and not a straightforward physical description of the interface.

3.3. XPS: characterization of the passive films

The previous electrochemical results pointed out that the protectiveness of the passive layer formed on the steel immersed in OPC and BYF pore solutions is similar. However, the electrochemical techniques did not provide detailed information about the compositional characteristics of the passive film. Furthermore, as discussed before, the calculation of the thickness of the passive film from the EIS data is potentially unreliable. Considering these difficulties, XPS was conducted on the different samples as soon as the electrochemical results started to indicate negligible corrosion rates, i.e., after 1 and 2 days of immersion.

The general survey spectra of the steel immersed in OPC and BYF solutions, **Fig. 8**, indicate the presence of C, Ca, Fe, and O. Other elements present in the pore solution such as Na, K, Al, S, and Si are not expected to be present in passive layer and were washed out prior to XPS during the rinsing step. The expressive C peak is related to both the adsorbed ethanol

and its evaporation residue remaining on the specimen surface upon drying. Calcium compounds are associated to precipitated mineral scales, which are a common occurrence in steel passivation studies in concrete pore solutions [23]. Consistently, as seen in **Fig. 8**, these Ca-rich compounds are not present in steel exposed to air. Iron oxides/oxyhydroxides, hydrocarbons, and calcium-based mineral scales accounts to the oxygen signal. Iron peaks are attributed to the steel substrate and to the iron oxides and iron oxyhydroxides products, which are the scope of this study.

Specific Fe spectra at 90° and 30° for steel immersed for 1 and 2 days in OPC and BYF extracts are shown in **Fig. 9** and **10**, respectively. The large broad peak of the Fe $2p_{3/2}$ is ascribed to iron oxides and oxyhydroxides while the much smaller peak allocated at lower binding energies is associated to metallic iron. The presence of the metallic iron peak in all samples regardless of the media and immersion time indicates that the layer thickness on the steel substrate is inferior to 10 nm, the maximum escape depth of photoelectrons. However, for the steel specimen exposed to air, **Fig. 9a** and **b**, it is clearly seen a higher intensity of the iron metallic peak Fe-1 indicating thinner layer formation on the air-exposed steel substrate compared to those formed on steel immersed in OPC and BYF solutions.

Steel immersed in OPC and BYF solutions exhibit similar spectra at 90° and 30° after 1 day, **Fig. 9**, and 2 days, **Fig. 10**, of immersion. This suggests that the chemical composition and the amount of iron compounds, therefore the average thickness of the iron oxide layer, of the passive film on the steel substrate immersed in OPC and BYF solutions are similar.

The relative fraction of each iron oxide and oxyhydroxide compounds can be calculated from the ratio between each individual area and the sum of the areas of the iron oxide and oxyhydroxide compounds. Different iron compounds have different resistance against corrosion, being the Fe-II-rich ones (FeO and Fe₃O₄) recognized as the most resistant one [47–49]. **Fig. 11** reveals that the passive layer formed in OPC and BYF solutions present

almost the same proportion of low (FeO and Fe₃O₄) and high (Fe₂O₃ and FeOOH) oxidation level compounds (ca 1/3 and 2/3, respectively). Since Fe-III compounds are more likely to have been in direct contact with the solution, the film is probably composed of an inner Fe-II-rich highly protective oxide layer and an outer Fe-III-rich less protective one. The similarities in the chemical composition of the passive film shown in **Fig. 11** indicate that the protectiveness of the passive film formed on the carbon steel immersed in OPC and BYF is comparable. This is of importance because in the presence of aggressive species such as chlorides, if it is not considered the role of the hydroxyl concentration in the solution, both passive films formed on steel immersed in OPC and BYF solutions are expected to exhibit similar resistance against pitting corrosion.

The thickness of the passive film, D , was calculated according to the following equation [50], assuming an uniform iron-oxygen-rich film on the steel sample:

$$D = \lambda_{ox}^{Fe} \cdot \cos(\theta) \cdot \ln \left(\frac{I_{ox}^{Fe}}{I_m^{Fe}} \cdot \frac{N_m^{Fe}}{N_{ox}^{Fe}} \cdot \frac{\lambda_m^{Fe}}{\lambda_{ox}^{Fe}} + 1 \right) \quad (\text{Eq. 4})$$

where I_m^{Fe} and N_m^{Fe} are the intensity and the atom density of metallic iron, respectively, while I_{ox}^{Fe} and N_{ox}^{Fe} are the intensity and the atom density of iron-rich-oxygen compounds, respectively; the electron inelastic mean free path in metallic iron, λ_m^{Fe} , and in iron-oxygen-rich compounds, λ_{ox}^{Fe} , can be calculated from [51]:

$$\lambda_m^{Fe} = 0.41 \cdot (a_m)^{3/2} \cdot (E_k)^{1/2}; a_m = \left(\frac{1}{N_m^{Fe}} \right)^{1/3} \quad (\text{Eq. 5})$$

$$\lambda_{ox}^{Fe} = 0.72 \cdot (a_{ox})^{3/2} \cdot (E_k)^{1/2}; a_{ox} = \left(\frac{1}{N_{ox}^{Fe}} \right)^{1/3} \quad (\text{Eq. 6})$$

with E_k the kinetic energy of the considered photoelectrons, 779 eV for iron, and a the mean distance between two atoms. For calculations, it was considered $N_m^{Fe} = 84 \text{ atom/nm}^3$, $N_{ox}^{Fe} = 38 \text{ atom/nm}^3$ [51], and the intensities I_m^{Fe} and I_{ox}^{Fe} at 0° using the procedure described in Ghods et al. works [22,23].

The calculated thicknesses of the passive layer formed on the steel immersed for 1 and 2 days in OPC and BYF solutions are summarized in **Table 5**. As might be expected from the electrochemical results of steel immersed in BYF and OPC pore solutions, steel readily starts to passivate when immersed in these media with the formation of a passivating layer of about 5 nm regardless of the media and immersion time of 1 and 2 days.

As a final remark, it is worth reminding that experiments in the present paper have been performed with leachates and not actual pore solutions — hardly obtainable experimentally. As in any simplified representation of a complex physical system, leachates are nothing more than an experimentally feasible reproduction of the actual chemistry we were trying to investigate. In other words, this protocol can be accepted as a reasonable approximation, but it must be borne in mind that the interpretation has been objectively conducted from results obtained with an electrolyte that is not the actual pore solution. Strictly speaking, the conclusions raised here are to be analyzed in the context of our experimental conditions, even if they seem to constitute a robust evidence of BYF passivating ability. Much work is still needed from experimental, theoretical and modelling points of view for these results to be fully and unambiguously validated and, consequently, for BYF to be a reliable alternative to OPC in terms of reinforcing steel passivation / corrosion behavior.

4. Conclusions

Both tested BYF and OPC electrolytes enabled effective passivation of mild steel in less than 24 h of immersion, with a similar evolution of the interface steel/solution. The protective passive layer formed in BYF and OPC solutions was about 5 nm thick consisting of a similar fraction of Fe-II and Fe-III compounds as determined by XPS measurements. The use of the modified Randle's circuit to interpret the EIS data was not able to distinguish, in our study, the different capacitances from the steel/electrolyte interface. This lack of resolution led to

overestimated capacitance values and, consequently, to an underestimation of the thickness of the passive film, which was, thus, more accurately determined from XPS measurements.

Even if some previous studies claimed that early BYF pore solution could be potentially corrosive, this work showed that as the hydration of BYF progresses, its pore solution may be as protective as that found in Portland equivalents at 28 days of curing. These results might increase the domain of application of BYF cement, leading to the production of low-cost reinforced concrete structures with reduced CO₂ footprint.

Acknowledgements

The authors gratefully acknowledge the financial support of the Brazilian institution CNPq (grant number 229886/2013-2), of the French institution ANRT (grant number 2013/1440), and of the LafargeHolcim group.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

5. References

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Fig. 1 Main phases at 28 days of hydration of OPC and BYF cement pastes with water to cement ratio of 0.50. AFm is shorthand for a family of hydrated calcium aluminate phases structurally related to hydrocalumite and occurring mainly in hydrated cement paste. Si-Hg and C-S-H stand for siliceous hydrogarnet and calcium-silicate hydrate, respectively.

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Table 1 Characteristics of the binders of the study (Rietveld quantitative phase analysis, readily soluble alkalis, and Blaine specific surface according to NF EN 196-6).

<i>Rietveld Quantitative Phase Analysis g / 100 g cement</i>			
<i>Phases</i>	<i>OPC</i>	<i>Phases</i>	<i>BYF</i>
Alite, Ca_3SiO_5	60.2	Ye'elimite, $\text{Ca}_4\text{Al}_6\text{O}_{12}(\text{SO}_4)$	31.1
β -Belite, Ca_2SiO_4	17.9	α' -Belite, Ca_2SiO_4	29.0
Ferrite, $\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$	10.5	β -Belite, Ca_2SiO_4	8.0
Aluminate, $\text{Ca}_3\text{Al}_2\text{O}_6$	5.1	Ferrite, $\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$	17.7
Gypsum, $\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$	1.8	Anhydrite, CaSO_4	6.5
Hemihydrate, $\text{CaSO}_4 \cdot 0.5(\text{H}_2\text{O})$	1.8	Gypsum, $\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$	1.5
Calcite, CaCO_3	1.5	Periclase, MgO	0.9
Periclase, MgO	0.1	Other phases (inert)	5.9
Free lime, CaO	1.1		
Readily soluble Alkalis*			
K_2O	0.77	K_2O	0.36
Na_2O	0.07	Na_2O	0.02
		$\text{B}_2\text{O}_3^{**}$	1.36
Blaine specific surface (cm^2/g)	3680	Blaine specific surface (cm^2/g)	4430

* The soluble alkali contents represent the part of alkali that can be extracted from the cement in water for 15 minutes (analysis of the solution by ICP-AES).

** Boron content is the amount extracted in acid solution, 1/6 vol. HCl, during 10 min (analysis of the solution by ICP-AES).

Table 2 Measured total concentrations in OPC and BYF solutions used as electrolytes in electrochemical and XPS analyses.

<i>Solution</i>	<i>pH</i>	<i>Si</i> <i>mmol/L</i>	<i>Al</i> <i>mmol/L</i>	<i>Ca</i> <i>mmol/L</i>	<i>K</i> <i>mmol/L</i>	<i>Na</i> <i>mmol/L</i>	<i>S^a</i> <i>mmol/L</i>	<i>B^b</i> <i>mmol/L</i>	<i>Is*</i> <i>(mol/L)</i>
OPC ^a	13.2	0.018	0.018	6.04	204	16	0.11	---	0.122
BYF ^b	12.9	0.037	0.09	4.74	116	8	0.08	0.09	0.072

* $Is = \text{Ionic Strength} = \frac{1}{2} \sum_{i=1}^n c_i z_i^2$, where c_i is the molar concentration of ion i (mol/L) and z_i is the charge number of that ion.

^a Considered in solution as SO_4^{2-}

^b Considered in solution as B(OH)_4^-

Table 3 Peak parameters of Fe-based compounds used for XPS fitting.

<i>Element (core level)</i>	<i>Peak ID</i>	<i>Assignment</i>	<i>Peak position (± 0.2)</i>	<i>FWHM^b (± 0.2)</i>
<i>Fe (2p)</i>	Fe-1	Fe ^o	706.5 ^a	1.9
	Fe-2	FeO, Fe ₃ O ₄	709.0	2.8
	Fe-3	Fe ₂ O ₃	710.4	2.6
	Fe-4	FeOOH	712.2	3.0

^a T_{Hgt} / T_{Mix} / T_{Exp}: 0 / 0.20 / 0.08. The other peaks were considered symmetric.

^b Full width at half maximum.

Table 4 Fitting parameters of EIS data considering the equivalent circuit in Fig. 6.

Sample	Time (days)	R_e ($\Omega \cdot \text{cm}^2$)	R_p ($\text{k}\Omega \cdot \text{cm}^2$)	Q Y_o ($\mu\Omega \cdot \text{cm}^{-2} \text{s}^{-\alpha_1}$)	α	C_{eff}^* $\mu F/\text{cm}^2$
OPC	1/2	10	372	50	0.94	30.7
	1	10	614	47	0.94	28.8
	2	10	938	44	0.94	26.8
	3	10	1274	43	0.94	26.2
	4	10	1505	42	0.94	25.6
	5	10	1786	41	0.94	24.9
	6	10	1941	41	0.94	24.9
	7	10	2018	41	0.94	24.9
BYF	1/2	19	465	45	1.00	45.0
	1	19	680	44	0.95	30.3
	2	19	926	43	0.95	29.6
	3	19	1018	42	0.95	28.8
	4	20	1093	42	0.95	28.8
	5	20	1137	41	0.95	28.2
	6	20	1184	41	0.95	28.2
	7	20	1222	41	0.95	28.2

* Effective capacitance calculated using Eq. 2.

Table 5 Calculated layers thickness from XPS results.

<i>Solution</i>	<i>Immersion (days)</i>	<i>D (nm)</i>
OPC	1	5.1
BYF	1	4.9
OPC	2	4.6
BYF	2	4.7

Fig. 1 Main phases at 28 days of hydration of OPC and BYF cement pastes with water-to-cement ratio of 0.50. The phases were estimated by Rietveld refinement as in [13]. AFm is shorthand for a family of hydrated calcium aluminate phases structurally related to hydrocalumite and occurring mainly in hydrated cement paste. Si-Hg and C-S-H stand for siliceous hydrogarnet and calcium-silicate hydrate, respectively.

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