

Article

Improving Sustainability through Corrosion Resistance of Reinforced Concrete by Using a Manufactured Blended Cement and Fly Ash

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Abstract: The objective of this paper is to report the improvement of sustainability through the increase of reinforced concrete corrosion resistance by using a blended cement and fly ash. Different reinforced concrete mixtures were prepared with partial substitution of a manufactured blended cement with fly ash from a thermal power plant in Andorra (Teruel, Spain). These mixtures were manufactured using three different water/cement ratios (0.46, 0.59, and 0.70) and three substitution percentages of cement by fly ash (0%, 25%, and 50%). The test cylinders underwent an accelerated carbonation process and exposure to different chloride levels, with the aim of characterizing the corrosion level of the different mixtures. The addition of local FA matched or even improved the resistance of the control mixture against carbonation and chlorides.

Keywords: fly ash; corrosion; durability

1. Introduction

Its relatively low cost and high compressive resistance and molding capability make concrete a frequently used construction material worldwide [1]. However, several agents that are found in the environment degrade cement and concrete. Such agents include carbonation produced by carbon dioxide (CO₂) and the introduction of chlorides from sea water, which can corrode reinforced steel [2]. Thus, from an economics perspective, it is important to address this issue. It may even be necessary to replace structures before they fulfill their projected life cycle.

There is a general consensus that the majority of concrete deterioration processes are related to the corrosion of reinforcement due to carbonation or chloride induced depassivation of steel bars. Concrete carbonation is a complicated physicochemical process. The process includes the diffusion of CO₂ in the gaseous phase into the concrete pores, its dissolution in the aqueous film of these pores, the dissolution of solid Ca(OH)₂ in the water of the pores, the diffusion of dissolved Ca(OH)₂ in the pore water, its reaction with the dissolved CO₂, and the reaction of CO₂ with CSH and with the yet unhydrated C₃S and C₂S [1]. Carbonation does not only affect portlandite, but also other phases, including CSH, Etringite, and CAH phases. When CO₂ penetrates into the hardened concrete, it reacts with those phases in the presence of moisture yielding CaCO₃ [3].

The attack that is produced by the ingress of chloride ions into concrete can locally break the passive oxide layer of the steel surface, when sufficient chloride concentration reaches the reinforcement surface [4–7]. The critical chloride concentration needed to break the passive state is not constant, but it depends on several factors, such as the cation type of the chloride salt. When a chloride-induced corrosion process occurs, corrosion pits develop on the surface of the steel reinforcement, so a local corrosion phenomenon takes place, unlike the generalized corrosion mechanism that is produced under carbonation-induced corrosion. This local corrosion process is especially harmful since a progressive acidification of the environment inside the pit takes place due to the increase of the Fe^{2+} concentration, and therefore the corrosion rate increases as a consequence of the low pH solution that is created inside the corrosion pit.

On the other hand, the use of cement in the construction industry has generated great environmental concern because their raw materials come from the environment and the exhaustion of these makes them environmentally unsustainable. In addition, these raw materials need to consume a lot of energy in their manufacture in order to obtain the final product and transport to the site of the work. For the production of raw materials, large CO_2 emissions are generated that are highly harmful and alter the environment. Additionally, it is well known that the cement production accounts for approximately 5% of global CO_2 emissions [8]. This has been seen notably in recent years in climate change, changes in temperature, and the impact on human health.

It has also been found that the ashes (as fly ash) that remain of any industrial process are characterized as highly damaging materials, and due to their low density and high volumes they cause the contamination of soils, groundwater and also health problems [9]. The use of Supplementary Materials does not contribute to the depletion of natural resources, and therefore the impact to the environment that is generated by the production of these raw materials is satisfactorily reduced, and the problem generated by the handling of the remaining residues is solved when they are used as additions in mortar and concrete mixtures.

Fly ash is a byproduct from the thermal power industry that is currently used in several countries as an addition to concrete because improves handling of fresh concrete, reduces cracks, and increases resistance against aggressive agents by creating a more intricate matrix [4–7]. Also, it considerably reduces chloride diffusion in concrete by improving the microstructure [4,6,10–12] and obtaining a denser cement paste [4,6,10–20].

However, it has been reported that, as the fly ash content increases, the development of pozzolanic reactions decreases because there is not enough calcium hydroxide in the system to react with all of the available fly ash [21], which in turn leads to the development of a porous microstructure. It is thus important to define the most proper usage of fly ash in each case.

One disadvantage of using cements with fly ash from steelmaking slag is their susceptibility for carbonation when compared with CPO [4,22]. It is therefore necessary to define the maximum allowed addition without affecting the final durability.

Therefore, the purpose of the current study was to manufacture concrete with greater durability and improved sustainability, which would lower maintenance and repair costs when compared to other construction products. This ongoing research assessed the behavior of nine reinforced concrete mixtures based on Portland cement and fly ash to define its performance after 56 days of curing time against chlorides and accelerated carbonation degradation. This type of information is little studied in the literature; the durability tests previously reported usually had shorter curing times (28 days). Finally, a comprehensive longer-term study is needed to resolve confusing or contradictory data in the literature. Then, the aim of this paper is to provide original knowledge based on research about corrosion resistance by carbonation and chloride of these types of concretes with 56 days of curing. This has a direct improvement of concrete contribution to sustainability.

2. Materials and Methods

For this research, three different water/cementitious material (w/b) ratios were selected—0.46, 0.59, and 0.70—and three different contents of fly ash (FA)—0%, 25%, and 50%—in substitution by the weight of Portland cement, the mixtures selection considered the typical values in the concrete industry. After mixing, the curing process was performed in a wet chamber for 56 days, in order to increase the hydration of fly ash. Figure 1 shows a matrix of the mixtures that were used and Table 1 lists dosing from each of the used concretes, which has been adapted from Castro-Borges [23].

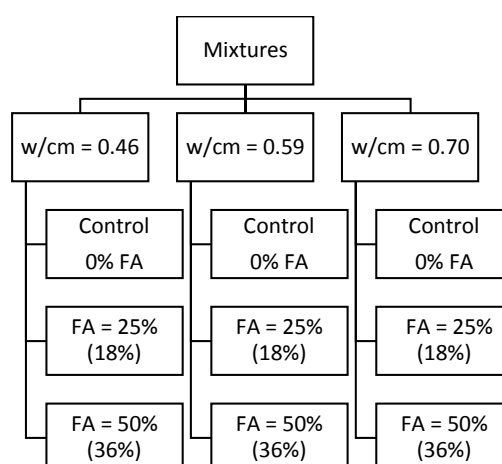


Figure 1. Matrix of mixtures used in the experiment. Between parentheses values of fly ash (FA) with respect to the content of clinker in the cement used (72%).

Table 1. Quantification of materials per mixture [21].

Specified Compressive Strength (ACI 211.1) (N/mm ²)	Portland Cement Content (kg/m ³)	0% FA (kg/m ³) in Substitution of Portland Cement	25% FA (kg/m ³) in Substitution of Portland Cement	50% FA (kg/m ³) in Substitution of Portland Cement	w/b Ratio	Water Content (kg/m ³)	Sand (kg/m ³)	Coarse Aggregate (kg/m ³)
34.3	533.0	0.0	—	—	0.46	245.2	558	754
24.5	402.0	0.0	—	—	0.59	237.2	637	754
19.6	346.0	0.0	—	—	0.70	242.2	645	754
N/A	399.8	—	133.3	—	0.46	245.2	558	754
N/A	301.5	—	100.5	—	0.59	237.2	637	754
N/A	259.5	—	86.5	—	0.70	242.2	645	754
N/A	266.5	—	—	266.5	0.46	245.2	558	754
N/A	201.0	—	—	201.0	0.59	237.2	637	754
N/A	173.0	—	—	173.0	0.70	242.2	645	754

2.1. Test Cylinders

The test cylinders were manufactured using CEM II/B-L 32.5 R Portland cement (UNE-EN 197-1: 2000 standard) [24] with a characteristic resistance of 32.5 N/mm², aggregates with a maximum size of 12 mm from a quarry, water from a local drinking water network (Alicante, Spain), a corrugated steel-reinforced bar 10 mm in diameter with an approximate length of 15 cm, and FA from the Andorra thermal power station (Teruel, Spain), which was used as received, without applying any treatment before its usage. The characteristic composition of the FA is listed on Table 2 and the clinker content is shown in Table 3.

Table 2. Chemical composition of FA, expressed in %. Low-calcium fly ash (class F according to ASTM C-618) from the thermoelectric power plant Andorra (Teruel, Spain).

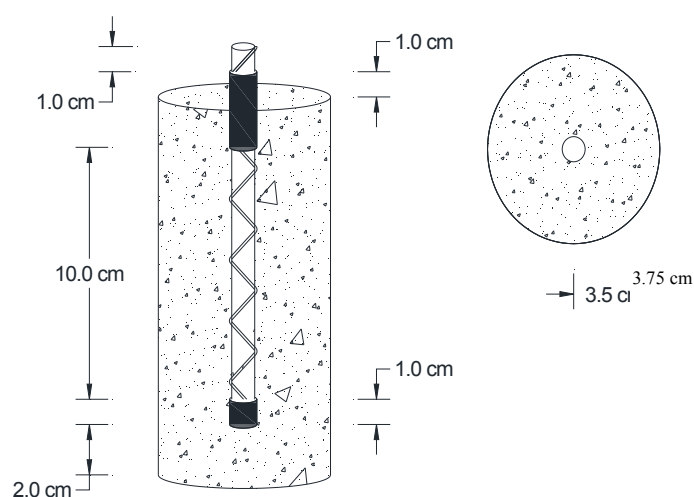
Composition	FA (%)
SiO ₂	40.94
Al ₂ O ₃	24.65
Fe ₂ O ₃	13.59
CaO	9.83
MgO	1.59
Na ₂ O	0.34
K ₂ O	1.40
SO ₃	1.60
P. F.*	2.44

P.F.*: loss to fire by ignition.

Table 3. Clinker content CEM II/B-L (percentage by mass %) [25].

Main Types	Name	Notation	Clinker	Limestone	Minor Additional Constituents
CEM II	Portland–Limestone cement	PC 35L	65–79	21–35	0 to 5

From each of the nine cement mixtures, we prepared three series of 75 mm × 150 mm test cylinders with 10 mm × 150 mm embedded steel (110 mm of exposure length) with a 33-mm-thick cover, as shown in Figure 2. The first series underwent CO₂ degradation for the purpose of comparing the different mixtures under accelerated carbonation. The second series was exposed to chloride activity by the partial immersion of the samples in a solution of 0.5 M NaCl with water. Finally, the third series was exposed to various chloride percentages in the water for the mixtures (1%, 2%, and 4% of the mass of the cement material). The cement mixture process fulfilled the UNE-EN 12390-2: 2001 [26] standard, and previously pickled steel was used. For the chloride migration tests (NT BUILD 492 standard) [27], test cylinders 100 mm × 200 mm without steel embedded in them were built.

**Figure 2.** Scheme of concrete test cylinder used during corrosion tests [20].

2.2. Exposure Conditions

After the test cylinders completed 56 days of curing in a wet chamber, the monitoring and exposure in different selected environments was carried out. The curing time was selected to facilitate

the FA reaction. It is worth mentioning that, for the test cylinders with chloride added to the mixture water, curing was not performed because of the expected initial high corrosion levels. It is interesting to analyze these levels together with the test cylinder reaction to the degradation of reinforced steel because of the capacity for releasing OH^- ions and the decreased corrosion levels of the cement matrix.

The exposure to accelerated carbonation comprised three stages. In the first stage, the test cylinders were exposed to an atmosphere of 100% CO_2 and between 60% and 70% relative humidity (RH) in order to favor the process and conditions of carbonation equipment. After 50 days in the carbonation chamber, the test cylinders were stored in laboratory humidity conditions (50–60% RH) and ambient temperature (20–25 °C) in order to monitor the evolution of the corrosion rates in ambient atmosphere with higher oxygen concentrations; this was the second level. At the final stage, a desiccator was used for the test cylinder having an atmosphere of 100% RH for the purpose of avoiding the resistive control of corrosion attack by the lack of humidity (a condition that can occur with RH between 50% and 60%). On the other hand, the carbonation chamber consisted of a desiccator that was connected to a CO_2 tank (environment > 99.9% dry). The CO_2 flow was intermittent (one daily discharge of 5 min) with a 10 L/min flow. To simplify, in this paper, the atmosphere that was created in the chamber is considered to be 100% CO_2 , although because of the humidity in the desiccator, the CO_2 concentration was slightly lower. The temperature of the carbonation chamber was maintained between 20 °C and 25 °C and the RH was controlled to the desired interval. For this purpose, a mixture of glycerine with distilled water was introduced at the bottom of the desiccator to suppress the excess humidity that was produced during the carbonation process, according to DIN 50 008 standard [28]. These carbonation T and RH conditions were chosen in accordance to previous experience from the authors and literature [29]. Sanjuan et al. also have stated that accelerated and natural conditions can be adequately linked only if concretes come from the same family (including additions). The concrete samples were dried prior to accelerated carbonation. To measure the carbonation rates, we made cylinders of the same setting, but without steel that was broken at different ages to know the carbonation depth. Once the electrochemical data showed corrosion rates greater than $1 \mu\text{A}/\text{cm}^2$, cylinders were broken to corroborate the completely carbonation using a phenolphthalein indicator.

The evaluation of chloride penetration was made by partial immersion of the test samples in a 0.5 M NaCl with water solution in an effort to achieve seawater concentration. During the study, the test cylinders were first submerged in the saline solution. After 50 days, they were dried at laboratory humidity (between 50% and 60% RH). From day 190, the test cylinders were placed in a desiccator at an RH of 100%, and for the final stage (from day 230), they were again placed in the saline solution.

For the chloride addition to the mixture water, 1%, 2%, and 4% of chloride per weight of cement material were added during the preparation of test samples. After 24 h, the test cylinders were removed and the instantaneous corrosion rate started to be monitored. The test cylinders were then exposed to three different RH levels: For the first 50 days, they were placed in a desiccator with 90% RH; from day 50 to day 190, they were under laboratory conditions at 50% and 60% RH. For the final stage of the study (from day 191 to day 280), the test cylinders were returned to the desiccator at 100% RH.

2.3. Corrosion Rate Monitoring

The corrosion potential (E_{corr}) and the instantaneous corrosion current (i_{corr}) were monitored and defined by the electrochemical method that is known as polarization resistance (R_p) [30] in a Princeton Applied Research model 362 EG&G potentiostat/galvanostat using a three-electrode configuration, with a saturated calomel electrode (SCE) as reference, a stainless-steel mesh electrode as the auxiliary electrode, and the reinforced steel as the working electrode. The R_p method was applied using a scanning rate of 0.5 mV/min and a perturbation of 10 mV from the anodic sense to 10 mV in the cathodic sense with regard to the E_{corr} value of the working electrode. Figure 3 shows the three-electrode configuration that was used in the measurement.

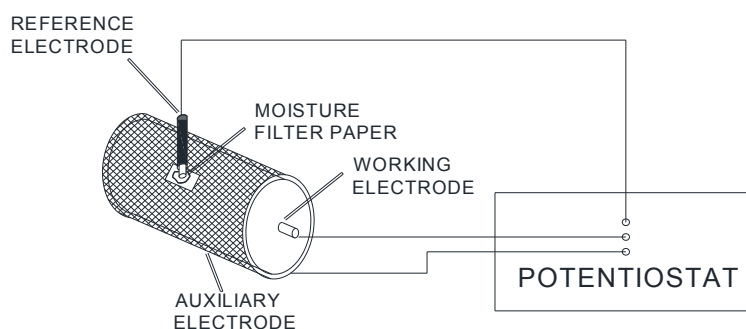


Figure 3. Measurement configuration of test cylinders.

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2.4. NT BUILD 492 (1999) Chloride Migration Test

The chloride migration test was performed according to the NT BUILD 492 standard, which uses three saturated test cylinders 100 mm in diameter and 50 mm in width. Each test cylinder is placed in a plastic cover containing a 0.3 N NaOH solution, which in turn, is placed in a vessel with a 10% NaCl solution. Then, a differential potential of 30 V is applied through the test cylinder and the initial current is measured. Based on the initial current, the essay duration and voltage are defined. Then, the test cylinder is diametrically cut and 0.1 M silver nitrate solution is sprayed onto the fracture surface to define the chloride's penetration depth. Finally, based on measured penetration and test conditions, the chloride's migration coefficient is calculated. Figure 4 shows the monitoring system configuration.

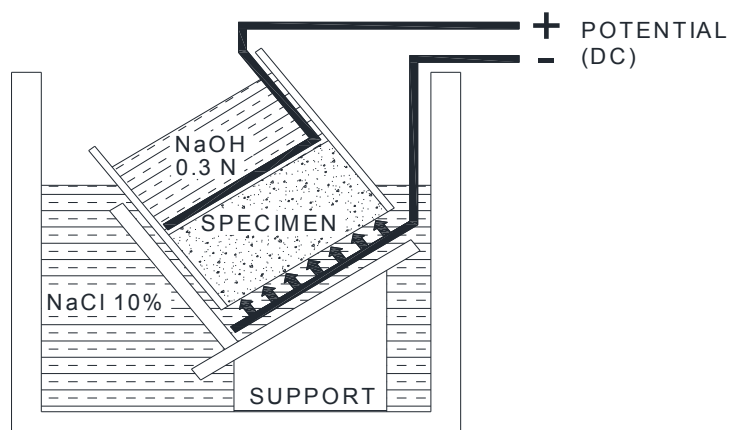


Figure 4. Monitoring configuration where test cylinders are induced with an electric current from a continuous current source (source: adapted from the NT BUILD 492 standard [27]).

3. Results and Discussion

3.1. Results of Exposure to Accelerated Carbonation

Figures 5–7 show the evolution of the corrosion potential and the corrosion rate of the selected nine types of concrete for the accelerated carbonation study. During the first 50 days of conservation (first conservation stage) of these test cylinders, they were exposed to an atmosphere of 100% CO₂ and between 60% and 70% RH. During this conservation stage, a slightly greater corrosion rate for the steels from mixtures with 50% FA substitution was detected. On the other hand, steels with 25% FA substitution showed corrosion values that were very similar to those of the steels with control

mixtures (0% FA), behavior that was detected for all the w/b ratios. After this first conservation stage of 50 days in the carbonation chamber, it started a second stage where the samples were dried at ambient temperature (20–25 °C) with 50% and 60% RH for 140 days (from day 50 to day 190), were, despite the fact that during the first 17 days of this period of time (between day 50 and 67 of exposure), the test cylinders maintained the same behavior as in the first stage, a decrease on the corrosion levels in general is noted from day 162. The reason for this decrease is essentially because of the resistivity of the cement matrix, which prevails in such conditions. For the final stage of the research (from day 190 to day 275), the samples were stored in a desiccator and maintained at 100% RH. The greater the substitution content of FA, the greater the corrosion rates detected for w/b ratios of 0.46 and 0.59. However, at the w/b = 0.70 ratio, the performance of the steel with the 25% FA substitution was similar to that of the steel with the control mixture. This was unexpected behavior because the substitution of fly ash uses calcium hydroxide for its hydration, leading to the conclusion that the greater the substitution content of FA, the greater the pH drop. Although the matrix is denser with FA, this densification in some cases is not enough to compensate for the loss of alkalinity as a consequence of the hydration of FA. It is worth mentioning that in previous studies [16,17,31], a low alkaline reserve only affected the time during which degradation occurred when porosity was high; if low porosities prevailed, then with a minimum alkaline reserve, it was possible to protect the reinforcing steel during the initial phase.

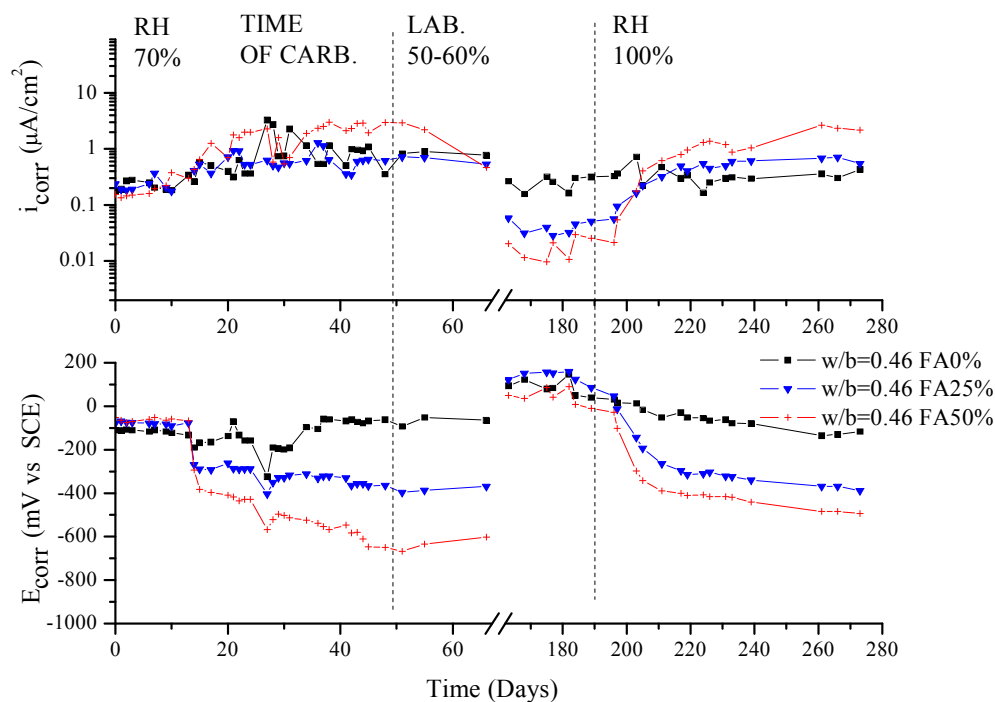


Figure 5. Evolution of i_{corr} and E_{corr} on steels embedded in concretes with accelerated carbonation. The w/b ratio = 0.46.

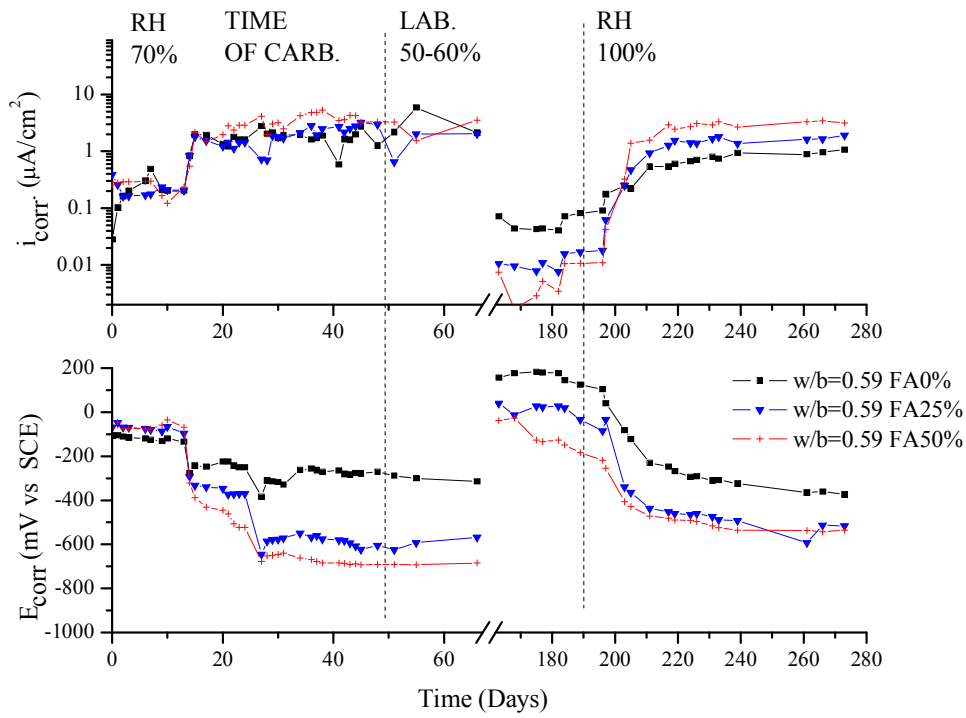


Figure 6. Evolution of i_{corr} and E_{corr} on steels embedded in concretes with accelerated carbonation. The w/b ratio = 0.59.

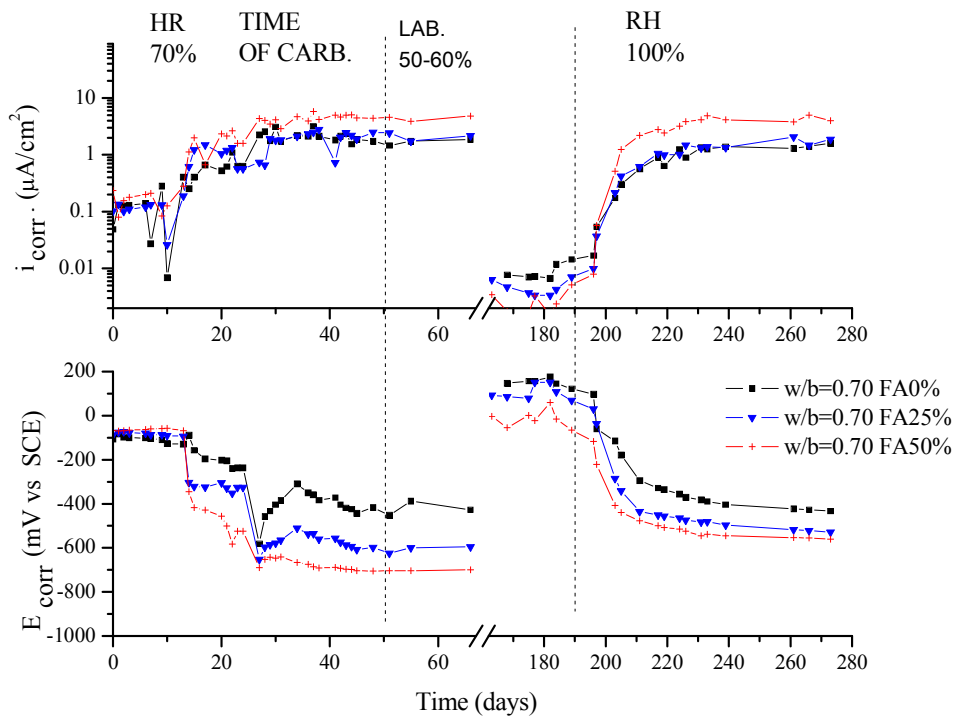


Figure 7. Evolution of i_{corr} and E_{corr} on steels embedded in concretes with accelerated carbonation. The w/b ratio = 0.70.

3.2. Results of Immersion in 0.5 M NaCl Solution

Figures 8–10 show the evolution curves of the corrosion current density and the corrosion potential of steels embedded in the selected nine types of concrete that were exposed to degradation by external chlorides by immersion in water with 0.5 M NaCl. Figure 8 shows samples that were produced with w/b ratio = 0.46 and different FA contents (0%, 25%, and 50%), as is shown in Table 2. The figure shows that the corrosion rates were very similar between the three steels. This is related to the low w/b ratios, which prevent the degrading agent from entering. To detect the contribution of FA, greater exposure times are needed to define behavior and performance.

The results of the $w/b = 0.59$ and $w/b = 0.70$ ratios for the same FA substitution content are shown in Figures 9 and 10. The steels have corrosion rates very similar to those of the first two stages. However, after day 200, the corrosion rates started to differ between the three steels. After day 200 for the $w/b = 0.56$ ratio (Figure 9), the mixture with 25% FA had a lower corrosion rate, whereas the steel with the mixture without FA added showed the highest corrosion rate. The steel with a mixture of 50% FA maintained an average corrosion rate as compared to the other two. For the $w/b = 0.7$ ratio (Figure 10) for the same period of time (after day 200), the corrosion rates of the steels embedded in mixtures with 25% and 50% FA had similar values, whereas the steel that was embedded in the control mixture showed an increase in the corrosion rate that was clearly greater than the other two. This behavior, where in general the greater the content of FA, the greater the protection of concrete against exposure of chloride ions, is mainly owing to the pozzolanic reaction, which increases the intricate matrix and reduces chloride diffusion. FA usually has a higher content of aluminates than Portland cement (24.65% Al_2O_3 for the FA in this study). As a result, the chlorides that try to penetrate the matrix bonded with the aluminates, thus forming Friedel's salt [32,33]. However, obtaining lower corrosion rates for steel with the substitution of 25% FA at the $w/b = 0.56$ rate and similar rates for steels with substitutions of 25% and 50% FA at the $w/b = 0.70$ ratio, defined that an increase in the substitution of FA does not clearly lead to a more intricate matrix, because the lack of calcium hydroxide [$Ca(OH)_2$] prevents the pozzolanic reaction from occurring.

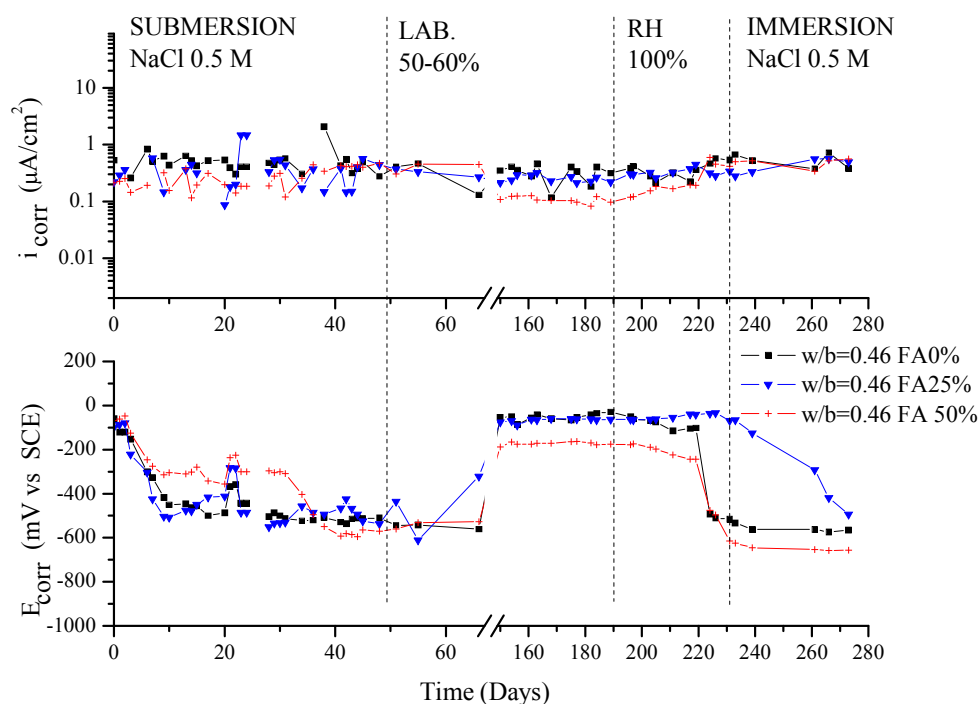


Figure 8. Evolution of i_{corr} and E_{corr} of steels embedded in concrete exposed to partial immersion in water with 0.5 M NaCl w/b rate = 0.46.

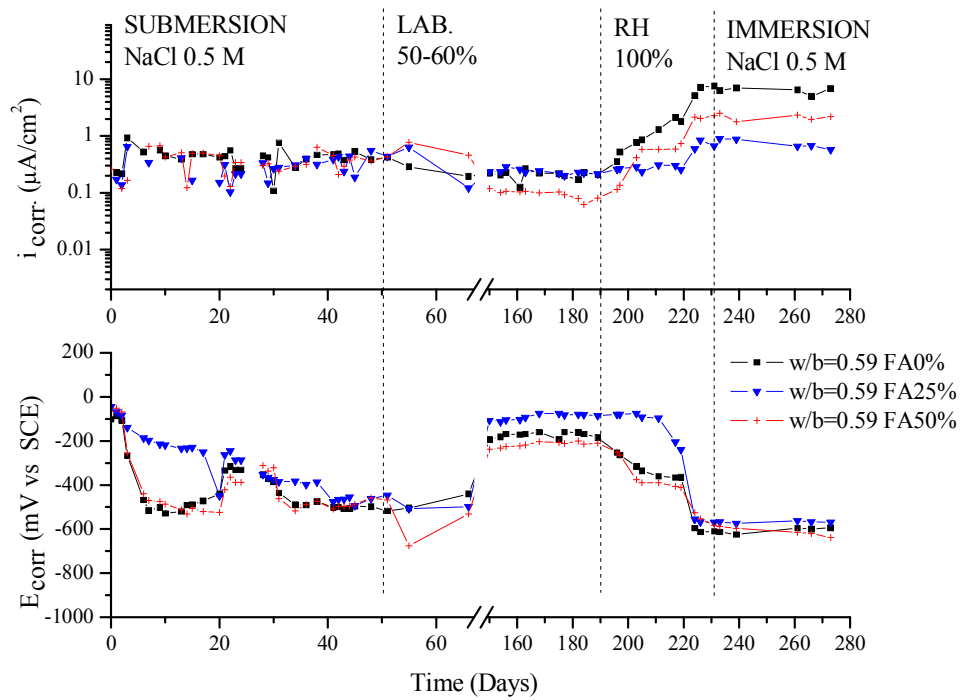


Figure 9. Evolution of i_{corr} and E_{corr} of steels embedded in concrete exposed to partial immersion in water with 0.5 M NaCl and w/b rate = 0.59.

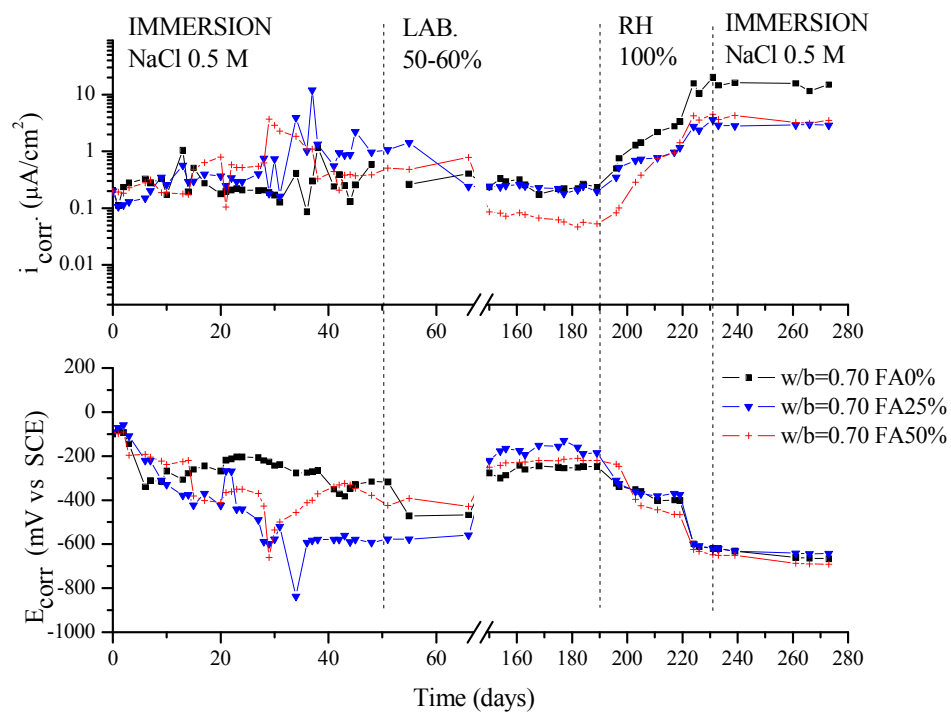


Figure 10. Evolution of i_{corr} and E_{corr} of steels embedded in concrete exposed to partial immersion in water with 0.5 M NaCl and w/b rate = 0.70.

3.3. Results of Corrosion Rates of Samples with Chloride Ions Included in the Water of Mixture

Figures 11–14 show the analyses of samples that were degraded with chlorides added to the water of mixture (1%, 2%, and 4% of weight of cement material) for the same w/b ratio of 0.59.

Figure 11 shows the comparison between steels with different FA contents for the 1% chloride addition. During the first 60 days and then between days 230 and 260, the steel of the control mixture showed low values of i_{corr} . On the other hand, and only for the time elapsed between 150 and 200 days, the steel of the mixtures with FA substitution showed similar corrosion rates during the time of the test. The mixture with 50% FA substitution decreased the steel's corrosion rate below that of the steel of the control mixture, which in turn, showed corrosion rates that were very similar to those of the steel with mixtures of 25% FA. However, at the end of the study (between day 260 and 280), the steels showed similar corrosion values. Based on these results, better performance was obtained for none of the three mixtures. The results also indicate that a longer period of time is needed to study the effect on corrosion rates of adding FA for that percentage of chloride ion. Figure 12 shows the comparison between steels with different FA contents with 2% chloride ions. During the first 60 days, the steel with the control mixture had slightly lower corrosion rates, although during the last 50 days of the study, this same steel showed higher corrosion rates. The steel with 50% FA showed better performance between 150 and 280 days, and the performance of the steel with 25% FA was very similar to that of the steel with 50% FA during the first 67 days of the study; between days 150 and 240, its behavior was similar to that of the steel with the control mixture. Finally, Figure 13 shows the comparison between the steels with different FA contents with 4% chloride ions. In the first 70 days, the steel with the control mixture showed slightly lower corrosion rates; after 150 days and up to the end of study, it exhibited greater corrosion rates when compared to concretes with FA that had lower and very similar values of i_{corr} . The best performance was obtained for FA mixtures with 2% and 4% chloride ions, which clearly shows the positive effect of adding FA to Portland cement. This allows for economical savings and provides a sustainable option because it decreases the consumption of cement and takes advantage of a byproduct from the thermal power industry, such as FA. A possible reason for this behavior is the ability of chloride ions bond to FA related to their high aluminum content, which in turn yields greater formation of Friedel's salt [32,33]. However, other authors attribute it to the creation of more gel during the hydration process, thus facilitating the adsorption of chloride ions [34].

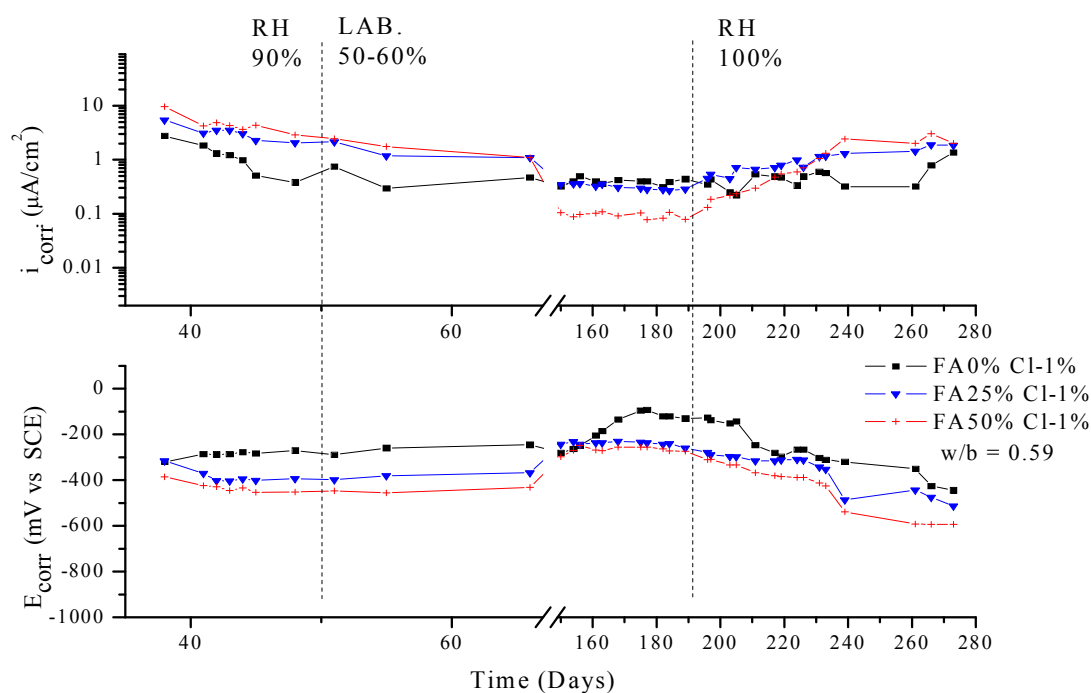


Figure 11. Evolution of i_{corr} and E_{corr} of steels embedded in concrete with 1% chloride ions added per weight of cement material.

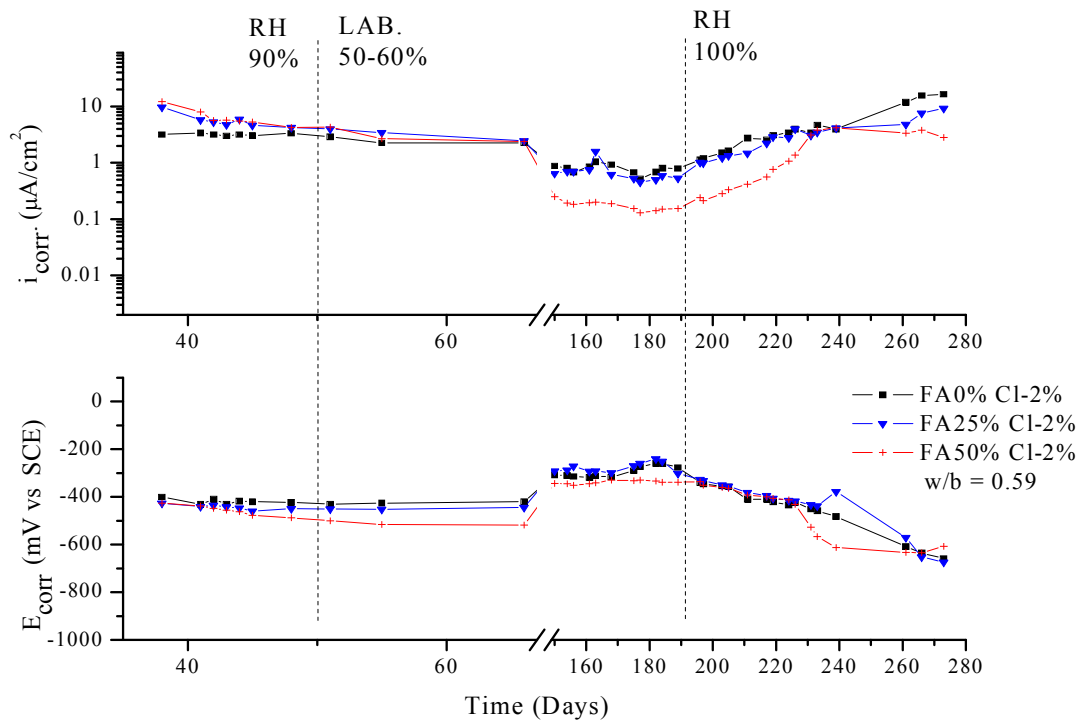


Figure 12. Evolution of i_{corr} and E_{corr} of steels embedded in concrete with 2% chloride ions added per weight of cement material.

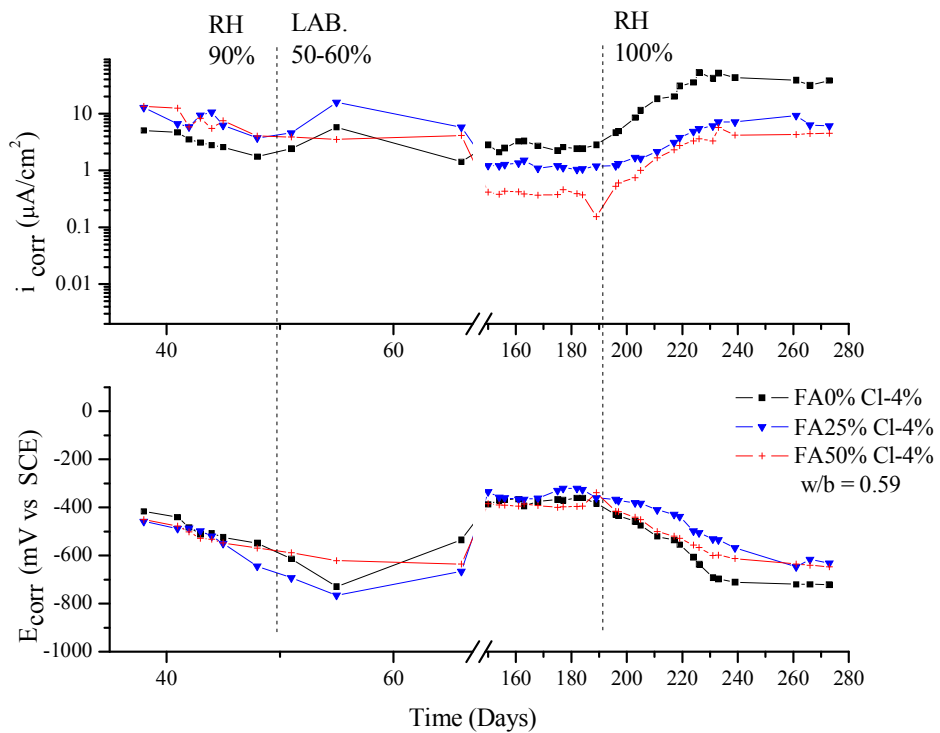


Figure 13. Evolution of i_{corr} and E_{corr} of steels embedded in concrete added with 4% chloride ions added per weight of cement material.

3.4. Results of Standard NT BUILD 492 Migration Coefficients

Figure 14 shows the values of the migration coefficients of chlorides, according to Standard NT Build 492, where the addition of FA improved, although at the same level of magnitude, the resistance against chloride migration. However, this improvement was limited, as shown by the very similar coefficients for 25% and 50% FA. These results coincide with the results of the corrosion rates in steels that were exposed to a 0.5 M NaCl solution and with the addition of chloride ions in the water for mixture, which also showed good performance of the mixtures with the substitution of FA.

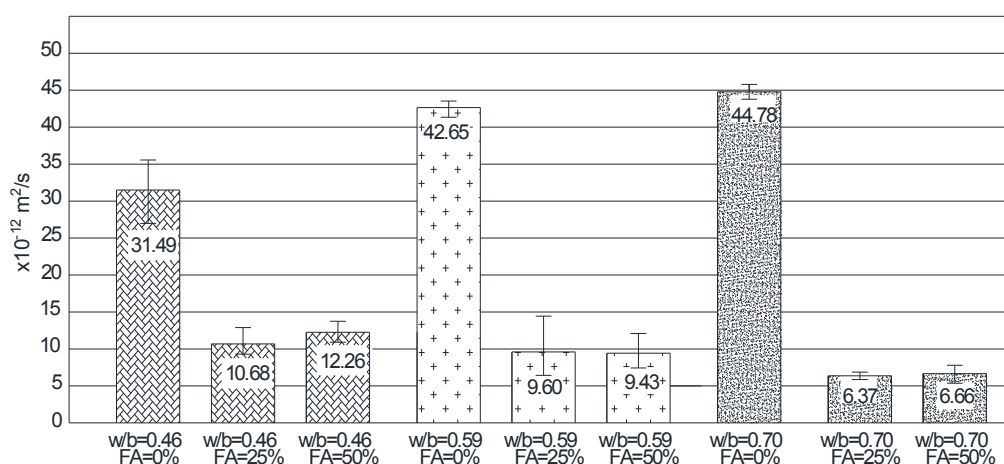


Figure 14. Comparison of migration coefficients obtained in each of the nine study samples (units $\times 10^{-12} \text{ m}^2/\text{s}$).

4. Conclusions

The following conclusions apply for the tests, methods, and circumstances that are discussed in the paper. Any extrapolation to different circumstances must be validated with more results. These conclusions apply for specimens of reinforced concrete cured for 56 day, where blended cement CEM II/B-L 32.5 R had partial substitution with fly ash.

- (1) The mixture without the addition of FA (0% FA) showed a lower corrosion rate under accelerated carbonation; however, the replacement of 25% FA showed similar behavior, and in some cases, the corrosion rate was similar to the sample with a w/b ratio = 0.70 with 0% FA. Thus, under carbonation attack, it is recommended to perform previous studies to define the optimum content of FA that replace Portland cement with no negative effect on the durability against CO₂ presence.
- (2) In general, the greater the replacement amount of FA, the greater the concrete's protection under chloride attack in a solution of water with 0.5 M sodium chloride. This same beneficial behavior was observed when the test cylinders were exposed to a solution with chloride ions added into the mixture water. The sample showed increased resistance to chlorides migration, according to Standard NT Build 492. Thus, the use of the tested FA as a replacement for Portland cement in high contents and after a reasonable curing time will improve the durability against the presence of chloride ions.
- (3) The improvement of corrosion resistance against carbonation and chlorides through the use of a manufactured blended cement plus fly ash has a direct and potential contribution on infrastructure sustainability.

Author Contributions: P.G.T., E.Z. and J.M.M.-R. conceived and designed the experiments; H.G.C.S. performed the experiments; P.G.T., and J.M.M.-R. and P.C.-B. analyzed the data; C.A.J.A. contributed reagents/materials/analysis tools; H.G.C.S., J.M.M.-R. and P.C.-B. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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