Analysis of the chloride diffusion coefficients by different test methods in concrete mixtures containing metakaolin and high-slag blast-furnace cement

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ABSTRACT

This study aims to evaluate the chloride diffusion coefficient and the service life (SL) of concretes containing metakaolin and high-slag blast-furnace cement (HSBFC). Accelerated methods of chloride ion diffusion and migration (RCPT, RMT, BDT and multiregime test method) were used. To produce the specimens, HSBFC resistant to sulphates (CPIII 40 RS) was partially replaced by metakaolin in the contents of 4%, 8% and 12%. Statistical analysis was performed by means of Analysis of Variance (ANOVA) and Tukey's Test to the chlorides diffusion coefficients obtained from different test methods. Similarity between diffusion by immersion (BDT) and non-stationary migration test (RMT and multiregime method) results was noted, however, with differences regarding to the stationary regime. The average diffusion coefficient obtained in the concrete specimens with 8 and 12% metakaolin as HSBFC partial replacement was 40-45 % lower than the reference mixture, providing an SL increase of approximately 70%. The most efficient metakaolin content obtained for overall mechanical and durability properties of concrete was 8%. This study also showed that HSBFC partial replacement by metakaolin can be beneficial even at later ages, as in 150 days.

Keywords: Concrete durability; Chloride diffusion; Service life; Granulated blast-furnace slag; Pozzolan.

1. INTRODUCTION

The cement industry is responsible for nearly 7% of the CO_2 global emissions, being a significant contributor to the global warming [1]. In this scenario, the cement partial replacement by supplementary cementing materials (SCM) emerges as a solution for reducing the CO_2 emissions and the consumption of energy and natural resources. The SCM use can occur in the production of blended cement or in the concrete batching, at fresh state. One of the SCM widely used in cement production is the granulated blast-furnace slag (GBFS). A high-slag blast-furnace cement (HSBFC) is a blended cement that has around 60 to 80% of GBFS, producing concretes with elevated chloride ion penetration resistance (CPR), being adequate for mitigating the harmful effects of corrosion in reinforced concrete structures [2-5]. Studies have indicated that HSBFC can reduce chlorides diffusion up to 600% [6-8]. Furthermore, the GBFS use in concrete has a positive environmental effect, due to GBFS be a by-product of iron production. The global production of pig iron according to WORLDSTEEL ASSOCIATION [9] was approximately 1.16 billion tons in 2015, being around 27.8 million tons in Brazil. Since for each ton of pig iron produced, 300 kg of slag is generated [10], an annual global generation of approximately 350 million tons is expected.

Another SCM commonly used in concrete production is metakaolin, a fine pozzolanic material, highly reactive, capable of accelerating the pozzolanic reaction and contributing to the pore-filling effect [11, 12]. It presents a silico-aluminous chemical composition derived from the calcination between 600 to 900ºC of a special type of clays, the kaolin [13, 14]. Its use as a cement partial replacement provides better resistance to aggressive agents and it improves the mechanical properties of concretes [11, 15-17], mainly at contents of 8 to 10% [11]. TAFRAOUI *et al.* [18] found that metakaolin can provide an increase in concrete CPR similar to silica fume. Regarding the increase in concrete compressive strength, DUAN *et al.* [19] found metakaolin to be more effective than silica fume and GBFS. Since metakaolin can be produced with lower energy con-

sumption than cement, its use also presents economic and environmental advantages [11].

Carbonation and chloride penetration are widely known aggressive mechanisms that cause reinforced concrete deterioration. These mechanisms (combined or separately) are considered in service life (SL) prediction models of reinforced concrete structures. The SL prediction by chloride penetration is important, especially for structures near the sea. Prediction by spontaneous mechanisms (real-life situation) is time consuming, being necessary the use of accelerated mechanisms of chlorides penetration, performed in laboratory tests. In the case of diffusion by immersion test, the exposure to the aggressive agent is increased [20-21]. Alternatively, in the migration test an electric current is used to propel the ionic movement from the cathode to the anode. From these tests results, represented by chlorides diffusion coefficients, it can be estimated the SL of the reinforced concrete structures [22-24].

Nevertheless, there is still debate on the most adequate methods for obtaining chloride diffusion coefficients and regarding its results sensitivity [23, 25-27]. The coefficients can be obtained by several methods, such as: 1) immersion in saline solution, presenting a chlorides concentration profile, as according to bulk diffusion test (BDT) - NT BUILD 443 [28]; 2) steady-state migration, by reading the conductivity, according to multiregime method - UNE 83987 [29]; and 3) migration with a colorimetric indicator, according to rapid migration test (RMT) - NT BUILD 492 [30]. Each method presents its advantages and limitations. The NT BUILD 443 [26] is more laborious and time-consuming in relation to the migration tests. Regarding the migrations tests, UNE 83987 [29] uses 12 V and NT BUILD 492 [30] can use up to 60 V in its procedures. However, a high value of potential difference may influence test results, causing excessive heat and damaging the concrete specimens [31]. Furthermore, some authors state that the use of pozzolans can cause oscillations in migration test results due to the reduction in the conductivity of specimens [32]. For the test using colorimetric indicator, discussions regarding the calculation method for SL prediction from its coefficients are also common [27]. Thus, the comparison of results from these different methods is of significant contribution in order to provide an improved diagnostic and increase the reliability of the chloride resistance assessment.

In this context, this study aims at assessing the possible further improvement of concrete CPR caused by metakaolin combined with HSBFC, and its effects on increasing the structure SL. In most studies, metakaolin is used with ordinary Portland cement (without SCM), thus, presenting a lack of investigations using commercial blended cements, such as HSBFC (CPIII 40 RS), commonly present in the Brazilian coastal region - the one under study. Studies suggested that this combination can improve the mechanical performance of concretes [19, 33, 34], and that this combination can be beneficial in relation to CPR. Nevertheless, there still a lack of studies on SL prediction and concrete durability of the combined use of these materials, mainly regarding CPR evaluated by different test methods. Therefore, this study analyses the chloride diffusion coefficient by different methods and performs a SL prediction of concretes using metakaolin combined with HSBFC.

2. MATERIALS AND METHODS

2.1 Materials

Materials used for producing the specimens included sulphate resistant cement CPIII 40 RS (classified as HSBFC, with GGBFS content ranging from 60 to 70%). This is a widely used cement in the Brazilian district of Espírito Santo, location where this study was conducted, due to its effectiveness against aggressive agents, such as chloride ions. High reactivity metakaolin was used as cement partial replacement in the contents of 4, 8 and 12 % - being the intermediate value (8%) the recommended by the manufacturer and commonly used in the region. Additionally, this value is close to 10%, a content found by some studies to be beneficial for mechanical and durability properties of concrete [11, 19, 34, 35]. The superior (12%) and inferior (4%) values were adopted for comparison. The physical and chemical properties of metakaolin and cement can be seen in Table 1. Local natural quartz sand previously washed and oven dried at 105 to 110 ºC was used as fine aggregate, along with granitic coarse aggregate, as seen in Table 2. The superplasticizer used was polycarboxylate based of normal setting time, liquid, with density 1,09 g/cm³.

Table 1: Physical and chemical properties of cement and metakaolin.

CHEMICAL PROPERTIES	CPIII 40 RS (HSBFC)	METAKAOLIN
SiO (%)	28.22	58.7
Al_2O_3 (%)	8.36	33.10
Fe_2O_3 (%)	1.78	1.80
CaO (%)	50.01	0.20
K_2O (%)	0.40	1.80
Na_2O (%)	0.26	0.20
MgO (%)	6.05	0.20
SO_3 (%)	1.77	0.20
Loss on ignition (%)	2.45	2.50
PHYSICAL PROPERTIES	CPIII 40 RS (HSBFC)	METAKAOLIN
True density (g/cm^3)	3.01	2.55
Bulk density (g/cm^3)	1.01	0.62
Fineness by sieve #200 (% retained)	0.4	0.92

Note: The chemical properties were provided by the cement and metakaolin manufacturers, determined using X-ray fluorescence (XRF).

Table 2: Aggregates properties.

MATERIAL	TRUE DENSITY (kg/dm^3)	BULK DENSITY (kg/dm^3)	FINENESS MODULUS	MINERALOGY/ LITHOLOGY
Sand	2.65	1.49	2.40	Quartz
Gravel (4,75/12,5mm)	2.73	1.45	5.96	Granite
Gravel (9,5/25mm)	2.75	1.47	6.95	Granite

The physical and chemical characterisation of the metakaolin was performed to verify its pozzolanic activity, as according to the requirements of Brazilian standard NBR 12653 [36] and can be seen in Table 3. Additionally, the average conductivity value according to the method of LUXÁN *et al.* [37] was used as a complement. It can be concluded that metakaolin fulfilled all the requirements according to the standard regarding pozzolanic activity. The test results of pozzolanic activity with lime, from NBR 5751 [38], with cement, from NBR 15894-2 [39], and according to LUXÁN *et al.* [37] presented values 92%, 52% and 158%, respectively, higher than the requirements, confirming the material reactivity. Furthermore, in Figure 1 can be seen the comparison of these test results of metakaolin and other SCM, such as silica fume, ornamental stone processing waste, and soda-lime glass waste.

Table 3: Metakaolin properties and the requirements for pozzolans according to NBR 12653 [36].

PROPERTIES	METAKAOLIN	NBR 12653 [36] REQUIREMENTS FOR POZZOLAN CLASS N
Retained on sieve #325	8.14%	< 20%
Pozzolanic activity with lime (MPa) at 7 days [38]	11.53 MPa	$\geq$ 6MPa
Pozzolanic activity with cement (%) at 7 days [39]	137%	$\geq$ 90%
$SiO_2 + Al_2O_3 + Fe_2O_3$ (%) [1]	93.6%	$\geq$ 70%
SO_3 (%) [1]	0.2%	$\leq$ 4%
Loss on ignition (%)	2.5%	$\leq$ 10%
Available alkalis in Na_2O_{eq} * (%) [1]	1.38 %	$\leq$ 1.5%
Pozzolanic activity according to LUXÁN *et al.* [35]	1.03 (ms/cm)	> 0.40 (ms/cm)

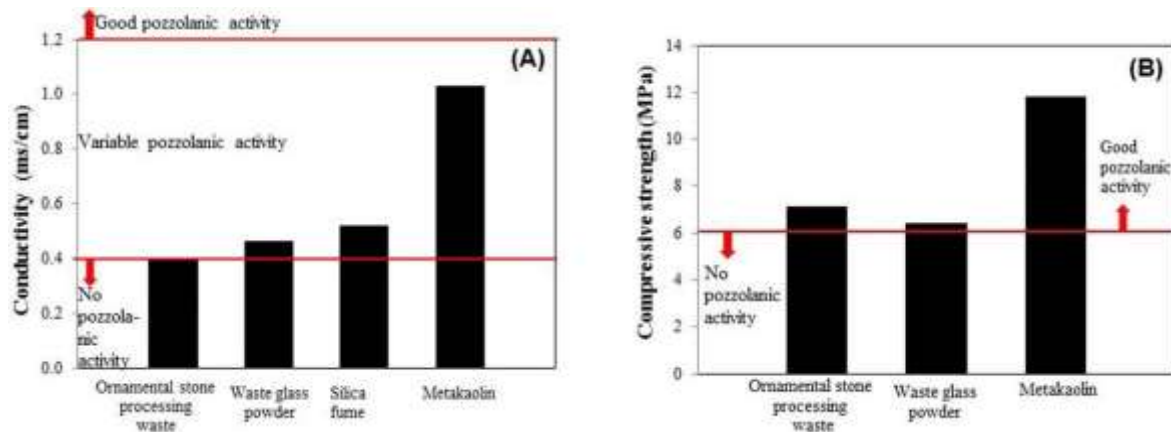Notes: [1] X-ray fluorescence (XRF). * $Na_2O_{eq} = Na_2O + 0.658 K_2O$.

Figure 1: Pozzolanic activity of metakaolin and other SCMs. (A) LUXÁN *et al.* [37]; (B) NBR 5751 [38].

2.2 Specimens preparation

Specimens were produced using a vertical axis mixer and then cured in a moist chamber for 28, 91 and 150 days. Table 4 presents the concrete mixtures proportions and the slump values. The water/cement (w/c) ratio was fixed at 0.55, being the upper limit value for concretes in aggressive maritime environment according to NBR 6118 [40]. The superplasticizer content adopted was 0.3% (by cement mass), within the manufacturer limits (0.2-2.0%), due to a previous mix design study, aiming to provide good plasticity and a slump of 100 ± 20 mm for the control mixture (REF) with the lowest superplasticizer content. Initially, the 0.2% content was attempted, and the slump range was reached for the REF mixture; however, the production of the specimens for the 8 and 12% (ME8 and ME12) metakaolin mixtures was problematic, whereas for the 0.3% superplasticizer content, it was conceivable, even with a low slump value (30 and 20 mm, respectively).

Table 4: Concrete mixture proportions.

MIXTURE	ME (%) [2]	W/C RATIO	CEMENT (kg/m³)	ME (kg/m³)	SAND (kg/m³)	GRAVEL (kg/m³)	SP (l) [3]	SLUMP (mm)
REF	0	0.55	325	0	813	1118	0.975	150
ME4	4	0.55	312	13	813	1118	0.936	80
ME8	8	0.55	299	26	813	1118	0.897	30[1]
ME12	12	0.55	286	39	813	1118	0.858	20[1]

[1] Despite the low values, it was possible to prepare the specimens according to NBR 5738 [41]. [2] ME= Metakaolin [3] SP = Superplasticizer

2.3 Testing procedures and service life prediction

Table 5 presents a summary of the standards used for the test procedures along with the size and quantity of cylindrical specimens and age of testing.

Table 5: Standards, specimens and age of testing.

PROPERTIES	STANDARD	DIAMETER x HEIGHT (QUANTITY)	MATERIAL	AGE (DAYS)
Pozzolanic activity with lime	NBR 5751 [38]	50 mm x 100 mm (6)	Mortar	7
Pozzolanic activity with cement	NBR 15894-2 [39]	50 mm x 100 mm (6)	Mortar	28
Compressive strength	NBR 5739 [42]	100 mm x 200 mm (4)	Concrete	28; 91
Rapid chloride permeability test (RCPT)	ASTM C 1202 [43]	100 mm x 50 mm (3)	Concrete	28; 91
Rapid migration test (RMT)	NT BUILD 492 [30]	100 mm x 50 mm (3)	Concrete	28; 91
Multiregime method	UNE 83987 [29]	100 mm x 20 mm (3)	Concrete	28
Bulk diffusion test (BDT)	NT BUILD 443 [28]	100 mm x 50 mm (4)	Concrete	28 (curing) + 150 (exposition)

2.3.1 Compressive strength

The test followed the procedures described in the standard NBR 5739 [42]. Four specimens of each mixture were tested at 28, 91 and 150 days.

2.3.2 Rapid chloride permeability test (RCPT) - ASTM C 1202

The rapid chloride permeability test (RCPT) followed the procedures of WHITING [44], as recommended by the standard ASTM C 1202 [43]. For each mixture, three specimens (50 mm thick and 100 mm in diameter) were extracted from the central part of the single original cylinder specimen (200 mm height, 100 mm diameter), procedure statistically validated by HELENE and MEDEIROS [45], and then tested at 28 and 91 days. The test consisted in exposing one side of the specimen to a sodium chloride solution (3% NaCl by mass) and the other to a sodium hydroxide solution (0.3 N NaOH). In each solution, a conducting copper plate was introduced, and connected to a 60 ± 0.1 V source. Electric current readings were taken every 30 min, totalling 6 h of test. The electric current multiplied by time, expressed in coulombs (C), represents the concrete resistance to chloride ions penetration. The Figure 2 presents the apparatus used and its diagram. This experiment is commonly adopted in the literature, in studies involving the concrete resistance to chloride penetration [46-48].
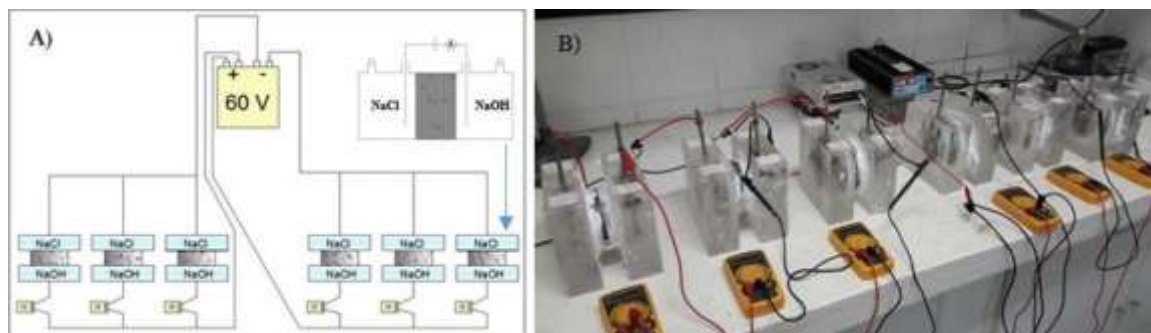

Figure 2: Rapid chloride permeability test according to ASTM C 1202 [41]. (A) Test diagram; (B) Ongoing test.

2.3.3 Rapid migration test (RMT) - NT BUILD 492

Proposed by LUPING and NILSSON [50] and consolidated in the standard NT BUILD 492 [30], the procedures of this method use potential difference and a colorimetric indicator (spray of $AgNO_3 - 0.1$ M). It provides quantitative data, as final chloride penetration depth and chloride diffusion coefficient. The test can last from 24 h, for ordinary concrete, to 96 h, for high performance concrete. The test duration and the voltage to be adopted will depend of the initial passing current reading in the concrete specimen when applied a potential different of 30 V. In this study, the average test duration for each specimen was 24 h. The test procedure is represented in Figure 3.
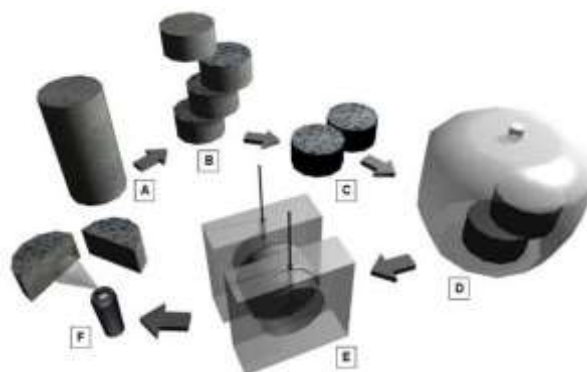

Figure 3: Procedure of migration test according to NT BUILD 492 [28]. (A) Original concrete specimen; (B) Extraction of test specimens; (C) Coating of side face; (D) Saturation; (E) Cells assembly; (F) Spray of $AgNO_3$.

To calculate the apparent chloride ion diffusion coefficient, the Equation 1 must be used, as according to NT BUILD 492 [30]. Where: D_{nssm} is the non-steady-state migration coefficient multiplied by 10^{-12} (m^2/s);

U is the absolute value of the applied potential (V); T is the average value of the initial and final temperatures in the anolyte solution (ºC); L is the thickness of the specimen (mm); x_d is the average value of the chloride penetration depth (mm), and t is the test duration (h). This equation has also been used by Kim *et al.* [28].

$$D_{nssm} = \frac{0.0239\,(273 + T)L}{(U - 2)t}\left(x_d - 0.0238\sqrt{\frac{(273 + T)Lx_d}{U - 2}}\right)$$

(1)

2.3.4 Steady-state chloride migration test (Multiregime method) - UNE 83987

For comparing the RMT - NT BUILD 492 [30] test results of non-steady-state chloride migration, the steady-state chloride migration test from UNE 83987 [29] was performed. The test is based in the migration of the ions present in an electrolyte to an opposite pole, as a response to an electric field when applied 12 V. The concrete specimen is placed between different solutions. In of the solutions, containing chloride ions (1 M NaCl), the potential difference applied attracts the ions from the negative to the positive electrolyte (anolyte), migrating and crossing the concrete specimen (Figure 4A). The increase of chlorides concentration in the anolyte is measured by the determination of the electric conductivity. The initial time period where the concentration of chlorides migration is negligible is determined as 'time lag' (t), as seen in Figure 4C, being used for the determination of the non-steady-state chloride diffusion coefficient (D_{ns}). After this period, the flow of chloride ions becomes constant, corresponding to the steady-state chloride diffusion coefficient (Ds). The test is finished when both coefficients are determined. The 100 x 20 mm specimens used in this test are obtained from the 100 x 200 mm original specimen core. PVC tubes (100 mm diameter) were used for the assembly of the apparatus, as adopted by MEDEIROS [51], according to Figure 5.
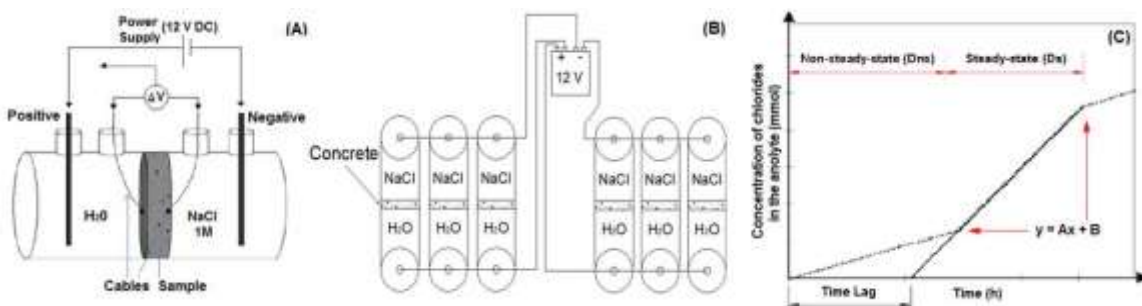

Figure 4: Steady-state chloride migration test. (A) and (B): test procedure; (C): schematic graph of test results.

Daily conductivity readings in the anolyte were made. The conductivity is then converted to chlorides concentrations by an equation, evaluating its development over time. According to the standard, the test time for ordinary concretes is approximately two weeks; however, for high performance concrete, this time can increase significantly, having been around eight weeks for the present study.
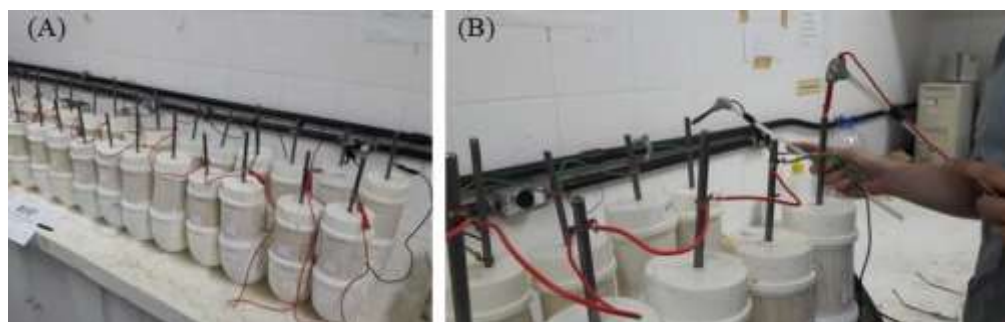

Figure 5: Chloride migration test. (A) Ongoing test; (B) Conductivity and potential difference readings.

2.3.5 Bulk Diffusion Test (BDT) - Diffusion by immersion - NT BUILD 443

The bulk diffusion test (BDT) is a method for obtaining chloride diffusion by immersion, represented in the NT BUILD 443 [28], and consists in keeping the concrete specimens immersed in a chloride solution (165g of NaCl by litre) to induce accelerated diffusion mechanisms. The specimens were cured for 28 days and immersed for 150 days. The aim of performing this test was to compare the coefficients obtained from a dif-

fusion test with those obtained by migration tests (UNE 83987 [29] and NT BUILD 492 [30]). The standard recommends splitting the cylindrical specimens in two, perpendicular to its axis. One half is used as the test specimen, being the sawed face exposed in the NaCl solution, in the other half, the initial chlorides concentration is determined. The immersed test specimen is placed in a hermetically sealed plastic container, being the solution agitated weekly. The chlorides profile is obtained by milling the material, parallel to the exposed surface. At least 8 layers must be milled. The thickness of the layers must be adjusted accordingly to the expected chloride profile, such that at least six places encompass the profile between the exposed surface and the depth reached by the chlorides. The content of chloride soluble in acid in the specimens is determined according to NT BUILD 208 [52]. The test results, superficial chlorides concentration (C_s) and non-steady-state chlorides diffusion coefficient (D_{ns}), are determined adjusting the Equation 2 for the chlorides content measured, by a linear regression analysis according to the least squares.

$$C_{(x,t)} = C_S - (C_S - C_i) \cdot erf\left(x / \sqrt{4 \cdot D_{ns} \cdot t}\right)$$
(2)

Where: C (x, t) (mass, %) is the chlorides concentrations, measured in the depth 'x' at the exposure time 't'; C_s (mass, %) is the boundary condition of the exposed surface; C_i (mass, %) is the initial chlorides concentration measured; x is the depth below the exposed surface (m); D_{ns} is the non-steady-state chlorides diffusion coefficient (m^2/s); t is the exposure time (s); erf is the Gauss error function.

2.3.6 Service life prediction

With the chloride diffusion coefficient and adopting the Fick's second law of diffusion in the non-steady-state, it becomes possible to draw a graph relating the chloride penetration depth with the SL of the reinforced structure [24, 51, 53]. The Equations 3 and 4 are developed from the Fick's second law.

$$P_{Cl} = 2(z)\sqrt{Dt}$$
(3)

$$erf(z) = 1 - \frac{C_{cl} - C_0}{C_s - C_0}$$
(4)

Where: D is the chloride diffusion coefficient (cm²/year), t is the SL (years), erf is the Gauss error function (z), P_{Cl} is the chloride penetration depth in which the chloride concentration reached a critical point for depassivation of reinforcement (cm); C_0 is the initial chlorides concentration inside the specimens (mass, %); C_s is the chlorides concentration in the specimens surface (%); C_{Cl} is the chlorides concentration over the P_{Cl} depth and time t (%).

For producing the graph, it was necessary to fix some parameters. The upper limit value considered for depassivation of reinforcement was 0.4%, related to the cement mass. This value is the upper limit of chlorides for reinforced concrete according to The International Federation for Structural Concrete (CEB-FIP) [54]. This is also an average value between the Brazilian standard NBR 6118 [40] of 0.5% and the American standard ACI-318 [55] of 0.3%. Additionally, 0.4% is the recommended value by HELENE [24] and BROWNE [56]. The chlorides concentration in the concrete surface (C_s) adopted was 0.9%, value recommended by Helene [24] as a reference for concretes with w/c ratio of 0.48 to 0.68, cement consumption of 280 to 400 kg/m³ and subjected to salt spray. However, this value is object of discussion. NUNES *et al.* [57] evaluated concrete structures older than 15 years and at different distances from the sea, obtaining the following values: C_s = 3.1% at 0 m sea distance; C_s = 1.1%, at 160 m; and C_s = 0.6%, at 630 m. GUIMARÃES *et al.* [58] suggest the following value for C_s: 3.2% at 0 m sea distance; 1.1% at 160 m; and 0.6% at a distance between 680 and 5,000 m from the sea. Thus, the 0.9% value adopted in this study is consistent with the presented literature, and a sensitivity analysis of ±0.3% was performed, being equivalent to a concrete structural application 160-680 m distant from the sea.

3. RESULTS AND DISCUSSION

A brief analysis of the test results is presented first, followed by a thorough analysis and discussion of the different test methods.

3.1 Compressive strength

Figure 6 presents compressive strength results at 28, 91 and 150 days. It can be noted that at 28 days, the me-

takaolin at 4 and 8% content (ME4 and ME8) provided an increase of compressive strength of 6%, compared to the control mixture (REF). This is justified by the pore filling effect provided by the fine metakaolin particles, along with the calcium silicate hydrate (C-S-H) gel formation in the hydrated cement compounds provided by the pozzolanic activity. [16, 17]. The pozzolanic reaction converts a material rich in silica and without cementing properties into C-S-H. Generally, the compressive strength gain remained until 150 days. At the 12% content (ME12), the cement replacement by metakaolin did not affect negatively the compressive strength, despite the decrease of clinker content (since a HSBFC is being used) - providing less $Ca(OH)_2$ (or CH) for occurring the pozzolanic activity.

DUAN *et al.* [19] evaluated concrete mixtures partially replacing cement by 10 and 20% metakaolin, and the combined replacement of 10% metakaolin and 10% GBFS. It was noted an increase in compressive strength at 28 days for the combined content; however, at 180 days, the compressive strength increase was the same for the 10% metakaolin and the combined content. Similarly, this research noted that there was no significant increase after 91 days, remaining the compressive strength somewhat stable, within the deviation limits. This is possibly also justified by the near completion of the pozzolanic reaction, when the cement enabling compounds (CH) are not available to further produce the chemical reactions.
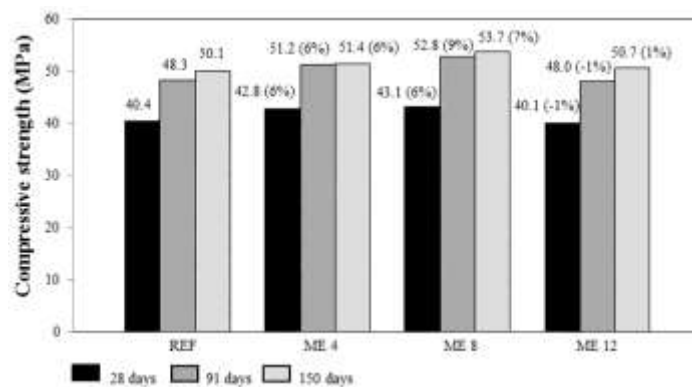

Figure 6: Compressive strength of concretes at 28, 91 and 150 days.
Note: The percentage values indicate the results variation related to the reference concrete of same age.

3.2 Rapid chloride permeability test (RCPT) - ASTM C 1202

A reduction is noted in the total charge passed of 35, 41 and 54% for the ME4, ME8 and ME12 mixtures, respectively, compared to the REF, at 28 days (Figure 7). This presents an increase in CPR of mixtures with higher metakaolin content. Furthermore, at 91 days, it can be noted a decrease higher than 50% of charge passed for the ME8 and ME12 mixtures, in comparison with the REF. The results at 28 days are consonant to that of BERNAL *et al.* [34], which assessed the CPR of concretes replacing HSBFC by metakaolin at 10 and 20% content, noting that the chloride ion penetration reduced at 28 days due to the use of metakaolin; however, at 91 days, there was not significant difference between the mixtures.
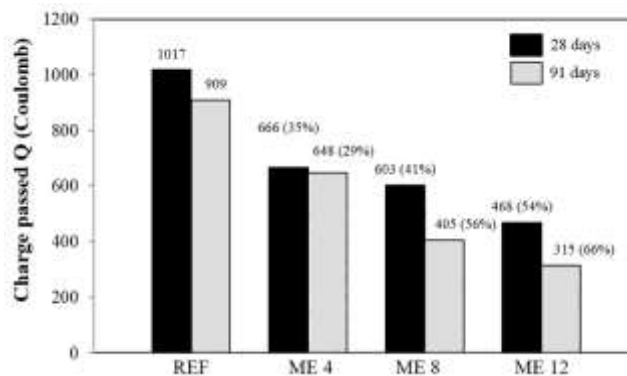

Figure 7: Total charge passed of mixtures.
Note: The percentage values indicate the results variation related to the reference concrete of same age.

3.3 Rapid migration test (RMT) - NT BUILD 492

In Figure 8, it can be seen the chlorides concentration in the specimens using the colorimetric indicator. ME12 presented a lower penetration depth compared to the other mixtures, demonstrating a better CPR at this metakaolin content. The final depth results were obtained by the average of seven depth readings, as seen in Figure 8E, and the coefficients were determined by Eq.1. A high precision digital calliper was used for the depth readings.
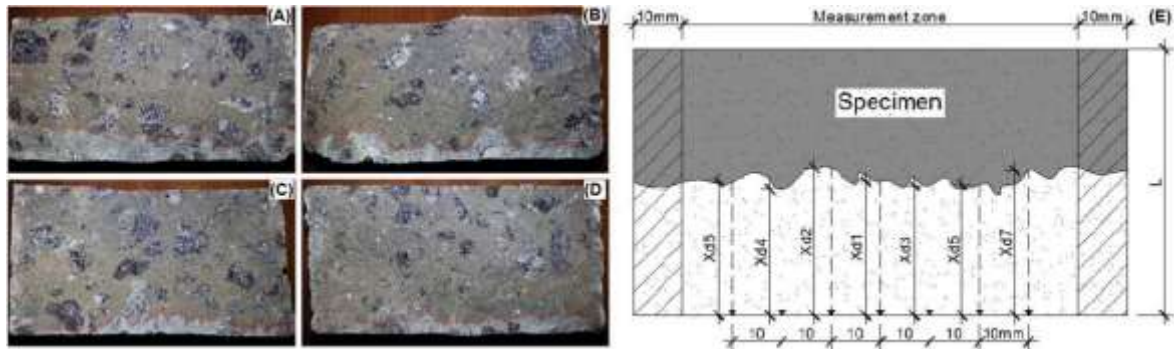

Figure 8: Specimens after spray of AgNO$_3$ – NT BUILD 492 [28]. (A) REF; (B) ME4; (C) ME8; (D) ME12; (E) Measurement of chloride penetration depths.

3.4 Steady-state chloride migration test (Multiregime method) - UNE 83987

Figure 9 presents the chloride concentration profile of the multiregime method for REF and ME8 mixtures. The REF mixture presented an earlier start of the steady-state compared to the ME8 mixture; thus, highlighting the improved CPR of the mixture with metakaolin. From the profile graphs of the mixtures, it can be determined the chloride migration coefficients.
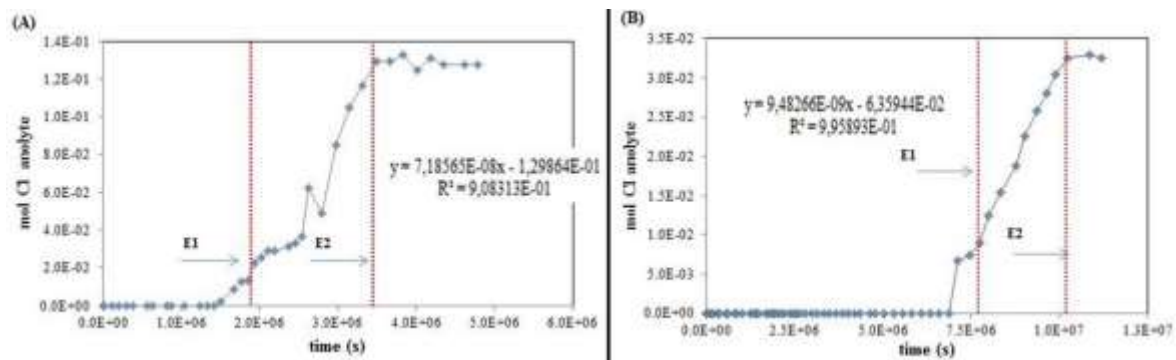

Figure 9: Steady-state chloride migration test results - UNE 83987 [29]. (A) REF mixture; (B) ME8 mixture.

3.5 Bulk Diffusion Test (BDT) - Diffusion by immersion - NT BUILD 443

Table 6 presents the superficial (C_s), initial (C_i) and final layer (14 mm) chlorides concentration of the mixtures along with the D_{ns}. It can be noted that at 14 mm depth, the only mixture with a concentration higher than 0.05% was the REF, supporting that metakaolin can reduce the chloride concentration in greater depth. Furthermore, there is a reduction of 29 and 9% in D_{ns} for the ME8 and ME12 mixtures, respectively, in comparison with REF, confirming the positive effect of metakaolin in increasing CPR, as also observed in the migration test results. For the ME4 mixture, the influence of metakaolin on D_{ns} is not significant, possibly due to the low influence of metakaolin at this content in improving the compactness of the cement paste and the interfacial transition zone.

Table 6: Bulk diffusion test results - NT Build 443 [28].

MIXTURES	Cs (%)	Ci (%)	CHLORIDES IN THE FINAL LAYER - 14 mm (%)	Dns (x 10^{-12} m²/s)
REF	0.358	0.0262	0.067	1.97
ME4	0.368	0.0248	0.019	2.05
ME8	0.445	0.0295	0.022	1.40
ME12	0.518	0.0246	0.019	1.79

3.6 Different methods – Mixtures classification and comparison of results

Table 7 presents D_{nssm} (NT BUILD 492 [30]), D_{ns} (UNE 83987 [29]) and the qualitative classification of the mixtures, according to ASTM C 1202 [41] and GJØRV [53]. It can be noted that all mixtures are classified as low or very low chloride ion penetration (according to ASTM C 1202 [43]) or having very high or ultra-high CPR (according to GJØRV [53]). This confirms the effectiveness of combining metakaolin with HSBFC in providing resistance against chlorides in an aggressive maritime environment. The REF mixtures presented coefficients in the range of 3 to 3.3 x 10^{-12} m²/s, approximately, being these results consonant to GJØRV [6], SENGUL [7] and BIJEN [8], who evaluated concrete mixtures with high GBFS content. DUAN *et al.* [19] evaluated concrete mixtures partially replacing cement by metakaolin and GBFS in 10 % content, separately, and the combined replacement of 10% metakaolin and 10% GBFS. The authors noted that the combined replacement provided the lowest coefficient (NT BUILD 492 [30], at 28 days), 1.5 x 10^{-12} m²/s, which was somewhat close to the one found in this study (1.81 x 10^{-12} m²/s) for the ME8 mixture; whereas for the metakaolin and GBFS separate replacements, the coefficient was 2 and 4 x 10^{-12} m²/s, respectively, being the control mixture (no replacement) with 10.0 x 10^{-12} m²/s.

Table 7: Total charge passed, chloride coefficients from migration tests and mixtures classification.

MIXTURE	AGE (DAYS)	RCPT – ASTM C1202 [43] CHARGE PASSED (Coulombs)	RMT – NT BUILD 492 [30] Dnssm (x 10^{-12} m²/s)	MULTIREGIME – UNE 83987 [29] Dns (x 10^{-12} m²/s)	ASTM C 1202 [43] CHLORIDES PENETRATION (Charge passed)	GJØRV [59] CPR CLASSIFICATION (Chloride diffusion coefficient)
REF	28	1017	3.67	-	Low	Very high
ME4	28	666 (-35%)	2.25 (-39%)	-	Very low	Ultra-high
ME8	28	603 (-41%)	1.81 (-50%)	-	Very low	Ultra-high
ME12	28	468 (-54%)	1.79(-51%)	-	Very low	Very high
REF	91	909	2.98	3.33	Very low	Very high
ME4	91	648 (-29%)	2.06 (-44%)	2.65 (-20%)	Very low	Ultra-high
ME8	91	405 (-56%)	1.49 (-50%)	2.37 (-29%)	Very low	Ultra-high
ME12	91	315 (-66%)	1.39 (-53%)	1.66 (-40%)	Very low	Ultra-high

This study shows that the HSBFC partial replacement by metakaolin at 8 and 12% content can reduce the chloride coefficients at 91 days by up to 53%, approximately (Table 7). Thus, the pozzolanic activity of metakaolin, as verified by the characterisation study (Table 3), added to the cementing properties of GBFS can provide a more compact concrete microstructure, as it was noted in the microstructure studies of TATRAOUI *et al.* [18], DUAN *et al.* [19] and LI *et al.* [60]. According to ZIBARA *et al.* [61], the chloride diffusion through concrete depends, mainly, of its microstructure and of the capacity of these ions fixation. For mixtures with ordinary Portland cement, the key fixation mechanism is the formation of Friedel's salt and aluminates related complexes from the tricalcium aluminate (C_3A) [62]. This fixation mechanism is similar for the concrete mixtures with SCM; thus, the metakaolin, by having in its chemical composition 33.10% alumina (Al_2O_3) (Table 1), fosters the formation of C_3A compounds and helps to increase the chloride ions fixation.

In Figure 10, a comparison of chloride ions migration and diffusion test results is presented. The average chloride diffusion coefficient obtained for the REF mixture was 2.76, reaching 1.61 for the ME12, reinsuring the positive effect of metakaolin. The average coefficient of variation (CV) of the mixtures amongst

the tests is 21%. As means of comparison, this value is close to the accepted (20.2%) in the ASTM C1556 [63], the American standard equivalent to the NT BUILD 443 [28], for tests performed at different laboratories. It can also be identified a higher correspondence between the test results of NT BUILD 443 [28] with NT BUILD 492 [30], presenting a CV between both tests results of 13%, similar to the CV accepted (12.3%) by the ASTM C 1202 [43] standard. This higher correspondence between both tests agrees to the observations of LUPING and SØRENSEN [23] and SCHIESSL and LAY [64]. LUPING and SØRENSEN [21] recommend the NT BUILD 443 [26] as a reference test method for verifying chloride penetration into concrete. Nevertheless, they also state that a rapid non-steady-state method, equivalent to NT BUILD 492 [30], can be used as an alternative method due to its simplicity, rapidity, good precision and compatibility with NT BUILD 443 [28] results. Furthermore, it can be noted an increase of chloride resistance at 150 days. This can be justified by the improvement of the interfacial transition zone (ITZ) between cement paste and aggregate, as observed by DUAN *et al.* [19] in concretes with metakaolin and GBFS at 180 days. Due to this fact, a more compact microstructure is obtained, enhancing the CPR. The beneficial aspect of using metakaolin at later ages was also noted by MENHOSH *et al.* [65].
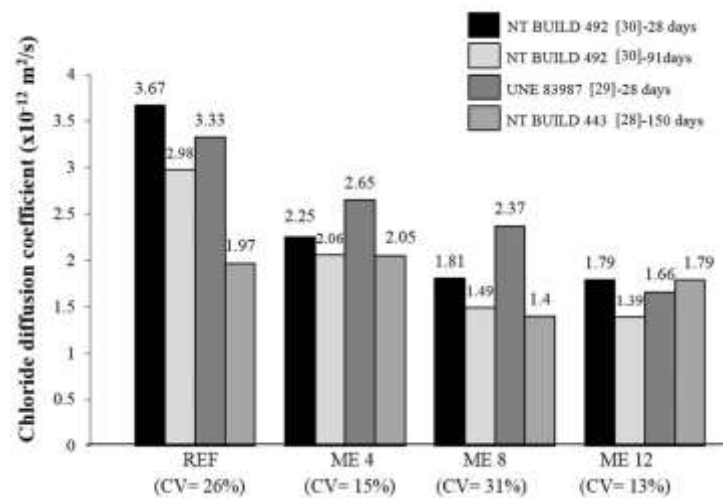

Figure 10: Representation of chlorides diffusion coefficient by different methods.

Since the RMT test (NT BUILD 492 [30]) presented to be a good test alternative to its more time-consuming counterparts (NT BUILD 443 [28] and UNE 83987 [29]), a further comparison is presented in Figure 11. A good relationship was noted between NT BUILD 491 and the total charge passed, from ASTM C 1202 [43] (Figure 11A) (qualitative test without coefficient results). Additionally, with the increase of compressive strength, the values of chloride diffusion coefficient decrease, thus, producing more chloride resistant concretes (Fig. 11B).
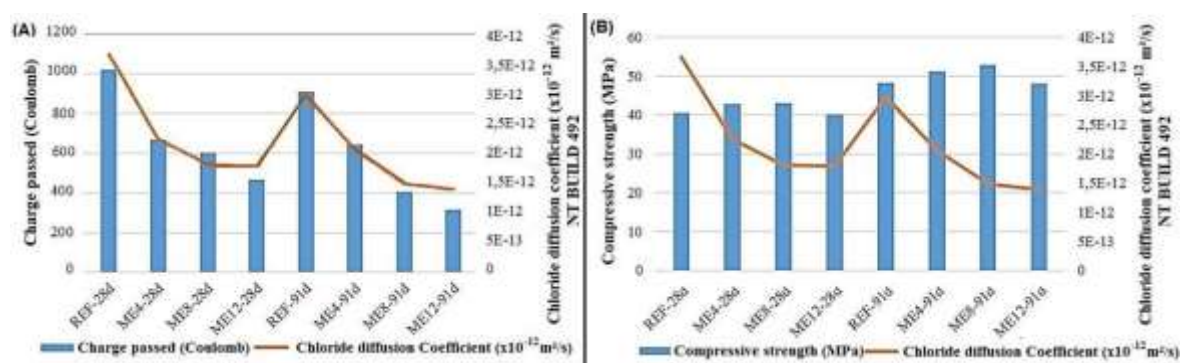

Figure 11: Relation between chloride diffusion coefficient from NT BUILD 492 [30] and: (A) Total charge passed from ASTM C 1202 [43]; (B) Compressive strength.

The summary of this study results can be seen in Table 8. It can be verified that the mixture with 8% metakaolin content (ME8) presented as the most efficient mixture analysed, reconciling the benefits of good mechanical strength and elevated CPR.

Table 8: Summary of the study results.

TEST	PERCENTAGE CHANGE [a]		
	ME4	ME8	ME12
Compressive strength (28 days)	6% ↗	6% ↗	Insignificant
Compressive strength (91 days)	6% ↗	9% ↗	Insignificant
Compressive strength (150 days)	6% ↗	7% ↗	Insignificant
28-day chloride diffusion coefficient (m²/s) (NT BUILD 492)	-39% ↘	-51% ↘	-51% ↘
91-day chloride diffusion coefficient (m²/s) (NT BUILD 492)	-31% ↘	-50% ↘	-53% ↘
91-day chloride diffusion coefficient (m²/s) (UNE 83987)	-20% ↘	-29% ↘	-50% ↘
150-day chloride diffusion coefficient (m²/s) (NT BUILD 443)	4% ↗	-29% ↘	-9% ↘
28-day total charged passed (coulombs) (ASTM C 1202)	-35% ↘	-41% ↘	-54% ↘
91-day total charged passed (coulombs) (ASTM C 1202)	-29% ↘	-56% ↘	-66% ↘

Note: [a] Related to the REF mixture.

3.7 Statistical analysis of the chloride diffusion coefficient test results

The chloride diffusion coefficient presented in Figure 12 is resulting from the Analysis of Variance (ANO-VA) obtained from the different test methods used. Statistical analysis has been employed to verify not only the comparative analysis between different methods, but also the influence of HSBFC partial replacement by metakaolin. The significance level (α) adopted was 5%. The null hypothesis analysis (H_0) adopted implied that all the averages are statistically equal, thus, the metakaolin use did not generate significant results. The p-value obtained from this analysis was 0.01%, which was inferior to the significance level adopted of 5%. Thus, it can be concluded that at least one of the averages is different from the other, thereby, demonstrating that the metakaolin provided significant changes in the concrete. Furthermore, it was adopted the Tukey's test (Figure 13), aiming to compare the average of each treatment pair, determining the difference between them for a given confidence interval.
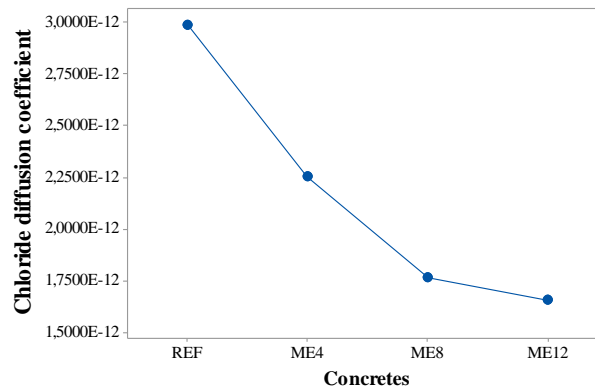
Figure 12: Individual values of chloride diffusion coefficient.

From this statistical analysis, it can be identified the values relating the chloride diffusion coefficient and the content of cement partial replacement by metakaolin (Figure 12). It can be noted a decrease in the chloride diffusion coefficient due to the use of metakaolin. The ME4, ME8 and ME12 provided a reduction of 22.44, 40.94 and 44.63%, respectively, related to the REF. For the Tukey's test (Figure 13), the analysis is performed in groups of two, therefore, those that do not share a group can be considered significant with each other. If the interval of the pair of averages does not include the zero, the difference between the averages is significant. Thus, it can be identified that the average chloride diffusion coefficient varied significantly from the REF related ME8 and ME12; whereas the ME4 did not present a significant increase in CPR.
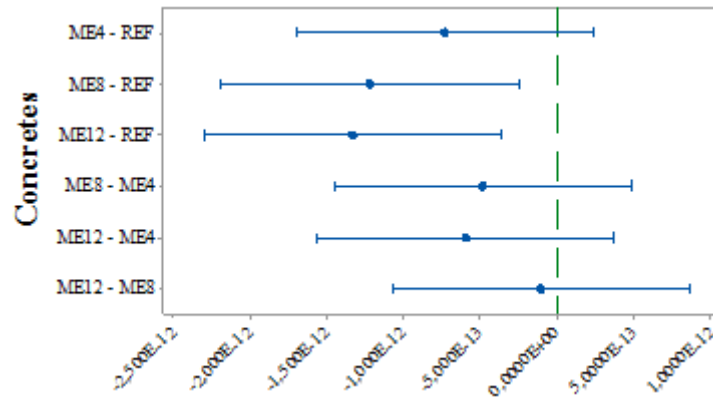
Figure 13: Tukey's test of chloride diffusion coefficient.

3.8 Service life prediction

The average values from the ANOVA were used to estimate the structure SL according to the Fick's law of diffusion, becoming possible to build graphs relating the chloride penetration depth and the structure SL (Figure 14). The value of C_s used was $0.9\pm0.3\%$, consistent with the presented literature. Additionally, the SL used in this study is equivalent to the initiation period (time to initiate depassivation) and does not include the propagation period of the corrosion. The use of Fick's Law for service life prediction was used for comparative purposes, and its absolute values should be considered with caution. According to Helene [24], it is one of the most important methodologies used for estimating the service life using chloride diffusion coefficient.

This coefficient in concrete structures is influenced by the electrolytes available, concrete microstructure (permeability), oxygen availability, temperature and the microclimate (wind and rain) of the region where the structure is built [24,51]. These factors combined can increase the chloride diffusion coefficient, fostering the chlorides ingression in the reinforced structure and initiating the corrosion mechanisms.

The reinforcement depth of 4 cm is specified in the Brazilian standard ABNT NBR 6118 [40] for reinforced concrete structures exposed to marine environments. Considering a C_s of 0.9%, the predicted SL at this depth for ME8 and ME12 mixtures are 25 and 26 years, respectively, representing an increase of approximately 70% compared to the REF (15 years). A similar value of SL attained by the ME12 mixture at 4 cm depth (26 years) is only reached in the REF mixture for a reinforcement depth of 6 cm (33 years); thus, for a considered structure SL of 25 years, the metakaolin can provide a reduction of reinforcement depth of approximately 30%. By adopting the 5 cm reinforcement depth – the highest value specified in the mentioned standard – the SL predicted for the REF is 23 years, whereas for the ME8 and ME12, the predicted SL is 39 and 41 years, respectively. Moreover, similar values of the SL predicted for the REF at 5 cm can be reached by using the ME8 and ME12 mixtures with 4 cm reinforcement depth. The pozzolanic activity of metakaolin, by reacting with the hydrated compounds of cement at later ages, provided significant gains in CPR, delaying the corrosion initiation - equivalent to the SL estimated.
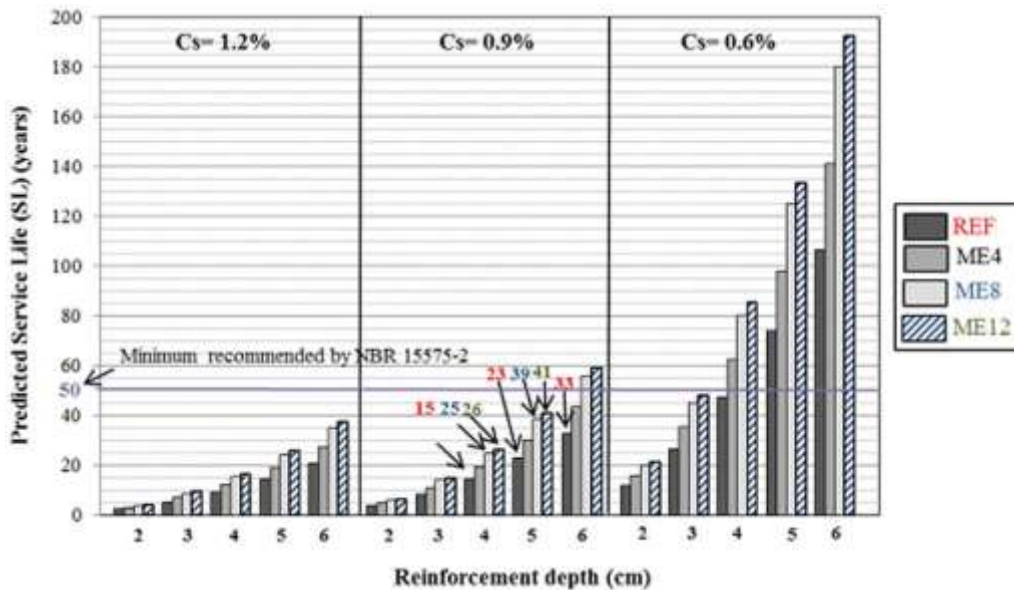
Figure 14: SL prediction of mixtures at different reinforcement depths.

According to the Brazilian standard NBR 15575-2 [66], named as 'the performance standard', the minimum recommended SL for reinforced concrete structures (such as foundations, pillars, beams, slabs, load-bearing walls, retaining walls) is 50 years. For a C_s of 0.9%, this SL could only be reached with 6 cm reinforcement depth and the ME8 or ME12 mixture. At an application with moderate salt spray (C_s of 0.6% - over 630 m distant from the sea, as reported by NUNES *et al.* [57] and GUIMARÃES *et al.* [58]), a reinforcement depth of 4 cm must be used for ME8 and ME12 mixtures to meet the performance standard requirements. Using this depth, the estimated SL for ME12 mixture is 85 years, whereas for the REF is 47 years. Additionally, for 3 cm reinforcement depth, the minimum (50 years) is almost reached for the ME12 mixture (48 years).

It should be emphasised that there are some limitations to the SL prediction, as it depends of other factors besides the chlorides concentration, such as oxygen availability, presence of electrolyte (humidity) and the concentration differences. Thus, this analysis serves more as a comparative measure, than an absolute one.

4. CONCLUSIONS

1. The use of metakaolin as a HSBFC partial replacement presents to be a viable option aiming at improving the technological, ecological and economic aspects of concrete, by increasing the CPR (thus, the SL), and by reducing the required reinforcement depth.

2. The use of metakaolin as HSBFC partial replacement at 4 and 8% content could slightly improve the compressive strength, and at 8 and 12% content, it significantly increased CPR.

3. The 8% metakaolin content mixture presented as the most efficient for overall mechanical and durability properties of concrete. At 91 days, the compressive strength increased 9% and the total charge passed reduced 56%, in comparison to the control mixture. Furthermore, the average diffusion coefficient (three test methods) reduced 40.94%.

4. The concretes produced with HSBFC without metakaolin presented a very high CPR, according to a qualitative assessment of the diffusion coefficient. Nevertheless, the use of metakaolin as partial HSBFC replacement could significantly increase the predicted SL, approximately 70% at 8 and 12% metakaolin content.

5. Compatibility was identified between the results of the non-steady-state chloride diffusion coefficient obtained by the chlorides migration and diffusion tests, with a CV of 21%. Between the migration tests, the one with the better correspondence with the BDT (NT BUILD 443) was the RMT (NT BUILD 492).

6. As noted in the literature, this study showed that the metakaolin use in concretes with high GBFS content can provide significant benefits related to the increase of CPR. Nevertheless, this study showed that this happens also at later ages (over 150 days).

7. The literature argued that the use of high voltage provided significant variation in the test results. Conversely, this study showed a similarity between diffusion coefficients from RMT (NT BUILD 492), which used high voltage, and BDT (NT BUILD 443).

8. The SL prediction analysis showed that the mixture without metakaolin usually required a concrete cover increase of over 1 cm to attain a SL similar to mixtures with 8 and 12% metakaolin. At the specified baseline scenario, the minimum SL of 50 years could only be attained by using 8 or 12% metakaolin as HSBFC replacement.

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