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Abstract:

In order to increase the durability of concrete in maritime environments, it is often recommended to use supplementary cementing materials such as silica fume or blast furnace slag. Metakaolin, even of low purity, also allows a significant improvement of the chloride diffusion. The aim of this work was to evaluate the characteristics of concretes based on flash metakaolin when exposed to a marine environment. Concretes based on CEM I cement (more than 95% of clinker) or CEM II/A cement and metakaolin were compared to a cement often used in a marine context (SR cement). The results show that a substitution of metakaolin for CEM I or CEM II/A allowed a reduction of the coefficient of chloride migration into the cementitious paste on the one hand and, on the other hand, gave results similar to those of sulfate resistant cements with a low C_3A content. Then, tests of accelerated corrosion confirmed the beneficial effect of metakaolin in a marine context. Finally, a predictive model was used to estimate the lifespan of the mixtures exposed to chloride ions. The model showed that the substitution of metakaolin for cement could significantly increase the lifespan of the structures.

1   Introduction

Several important concrete structures are built in marine environments. This special environment requires particular attention to be paid to the concrete formulation as, during its service life, chloride ions diffuse into the cement paste through the porous network toward the steel bar and corrode it. There are two main obstacles that can delay corrosion initiation:

1) The cement paste itself, as it is the quality of the porous network that manages the kinetics of chloride ion diffusion through the material.

2) The passivation layer of the steel, as this protective layer avoids the initiation of corrosion by the first chloride ions.

The main objective is to find solutions to improve the quality of these two barriers in order to increase the lifespan of the structure. Actually, some alternatives exist already, such as the use of specific cement (PM in France [1]) or the replacement of conventional cement by supplementary cementing materials (SCMs). Silica fume [2, 3], blast furnace slag [4, 5] and fly ash [6, 7] have already been studied in concrete exposed to chloride penetration. The use of metakaolin in concrete exposed to a marine environment has been studied in several previous works [8-20], mostly by authors working with pure, very reactive metakaolin. When part of the cement was replaced by metakaolin, the chloride migration coefficient was reduced [8, 9]. For instance, Courard et al. [9] showed that the migration coefficient decreased by 170% for a 10-15% substitution and, after one year of testing, no diffusion was observed with 20% of MK. This result was confirmed by Poon [11], Boddy [12] and Gruber [13], who showed that using 5% to 20% of metakaolin decreased the chloride diffusion and the chloride penetrability (total charge passed) by a factor of 2 to 7. Valipour et al. [14] showed that tests in natural conditions (e.g.

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tidal range area) gave results similar to those of the accelerated test: when metakaolin was used, the chloride penetration decreased in comparison with the control concrete results. The purity of the metakaolin was also important, as the decrease in chloride diffusion of concrete based on low purity metakaolin was smaller than with a highly reactive metakaolin [8]. The beneficial effect of metakaolin has been compared to the effects of other SCMs, like fly ash [15] or silica fume. The use of highly reactive metakaolin gave the same chloride diffusion as a concrete based on the same silica fume content [16, 17]; Poon et al. showed that this results was true whatever the Water/Binder (W/B) ratio (W/B=0.3 and 0.5 in this work) and with 5 to 15% of metakaolin versus 5 and 10% of silica fume and two W/B ratios: 0.3 and 0.5 [11].

It is also important to study the kinetics of the steel bar corrosion. Güneyisi et al. [18] showed that cement replacement by metakaolin improved the performance of concrete against corrosion. They showed that the current corrosion of reinforcing steel was lower in a concrete based on metakaolin (up to 15%). A similar result was found by Kuber Parande et al. [19], as they showed a relation between the quantity of metakaolin (up to 15%) and the improvement of concrete performance. Finally, Batis et al. [20] studied the effect of the metakaolin purity and found that, for pure (90%) and non-pure (50%) metakaolins, a maximum substitution rate of 10% allowed the corrosion resistance to be maintained.

The aim of the present work is to study the capacity of low purity flash metakaolin to protect concrete intended to be used in a marine environment. The metakaolin came from a flash calcination process, which refers to the combustion near a flame (temperature around 700 °C) of kaolinite particles for a few tenths of a second. Data involving chloride migration and accelerated corrosion tests are presented to highlight the effect of flash metakaolin used in replacement of a fraction of Portland cement (CEM I), in comparison with commercialized blended cements based on GGBS (CEM II/A-S and CEM III/A), which are already used in concretes destined for marine environments. A predictive model calculates the lifespan of a concrete structure from the time taken by the chloride to diffuse from the solution to the steel bar.

2   Materials and method

2.1   Materials

The binders used in this study were four French cements of the same strength class, 52.5, and in conformity with the European standard EN 197-1 [21]: two Portland cements with more than 95% of clinker (CEM I 52.5N from two different plants, named clinker a and clinker b), and two blended cements containing ground granulated blast furnace slag (GGBS) at 11% (CEM II/A-S 52.5N PM, made with clinker b) and 62% (CEM III/A 52.5 L PM-ES, made with clinker a). The GGBS cements complied with French standards NF P 15-317 [1] and NF P 15-319 [22] (in France, medium and low-C_3A cements are named "PM" and "ES" or "PM-ES", respectively. EN 197-1 uses the term "SR-cements" but not for CEM II/A-S and CEM III/A). The cement technical data gave by the producer are summarized in the table 1.

The metakaolin (MK) used came from a flash calcination process, which refers to the combustion near a flame (temperature around 700 °C) of kaolinite particles for a few tenths of a second [23]. This process is faster and consumes less energy than traditional methods (e.g. rotary kiln) [24]. Due to the low purity of the deposit, the MK used in this study contained an impurity rate near 50%, mainly

composed of quartz and mullite. The quartz content led to a significant decrease in the surface area and therefore to the water demand compared to a pure metakaolin. The strength activity index of this MK remained around 1 [24]. The properties of the MK are given in Table 1 and this metakaolin was in conformity with standard NF P18-513 [25], which is the specific French standard giving the specifications and conformity criteria for MK to be used in concrete.

The High Range Water Reducing Agent (HRWRA) was a polycarboxylate (PCE) type available as a commercial solution (density = 1.05 kg/m^3; active solid content by weight = 30.5%). The aggregates used were crushed limestone: a marine sand (0-4mm) and two gravels (6-10mm and 11-22mm).

Table 1 – Chemical, mineralogical and physical properties of the cements and metakaolin.

	CEM I (clinker a)	CEM I (clinker b)	CEM II/A-S (clinker b)	CEM III/A (clinker a)	Metakaolin
Chemical and mineralogical properties					
SiO_2 (%)	20.79	21.00	22.40	29.10	67.10
Al_2O_3 (%)	5.40	4.60	5.30	8.50	26.80
CaO (%)	65.90	64.00	63.00	49.90	1.12
MgO (%)	1.10	1.40	2.00	5.00	0.11
Fe_2O_3 (%)	2.22	2.50	2.40	1.00	2.56
Na_2O (%)	0.18	0.10	0.11	0.40	0.01
K_2O (%)	0.30	0.86	0.80	0.32	0.12
TiO_2 (%)	0.19	0.30	0.30	0.44	1.37
SO_3 (%)	3.40	3.30	2.40	2.67	---
Cl^- (%)	0.03	0.04	0.04	0.26	---
Loss on ignition (%)	1.20	1.00	0.60	1.35	0.84
Mineralogy of the clinker (Bogue, in %)					
C_3S	62.0	66.8	66.8	62.0	
C_2S	12.0	11.6	11.6	14.0	
C_4AF	6.0	7.5	7.5	6.0	
C_3A	12.0	8.0	8.0	12.0	
Blast furnace slag content (%)	0	0	11	62	
Physical properties					
Specific gravity (g/cm^3)	3.12	3.15	3.13	2.98	2.51
Blaine specific surface area (cm^2/g)	3500	3450	3840	4260	165000 (BET)
Compressive strength of mortars at 28 days (MPa)	67.3	64.1	65.6	64.6	-
Strength activity index (28 days) (20% MK)	-	-	-	-	1

2.2 Mix compositions/concrete mixture

The concretes were designed according to the French annex of European standard EN-206 [26], which defines the specifications and performance levels of concrete. The exposure class XS3, corresponding

to the most severe corrosion induced by chlorides from sea-water (tidal, splash and spray zones), was chosen. The prescriptive approach of the French standard for XS3 concretes required a minimum concrete strength class of C35/45 (i.e. compressive strength at 28 days of 35 MPa on cylinders or 45 MPa on cubes), a water-binder ratio lower than 0.50 and a minimum equivalent binder content of 350 kg/m^3. It should be noted that the concept of equivalent binder means that a given SCM can replace a limited fraction of the Portland cement. The SCM mass is affected by a coefficient k, usually equal to or lower than 1 and depending on the efficiency of the SCM. For instance, a coefficient of 1 means that 1 kg of Portland cement can be replaced by 1 kg of SCM, the total binder content being considered as unchanged in the formulation. The replacement rate is limited and depends on the nature of the SCM. In the case of metakaolin, the French annex of EN 206 allows the replacement of 15% of CEM I or 10% of CEM II/A by MK, with a coefficient, k, of 1 if the MK complies with standard NF P18-513 [25].

The concrete mixture designs are given in Table 2. All concretes had the same equivalent binder content (350 kg/m^3) and water/binder ratio (0.45). The aggregate content was the same for all mixtures and the grading curve was chosen according to the Dreux method [27]. The targeted slump was 150 ±30 mm. The HRWRA contents, adjusted to reach the targeted slump, were always lower than 3% in order to respect the limit values given by the technical datasheet.

Four reference concretes were cast, two for CEM I (clinkers a and b), one for CEM II/A (clinker b) and one for CEM III/A (clinker a). MK was used in different proportions (10 to 25%) in replacement of CEM I (15, 20 and 25%) and CEM II (10 and 15%). A supplementary concrete (CEM I (15+5)) was cast using 15% of MK in replacement of CEM I (clinker a), and 5% more MK in addition to the cement (i.e. replacement of the sand). The ranges of replacement intentionally exceeded the values permitted by the standard (15% for CEM I and 10% for CEM II/A) in order to evaluate the efficiency of MK beyond the actual, and conservative, regulatory practice. As the price of the MK was similar to that of the commercial cements, all formulations of this study were equivalent in price per cubic meter of concrete.

2.3 Methods

Concrete batches were mixed for 3 minutes. After demolding, concretes are kept during 28 days in a wet room (95%RH, 20°C).

2.3.1 Slump

Slump tests were performed with the Abrams' cone, following standard NF EN 12350-2 [28]. Compressive strength tests were carried out after 2, 7, 28 and 90 days [29] on specimens 11 cm in diameter x 22 cm high using a hydraulic press that could exert a pressure of up to 300 tons. Each measurement was the mean value of three replicate samples.

2.3.2 Water porosity

The connected open porosity of the concrete was evaluated as the water accessible porosity according to the French standard (NF P18-459) [30]. This standard is based on the AFPC-AFREM procedure and has been used in several published works ([31], [32], [33]).

Table 2 - Mixture proportions of concrete

| Mixtures | Mixture proportions of concrete (kg/m³) | | | | | | | W/B |
	Cement	MK	Sand (0-4mm)	Fine aggregate (6-10mm)	Coarse aggregate (11-22mm)	Total Water	HRWRA** (% of binder)	
CEM I a (clinker a)*	350.0	0.0	850	200	840	157	0.90	0.45
CEM I a 15	297.5	52.5	850	200	840	157	1.55	0.45
CEM I a 20	280.0	70.0	850	200	840	157	1.40	0.45
CEM I a 25	262.5	87.5	850	200	840	157	1.41	0.45
CEM I a (15+5)	297.5	52.5	850	200	840	157	1.54	0.44
CEM I b (clinker b)	350.0	0.0	850	200	840	157	0.90	0.45
CEM I b 15	297.5	52.5	850	200	840	157	1.18	0.45
CEM II/A-S	350.0	0.0	850	200	840	157	0.90	0.45
CEM II/A-S 10	315.0	35.0	850	200	840	157	0.90	0.45
CEM II/A-S 15	297.5	52.5	850	200	840	157	1.47	0.45
CEM III/A	350.0	0.0	850	200	840	157	0.76	0.45

* bold refers to reference concretes; ** HRWRA (in liquid form), in % wt. of binder, adjusted to reach equivalent slump.

The test consists of measuring the masses of dry sample, wet sample and wet sample immersed in water, the accessible water porosity being given by equation 1.

$$p = \frac{Ms - Md}{Ms - Mw} \times 100$$ (Equation 1)

where p is the porosity, Mw is the mass of wet sample immersed in water, Md is the mass of dry sample and Ms is the mass of the saturated sample. The tests were performed on three replicate samples after a curing period of 28 days.

2.3.3 Mercury porosity

Mercury intrusion porosimetry was carried out at 20 °C using two complementary models of mercury porosimeter: Thermo Finnigan Pascal 140 and Pascal 240 with respective pressure ranges from 0.1 to 400 kPa and 0.1 kPa to 200 MPa. The results were then combined to obtain the pore distribution over a radius ranging from 2.5 nm to 100 micrometers. Prior to testing, 90-day cured paste samples (water/binder ratio of 0.35) were dried in an oven at 50°C and then cooled to room temperature in desiccators. The drying was checked by regular weighing of the sample. The sample was considered dry when the mass loss was lower than 0.05% in 24h.

2.3.4 Chloride migration

Chloride diffusivity was assessed from the steady state migration test, Nordtest NT Build 492 [34], after 28 days of wet curing (95%RH, 20 °C) for all mixtures and after 3 years for mixtures CEM I, CEM I 15, CEM I 20 and CEM I 25. The tests were done on three replicate samples. This test consists of measuring the chloride penetration depth in an accelerated chloride migration test (constant electric field), the depth of penetration being measured thanks to the precipitation of chloride ions after spraying with a silver nitrate solution.

2.3.5 Gaz permeability

Gas permeability was tested using the XP P18-463 standard [35] using a Cembureau device. The measurements were made at relative pressures of 1.0 bar to assess apparent permeability, and between 1.5 and 4.0 bars to assess permeability by the Klinkenberg approach. The test was performed on three replicate samples after 28 days of cure and complete drying of the sample (105 °C).

2.3.6 Corrosion test

The chloride permeability (corrosion test) was assessed using the embedded steel method, NT Build 356 [36]. This test used a specimen (100 x 100 x 200 mm) with a reinforcing steel rod (ϕ10 mm) placed in its center. The specimen was partly immersed in a solution of 3 % NaCl and a direct current voltage (5 V) was applied between the embedded steel rod and the specimen surface. The test was carried out at 20 °C and 60% RH. The current flow and the time of failure of the specimen were measured and the results expressed as the time in days needed for the chloride ions to reach the steel rod and so raise the current. The tests were run on two replicate samples cured for 28 days.

2.3.7 Electric resistance

The electric (ohmic) resistance of the concretes, which was due to the loss of electric potential caused by the modification of mobile species movement into the matrix, was determined by means of an impedance test. The measuring system was an impedance scanner working in a data range from 40 Hz to 110 MHz [37]. The samples used were discs 11 cm in diameter and 3 cm in height. The test was performed after 2 years of curing, on two replicate saturated samples. Samples were saturated with a recomposed cement pore solution [38], containing (in mol/m^3): 31.5 of Na$^+$, 122.8 of K$^+$, 3.3 of Ca^{2+}, 1.7 of SO$_4^{2-}$, and 142.9 of OH$^-$.

3 Test results for concrete mixtures

3.1 Workability

Figure 1 gives the characteristics of the concretes in the fresh state, i.e. the slump and the HRWRA content relative to binder necessary to maintain the slump at equivalent values (only Ref CEM I with cement B had a lower slump and would have needed additional HRWRA). It can be seen that the use of MK led to an increase in admixture content, especially for MK contents higher than 15 % (up to +72% more HRWRA required). These results are in agreement with those found in the literature for the same type of metakaolin [39], and were to be expected considering the specific surface area of MK, which can be as much as 15 times higher than that of cement. However, this higher admixture demand remained limited compared to that found with very pure, for which the increase can reach more than 300% in certain cases [40].
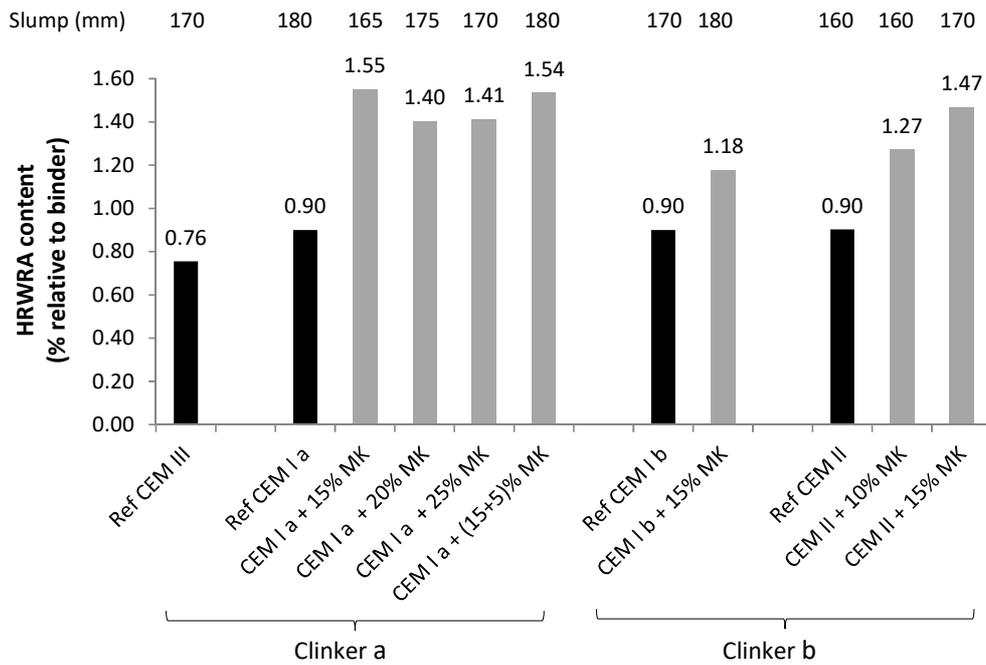
Figure 1 – HRWRA content (relative to binder) necessary to obtain a constant workability of concrete (except Ref CEM I with cement B, which had a lower slump).

3.2 Compressive strength

The compressive strength results between 2 and 90 days are given in Figure 2 for all concretes. The two horizontal lines (A and B) stand for the recommendation of minimal 28-day strength of an XS3 concrete (line A at 35 MPa, according to NF EN 206/CN [26]) and the targeted 28-day strength for concrete (line B at 40 MPa). These two minimal values were exceeded by all the concretes at 28 days, meaning that flash MK, even used at 25%, allowed concretes to be designed that satisfied the norm and specific project requirements in terms of strength.

Comparison with CEM I

The kinetics of strength development was lower for MK concretes at 2 and 7 days (30-50% decrease), but the strength gap no longer existed at 28 days for replacement rates of up to 20%. The behavior of the concrete with MK used in replacement of cement and sand (15+5) was equivalent to that of 20% MK concrete. In the case of cement b, the difference of strength between [b]CEM I and [b]CEM I + 15% MK was negligible as early as 7 days. The improvement of the strength with time was due to the well known pozzolanic activity of MK.

Comparison with CEM II

The use of MK in replacement of a fraction of CEM II/A-S (initially containing 11% of slag) did not lead to any delay in strength development, since the results were similar from 2 days to later ages. In that case, the pozzolanic reactions of the metakaolin did not hinder the speed of hydration of the binder based on clinker and slag. This shows the interest of using ternary blended cement involving slag and MK [41].

Comparison to CEM III

For all mixtures with MK (CEM I + 15, 20 or 25% MK and CEM II + 10 or 15% of MK), the compressive strength results at 2, 7, 28 and 90 days were higher than the ones obtained with the CEM III. In contrast with the concrete made with CEM III, concretes containing 15 and 20% MK (replacement of CEM I), and 10 and 15% MK (replacement of CEM II) reached the 28-day strength requirements as early as 7 days. These effects were due to the faster development of the reactivity of MK, already evoked in the literature, whereas slag usually slows down the hydration reaction [42].
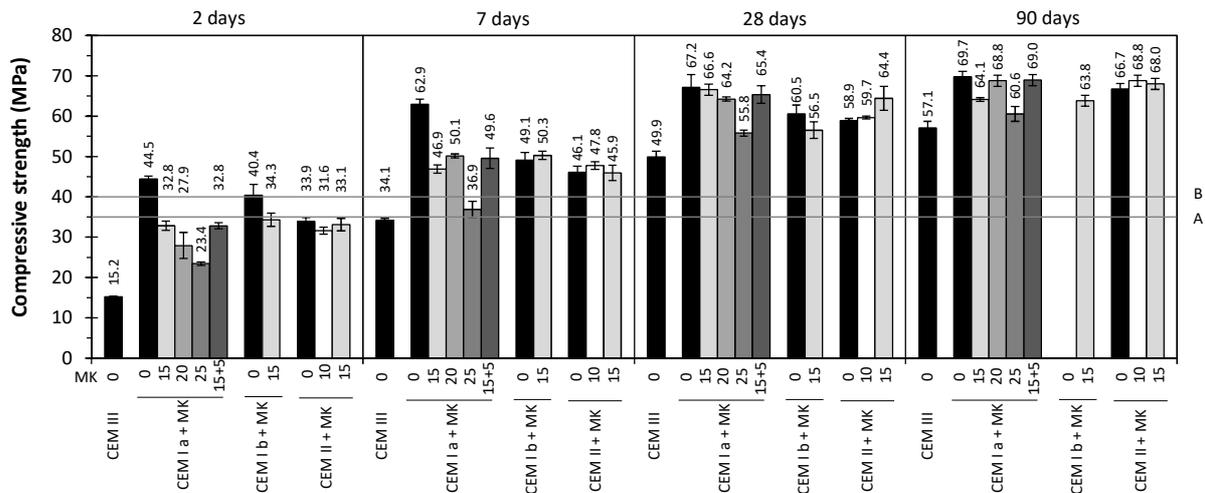
Figure 2 - Compressive strength of concrete mixtures between 2 and 90 days. A (35 MPa) is the minimum value of 28-day strength required for the XS3 exposure class, according to NF EN 206-1/CN. B is the design 28-day strength of the concrete mixtures.

3.3 Porous network

3.3.1 Water porosity

The porosity accessible by water, which gives an idea of the intrinsic characteristic of the porous network as it relates to the concrete composition (e.g. water-binder ratio), is summarized in Figure 3. All MK mixtures (except 25%) had an equivalent or lower porosity than the CEM III reference concrete. The general trend showed a slight increase of the porosity with increasing use of MK, which is in agreement with previous results [39]. These results were seen for CEM I and CEM II cements and had no apparent links with the compressive strength evolution (Figure 3). It cannot be excluded that the higher HRWRA content of the MK concretes led to a higher air content, since many PCE admixtures are known to have a slight air entraining effect. Nevertheless, all concretes formulated with up to 20% of MK were in the same durability class as their respective references (considering the dispersion of the results), when referring to durability classes given in the AFGC AFREM 2004 sustainability guide [43].
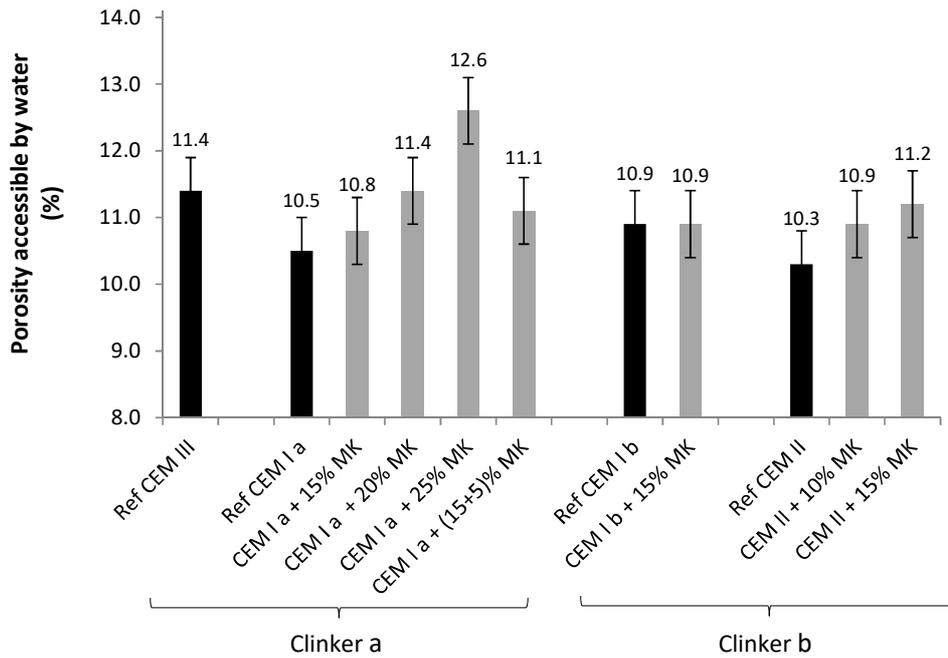
Figure 3 – Water porosity of concrete mixtures (28 days)

3.3.2 Gas permeability

The gas permeability of all concretes is given in Figure 4. Most of the results were in the same order of magnitude, especially when the dispersion of the results ($\approx$30%) was considered. This means that there was no significant gap between commercial cements (CEM I and CEM III) and mixtures containing MK. Only 20% MK concrete (with cement a) and 15% MK concrete (cement b) showed a slight decrease of their permeability. According to the AFGC AFREM 2004 sustainability guide [43], most of the concretes can be considered to have high durability (high durability class ranging from 10. 10^{-18}m^2.s^{-1} to 100. 10^{-18}m^2.s^{-1}). In the case of CEM II, a trend of increased permeability was seen when MK was used, especially for 15% MK. However, it remained within the values of the reference concretes (CEM I and CEM III). According to the results of this work, it was difficult to establish a clear relationship between permeability and compressive strength.
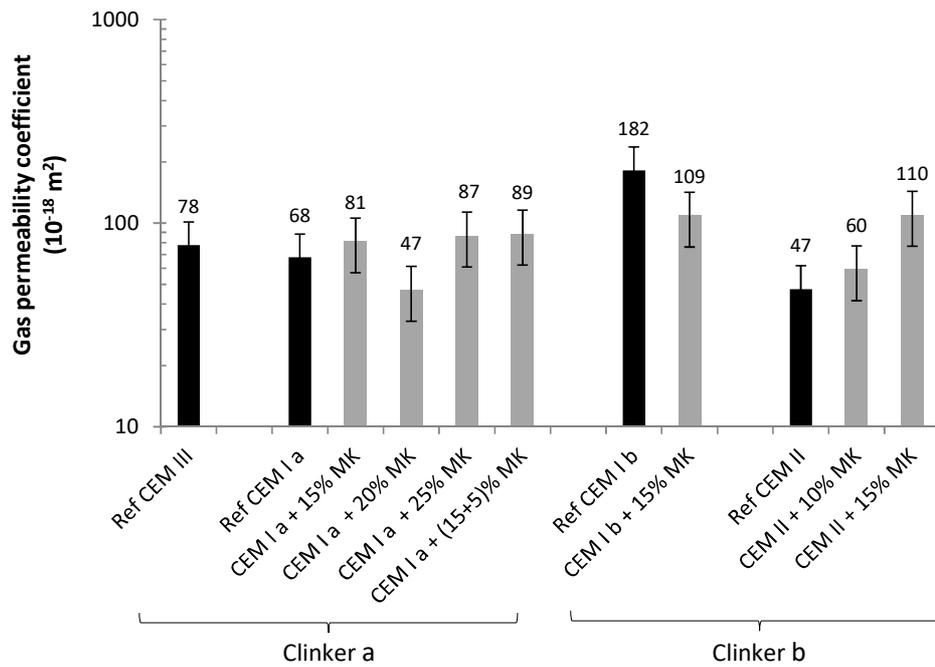
Figure 4 – Gas permeability of concrete mixtures (28 days)

3.4   Chloride and corrosion

3.4.1   Chloride migration

The chloride migration test helps to characterize the resistance of concrete to the penetration of chlorides. The results are summarized in Figure 5. It can be seen that the concretes with MK had a 28-day migration coefficient equivalent to or lower than those of the reference concretes made of CEM I and CEM II, but slightly higher than the CEM III reference. The variations in the chloride migration coefficients were not significant enough to strongly affect the durability class proposed in the AFGC AFREM 2004 sustainability guide [43]. All the results involving MK were within the values of reference concretes (Figure 6) and confirm the small variations among all the mixtures. The optimal replacement rate was around 15% of MK and led to a decrease of the coefficient by 30% and 45% relative to [a]CEM I and [b]CEM II, respectively.

The effect of MK regarding the chloride migration coefficient was less marked than in other studies reported in the literature. This could be due to:

- the lower reactivity of the MK used in the present study (less pure than the high purity metakaolin often found in other works). For instance, Boddy et al. [44] and Gruber et al. [45] saw a strong reduction in the migration coefficient at 28 days when they used very high purity metakaolin.
- the shorter curing time (28 days), a 28 days the pozzolanic reaction is not finished. For instance, Cabrera and Nwaubani [46] obtained lower chloride migration coefficients than control for 15% MK pastes cured for 60 days.

The beneficial effect of curing time on MK concretes was confirmed by the measurement of the chloride migration coefficient after three years of curing, for CEM I (clinker a) and replacement rates of 15, 20 and 25% (hollow bars on Figure 5). A significant decrease in the coefficient was seen for all

MK concretes, showing the improvement of the migration properties at later age, due to the development of the pozzolanic properties. According to San Nicolas et al. [47] and Siddique [48], the role of MK regarding the migration of chlorides would be to limit the ingress of these ions by increasing the tortuosity of the porous network and by binding them into new-formed products (Friedels salt).
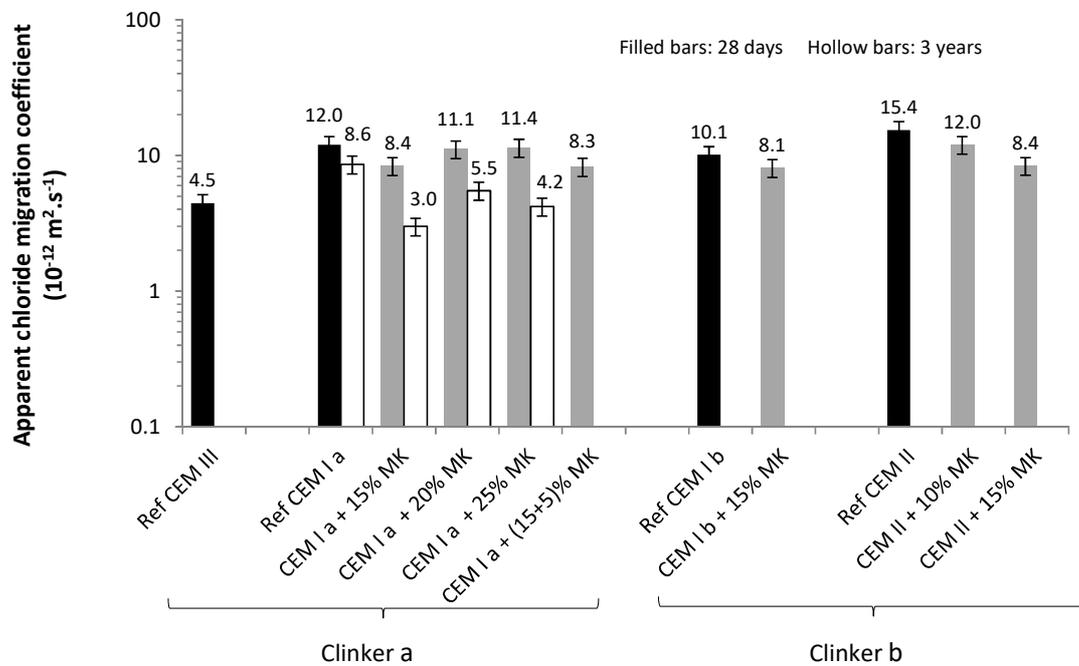
Figure 5 – Chloride migration coefficient of concrete mixtures (after 28 days and 3 years of curing)
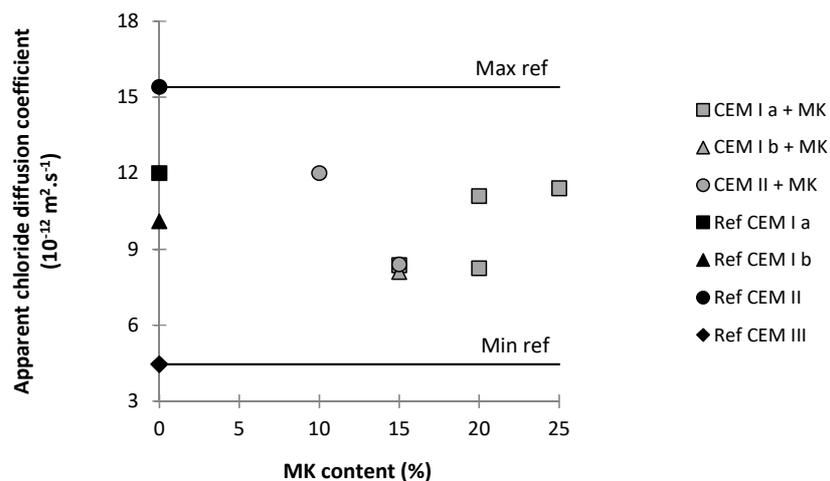
Figure 6 – Chloride migration coefficient of concrete mixtures versus MK content (28 days)

3.4.2 Accelerated corrosion

The accelerated corrosion test characterizes the capacity of a concrete to resist the penetration of chloride ions under an electric potential difference. The start of the corrosion is defined as the time when an increase occurs in the current measured in the samples. Figure 7 shows the different times obtained for the mixtures with and without MK.

The most evident observation that can be made from the results of this test is the significant effect of MK in delaying the corrosion initiation, which means that the chlorides took much more time to reach the steel bar than in all the other reference mixtures. It can be seen that, the higher the MK content in the concrete, the better the behavior against corrosion. This conclusion was true for the two CEM I tested, as well as for CEM II. The differences were much more marked in this test than in the chloride migration test presented in the previous section; this point is discussed later. It should be noted that, unlike the situation in migration tests, the CEM III concrete showed the worst behavior of all concretes, with a start of corrosion at 41 days, a delay four times shorter than the 160 days of the best results obtained with 25% of MK.
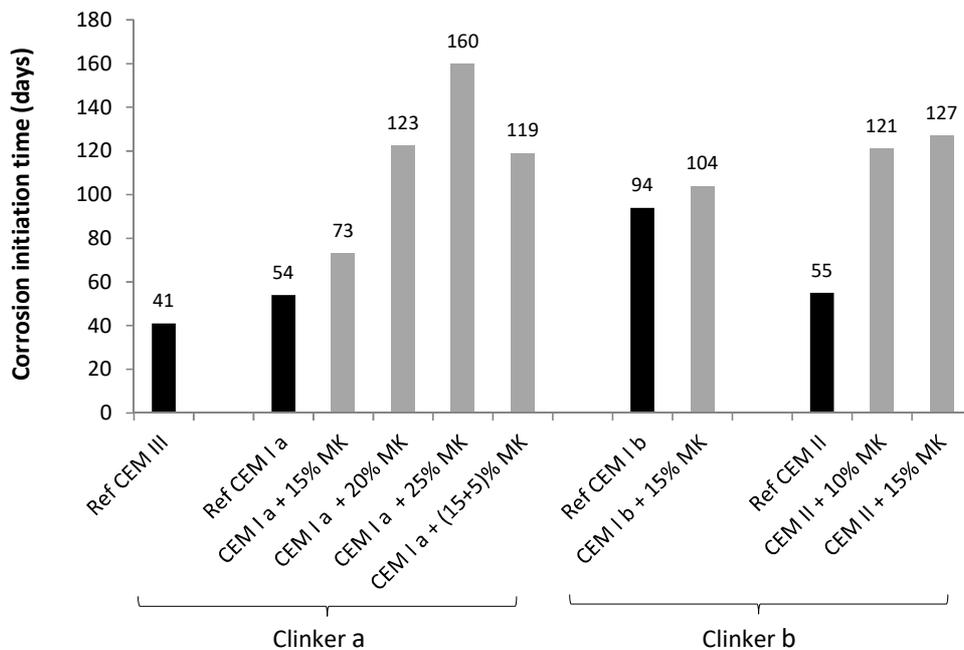
Figure 7 – Corrosion initiation time (accelerated tests) of concrete mixtures aged of 28 days

4 Discussion

4.1 Performance of MK concretes

4.1.1 Durability indexes

The first analysis of the results was carried out on the basis of the equivalence concept described in several performance based approaches. In order to highlight the effect of flash-calcined metakaolin and to evaluate its performance in comparison with reference, commercially available cements,

durability indexes were calculated for all MK mixtures. These indexes were defined as ratios between concrete containing MK and reference concretes (Figure 8). If durability was to be improved, the water porosity, chloride ion migration coefficient and gas permeability had to be as low as possible. In contrast, the corrosion initiation time had to be as long as possible. If these ratios were greater than 1, the durability of concrete with MK was considered to be improved. Indexes involving migration coefficient, gas permeability and corrosion were calculated in logarithms (base 10) as the phenomena responsible for these measurements (e.g. migration or permeability) obeyed power laws.

Figure 8 reports the durability indexes of MK concretes relative to CEM I (clinker a), CEM II and CEM III, the last two containing 11 and 62% of slag, respectively. The mean dispersion on the indexes is represented by the grey shadow (average dispersion values justified in sections 3.2 and 3.3).

Durability index vs porous network

The general trend regarding water porosity and permeability was that the durability index was of the same order of magnitude as for reference concretes. The index values for these parameters were sometimes slightly higher or slightly lower than 1, but the differences between the mixtures were not significant when the dispersion of the results was taken into account. Only the permeability index involving CEM II was lower for MK, due to a fairly low value of the permeability of CEM II concrete.

Thus it can be said that the porous network of concretes with up to 25% of MK is at least equivalent to those of reference concretes made of CEM I or CEM III/A-S.

Durability index vs chloride ingress

The performances of MK concretes against chloride ingress and their corrosion time were excellent most of the time (i.e. durability index > 1), especially when compared with the CEM I and CEM II references. Only CEM III presented peculiar behavior, since the chloride migration and the corrosion initiation time followed opposite trends. On the one hand, the performance regarding chloride migration was always better than in the case of MK, while, on the other hand, the behavior against corrosion was inadequate.

Reinforced concrete can be modeled by an electric circuit (Randles model) with two resistances in series:
- The concrete resistance depends on the porous network tortuosity and on the interactions between cement paste and chloride ions (the concrete resistance is inversely proportional to the chloride diffusion coefficient).
- The polarization resistance, R_p, depends on the interface conditions between steel and concrete (a passivation of the steel bar by iron oxide will increase the R_p).

According to Aguirre-Guerrero et al. [49], the R_p of a concrete containing 10% of metakaolin is higher than the control sample (100% CEM I). In this work, the concrete resistance (shown with the diffusion coefficient) of the concretes with metakaolin was better than for the CEM I. Addition of the two resistances explains why the start of the steel corrosion embedded in a metakaolin paste was postponed in comparison with the control sample. The R_p of GGBS concrete is supposed to be lower than that of the control sample [50, 51]. Even if the use of slag improved the chloride diffusion coefficient, it is possible for the sum of the concrete resistance and the R_p to be lower than for CEM I.

This could explain why the steel bar embedded in the CEM III matrix started to corrode earlier than the one in the CEM I (41 days against 54 days).

Thus, it can be said that the resistance to chloride ingress of concretes with up to 25% of MK is at least equivalent to those of reference concretes made of CEM I or CEM II/A-S.

Durability indexes

$\ast$ $\quad$ Water porosity index $= \dfrac{\text{Porosity of reference concrete}}{\text{Porosity of concrete with MK}}$

$\times$ $\quad$ Permeability index $= \dfrac{\log(\text{Gas permeability of reference concrete})}{\log(\text{Gas permeability of concrete with MK})}$

$-$ $\quad$ Chloride diffusion index $= \dfrac{\log(D_a \text{ of reference concrete})}{\log(D_a \text{ of concrete with MK})}$

$-$ $\quad$ Accelerated corrosion index
$= \dfrac{\log(\text{Corrosion inition time of concrete with MK})}{\log(\text{Corrosion inition time of reference concrete})}$

Dispersion on the indexes:

Figure 8 – Durability indexes defined as the ratios between concrete containing MK and reference concretes (CEM I, CEM II, CEM III)

4.2 Specific effect of MK on chloride ingress

4.2.1 Refinement of the porosity

Mercury intrusion porosimetry was performed on three cement pastes made of binders that gave high, medium and low migration coefficients on concrete (Figure 9): CEM I (12.0 x 10^{-12} m²·s^{-1}), CEM I+15% MK (8.4 x 10^{-12} m²·s^{-1}) and CEM III/A-S (4.5 x 10^{-12} m²·s^{-1}).

Despite a higher total porosity accessible by the mercury, the average diameter of the pores in MK mixture (16.6 nm) was about half that in the CEM I paste (26.6 nm). As seen in Figure 9, the refinement

of the porosity was mainly due to the high quantity of fine pores (8 nm). Similar results can be found in the literature with a micro pore proportion of 69.6%for the CEM I and 84.0% for the CEM I + 15% MK [47], the decrease of the diameter being attributed to a better hydrate development, due to the pozzolanic reaction producing extra C-S-H and C-A-S-H. The refinement of the porosity is known to be efficient in reducing the chloride ingress into the concrete matrix [52].

The refinement of the pore size did not explain the decrease in the migration coefficient in the case of CEM III, since this binder led to the largest average pore size. The large porosity of the network was probably due to the high slag content and the short curing time of the samples (28 days), slag being known to have a lower kinetics of hydration than MK.

	CEM I	CEM I a + 15% MK	CEM III
Total porosity (%)	12.4	15.0	15.
Average pore diameter (nm)	26.6	16.6	38.
Modes (nm)	8 and 50	8 and 30	8 and 4
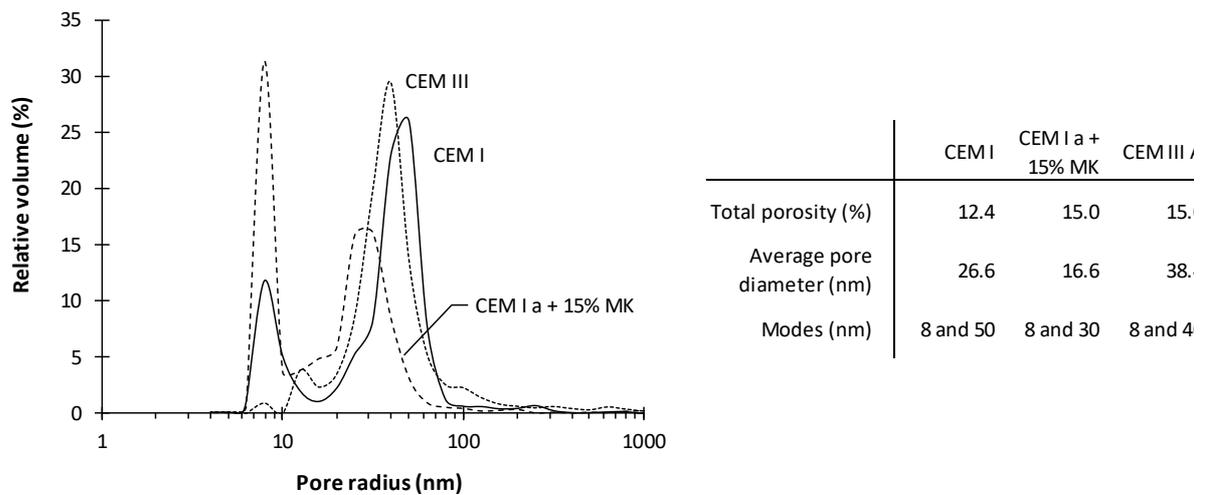
Figure 9 – Pore size distribution of cement pastes (CEM I, CEM I + 15% MK, CEM III) cured for 28 days, obtained by mercury intrusion porosimetry.

4.2.2   Paste-steel interface

Another effect usually seen with SCM is an improvement of the ITZ in mortars and concretes. It has been shown that MK allows the porosity of the ITZ to be reduced [53] due to the consumption of portlandite by the pozzolanic reaction. Micro-hardness measurements have also shown that metakaolin has a greater effect on the microstructural strength of the ITZ, suggesting that metakaolin contributes to a more homogeneous microstructure of the matrix [51]. In consequence, the ITZ produced in samples containing metakaolin does not differ significantly from that of the bulk paste in terms of its chloride diffusion resistance [53]. The wall effect responsible for the ITZ between cement paste and aggregates probably also exists between the paste and the steel bar, and might be partly responsible for the difference of behavior between CEM I and MK-based matrices.

Figure 10 illustrates the superficial aspects of steel pieces pulled out of a cement paste composed either of pure CEM I or of CEM I + 15% MK. It can be seen from the SEM images that the presence of MK in the paste led to better adhesion, probably because the interface was denser and stronger. A semi-quantitative calculation of the paste remaining on the steel (obtained from the binary image, where the black pixels correspond to the paste) showed that mixtures with MK left three times more paste than mixtures composed of cement only. This denser interface and better adhesion of the paste

on steel might be responsible for a local decrease in diffusion and could participate in the higher resistance to chloride ingress, as well as constituting a barrier to corrosion development at the interface.
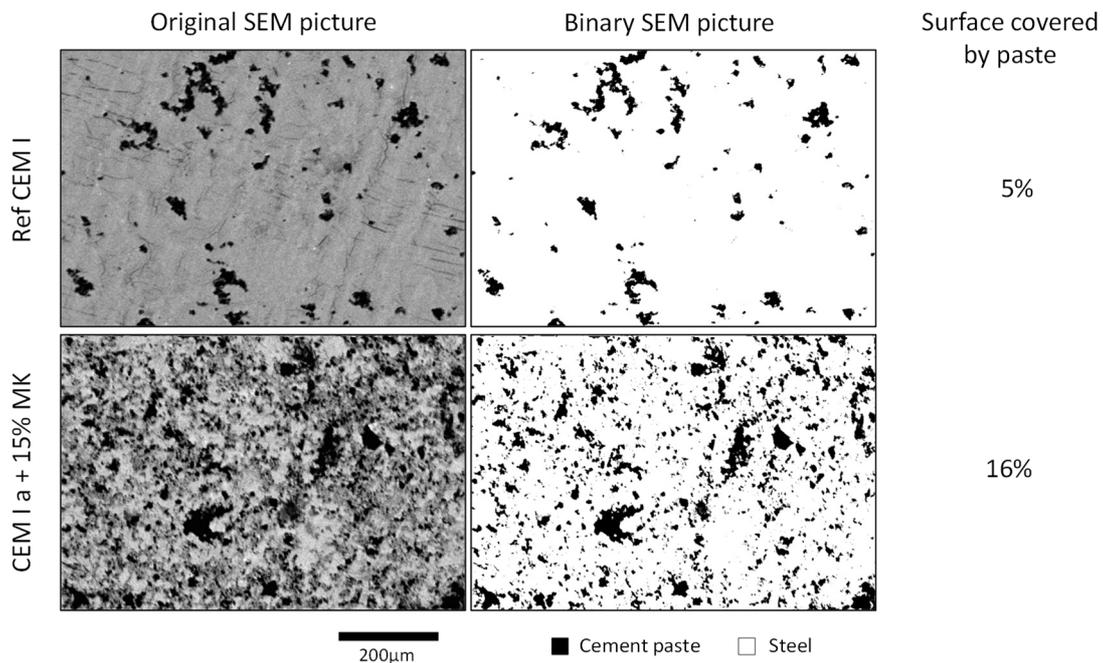
Figure 10 – SEM observations and surface quantification of the cement paste remaining on steel plates after the separation of the two materials. Cases of CEM I and CEM I + 15% MK.

4.2.3 Electric resistance

The resistance of four concretes (CEM I, CEM I + 15% MK, CEM I + 20% MK, and CEM I + 25% MK) was assessed by means of impedance tests. Prior to testing, the samples were saturated for 48 hours with a solution reproducing the pore solution of the CEM I concrete [54]. This step was used to limit the variation in the conductivity of the pore solution itself, as the composition can be quite different from one concrete to another, especially when reactive SCM such as MK are used [55].

Figure 11 plots the resistance against the corrosion initiation time. It can be seen that the resistance increased regularly with the substitution of metakaolin for cement, increasing by more than 30% between a control and a sample based on 25% of MK. This means that the use of MK could decrease the intensity of the current in the matrix, for a given difference of potential. The increase of the resistance in blended cements has already been noted by other authors. For instance, Mendoza et al. [30] measured values of 380 Ω and 750 Ω for concrete made of CEM I (pure clinker) and CEM V (clinker, slag and fly ash), respectively. Neithalath et al. [56] reported values of 600 Ω (cement alone), 900 Ω (cement with fly ash), and 2500 Ω (cement with silica fume). These authors linked the increase of the impedance to the refinement of the porous network.

Figure 11 also shows a good correlation between resistance and corrosion initiation time, so the very good behavior of MK against corrosion might be partly explained by the capacity of MK concrete to resist the propagation of a current.
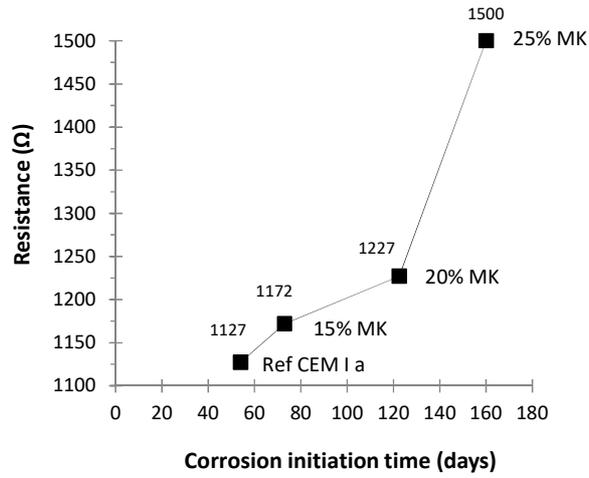
Figure 11 – Correlation between the resistance *of the concretes (impedance tests) and the time necessary for corrosion to be initiated (accelerated corrosion test), for concretes based on CEM I with and without MK.*

4.3 Service lifetime of concrete based on chloride ingress - Use of a predictive model

Models can estimate the chloride profile depending the immersion time of the civil engineering structure in question. A critical threshold is fixed for chlorides, above which the steel bar starts to depassivate and to corrode. The model used in this study was based on an analytic solution of Fick's second law (Deby et al. [57]). It takes the physical and chemical characteristics of the matrix into account. The chloride concentration (% of concrete mass), depending on the depth in the sample and the immersion time, is given by equation 1.

$$C(x,t) = C_{ref}^{tot} \, erfc\left(\frac{x}{2\sqrt{D_a t}}\right)$$

(1)

The apparent diffusion coefficient depends on the effective diffusion coefficient and the fixation isotherm C_b (equation 2).

$$D_a = \frac{D_e}{p + \rho_d \frac{\partial C_b}{\partial c}}$$

(2)

The isotherm slope is determined with equation 3.

$$\frac{C_b}{2 \times C_{ref}} = \frac{\partial C_b}{\partial C} = K(2ref)$$

(3)

The analytic equation is written (equation 4):

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$$C(x,t) = C_{ref}^{tot} \, erfc \left(\frac{x}{2\sqrt{\dfrac{D_e}{p + \rho_d.K(2c_{ref})}.t}} \right)$$

(4)

with :

C_{ref}^{tot} : Total chloride concentration in the concrete (% of concrete mass)

c_{ref} : Chloride concentration in the sea water (mol/m^3)

D_e : Effective coefficient of diffusion (m^2/s) (determined with the apparent coefficient of diffusion)

p : Porosity (%)

ρ_d : Density (kg/m^3)

C_b : Chloride fixation isotherm (parameters dependent on the quantity of C-S-H and Afm)

K : Isotherm slope

x : Depth (m)

t : Exposure time (s)

D_a : Apparent diffusion coefficient (m^2/s)

The physical and chemical characteristics of materials are derived from the tests studied in Section 3; the data are summarized in Table 3. In order to evaluate the time necessary for the chlorides to reach the steel bar, a coating thickness of 5 cm was fixed [47]. Figure 12 summarizes, for a fixed age, the chloride gradient of CEM I, CEM I + 15, CEM III/A, and CEM II/A-S. The age of 27 years was chosen because it corresponds to the time necessary to exceed the critical threshold in the case of the CEM I mix. The critical threshold corresponds to the chloride concentration that allows the steel bar corrosion to start and was taken as 1% of the binder mass, as proposed by Deby [57]. Equation 5 was used to determine the critical concentration (Cc) in kg/kg of concrete.

$$Cc = \frac{0.01 m_{binder}}{(\rho_d (1 - p))}$$

(5)

It could be noted that this moment corresponds only to the appearance of corrosion and not to the deterioration of the structure. Several years are necessary after corrosion initiation before structure deterioration becomes visible.

After 27 years of exposure to chlorides (Figure 12), the chloride concentration in CEM III and CEM I a + 15% MK concretes was below the critical threshold, meaning that, until this date, the steel bar might be protected against corrosion. However, according to the model, corrosion has started in CEM II A after 27 years.

Table 3 - Input data used in the predictive model

Type of cement	CEM I (clinker a)					CEM III	CEM I		CEM II A-S		
MK substitution rate (%)	0	15	20	25	15+5	0	0	15	0	10	15
D_{snnm} (m²/s)	12.0E^{-12}	8.4E^{-12}	11.1E^{-12}	11.4E^{-12}	8.3 E^{-12}	4.5E^{-12}	10.1E^{-12}	8.1E^{-12}	15.4E^{-12}	12.0E^{-12}	8.4E^{-12}
Water porosity (%)	10.5	10.8	11.4	12.6	11.1	11.4	10.9	10.9	10.3	10.9	11.2
D_e (m²/s)	1.3E^{-12}	9.1E^{-13}	1.3E^{-12}	1.4E^{-12}	9.21 E^{-13}	5.1E^{-13}	10.1E^{-13}	8.83E^{-12}	1.6E^{-12}	13.1E^{-13}	9.4E^{-12}
Binder (kg/m³)	350	350	350	350	358	350	350	350	350	350	350
ρ_d (kg/m³)	2391	2383	2380	2378	2382	2390	2391	2384	2390	2386	2383
C_{ref} (mol/m³)	465	465	465	465	465	465	465	465	465	465	465
CSH (kg/kg cement)*	0.556	0.557	0.558	0.559	0.556	0.469	0.591	0.586	0.547	0.563	0.562
Afm (kg/kg cement)*	0.197	0.168	0.158	0.148	0.160	0.144	0.221	0.188	0.170	0.157	0.147
C_b (kg/kg concrete) (Afm)	2.11 E^{-3}	1.97 E^{-3}	1.94 E^{-3}	1.92 E^{-3}	1.98 E^{-3}	1.68 E^{-3}	2.31 E^{-3}	2.14E^{-3}	1.95 E^{-3}	1.93E^{-3}	1.88 E^{-3}
C_{free} (kg/kg concrete)	8.10 E^{-4}	8.39 E^{-4}	8.92 E^{-4}	10.01 E^{-4}	8.65 E^{-4}	8.88 E^{-4}	8.45 E^{-4}	8.47 E^{-4}	7.93 E^{-4}	8.47 E^{-4}	8.74 E^{-4}
Critical concentration (kg/kg concrete) [53]	1.64 E^{-3}	1.65 E^{-3}	1.66 $^{--3}$	1.68 E^{-3}	1.69 E^{-3}	1.65 E^{-3}	1.64 E^{-3}	1.65 E^{-3}	1.63 E^{-3}	1.65 E^{-3}	1,65 E^{-3}
Immersion time (Afm)	27	41	30	26	41	93	27	38	25	29	42

*Calculated with equations in [58]
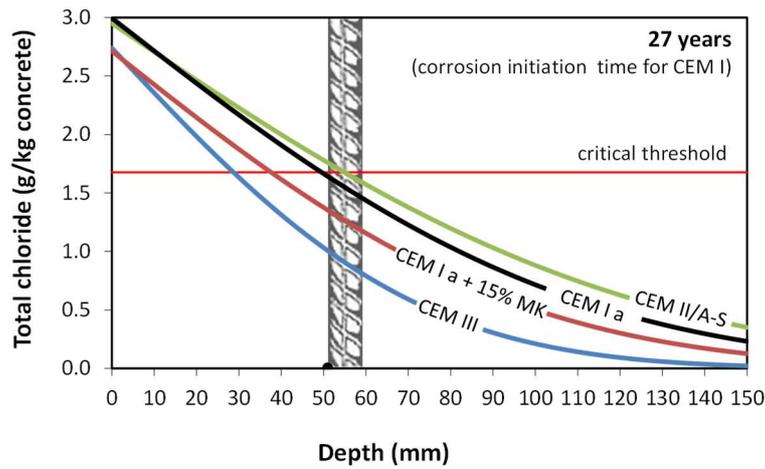
Figure 12 - Relation between quantity of chlorides and the chloride depth after 27 years of exposure (mixtures CEM I, CEM II/A-S, CEM I + 15 and CEM III/A)
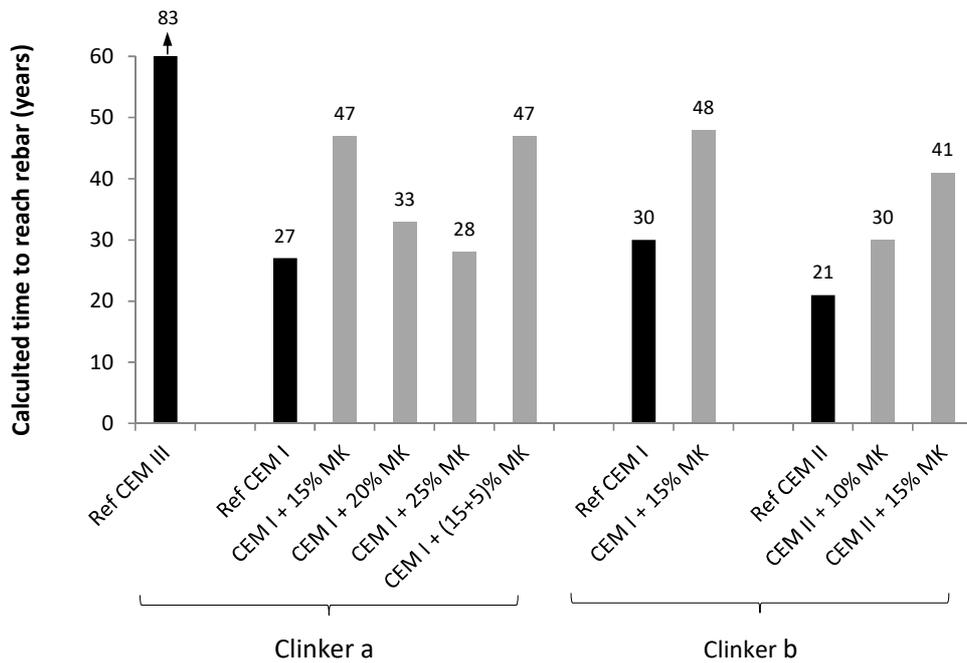
Figure 13 - Estimated lifetime of structures formulated with concrete a) CEM I, b) CEM I 15, c) CEM I 20 , d) CEM I 25, e) CEM III A and f) CEM II A-S

In order to estimate a lifespan, Figure 13 shows the time required for the chlorides to reach the steel bar with a quantity equal to the critical threshold, for all formulations. The formulation with the longest lifespan is the CEM III/A, as chlorides take 83 years to reach the steel bar. The lifespan of the other concrete based on PM-PMES cements is about 21 years. The CEM III/A concrete and the CEM II/A-S

concrete correspond to the longest and the shortest lifespan, respectively, of all formulations of this study. Concretes made with metakaolin are systematically found between the ranges of these two mixes based on PMES cement.

It should be noted that the model gives simply the diffusion time needed for chloride to reach the steel bar without considering the passivation state of the steel bar and the time to break this protective layer. In order to improve the quality of the model, an initiation threshold, depending on the embedded steel bar environment, has to be added. However, the knowledge of the initiation threshold will require further research before it can be used in the model [59]

4.4 Practical use of MK in concrete in chloride environment

4.4.1 How much MK in partial replacement of CEM I or CEM II?

On the basis of equivalent performance in terms of compressive strength, porous network, chloride ingress and accelerated corrosion tests, the results presented in this paper tend to show that MK can be used in partial replacement - at least up to 20% - of CEM I, and up to 15% in replacement of CEM II/A-S, without degrading the properties of concretes intended for use in chloride environments.

For exposure classes related to chloride environments (e.g. XS3 in EN 206), the limits proposed by the French annex to EN 206 (i.e. 15% in replacement of CEM I and 10% in replacement of CEM II) seems to be conservative, and could deprive concrete users of good technical and environmental performances. It should be recalled that the production of flash MK releases almost 10 times less CO_2 than the production of Portland cement [60].

4.4.2 Can MK be used as an alternative to PM or PMES cements in marine environments?

Marine environments can cause two types of concrete pathologies: steel bar corrosion after chloride diffusion into the concrete and cracking of the concrete due to ettringite formation. The data collected in this work show that the reduction of the pore size and the increase of the porous network tortuosity slow down the chloride diffusion. The comparison between concretes based on metakalolin and PM/PMES cements (Figure 5) shows a similar kinetics of diffusion and the accelerated corrosion tests (Figure 7) also show a beneficial effect of metakaolin use on the concrete lifespan.

The low quantity of C_3A in the PM and PMES results in better resistance against sulfates than is obtained with traditional cements. The work of San Nicolas [47] explains the benefits of metakaolin against sulfate attack, showing that a cement substitution rate of 25% leads to a significant reduction in the damage due to external sulfate attack. This could be due to a lower quantity of portlandite in these concretes and a decrease of their permeability, which would reduce gypsum and ettringite formation and so slow down crack formation.

5 Conclusion

The data found in this work has allowed us to assess the durability of a flash calcined, low-purity metakaolin with respect to chloride ingress and to estimate the lifespan of MK- based concretes through a predictive model. The main findings are:

1- The replacement of 15% of CEM I by metakaolin gave the best reduction of the chloride diffusion coefficient. On the other hand, with 20% and 25% of metakaolin, the chloride diffusion coefficient remained the same as for the control concretes. The higher the substitution rate of CEM II/A-S by metakaolin was, the lower the chloride coefficient became.

2- The kinetics of chloride diffusion into concrete based on metakaolin was equivalent to those of PM-PMES cements.

3- The delay in corrosion initiation on the steel bar embedded in the concretes with metakaolin increased as the substitution rate rose (from 15% to 25%).

4- Steel bar embedded in MK-concrete seemed to be better protected, as corrosion of the steel bar started later than in the control concretes without metakaolin.

5- The time for chlorides (at the critic concentration) to reach the steel bar was estimated by modeling the chloride diffusion into the concretes. This time is between 27 years (for CEM I) and 47 years for (CEM I 15 (15% MK)).

6 Acknowledgements

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