INFLUENCE OF METAKAOLIN ON THE CHLORIDE PENETRATION PERFORMANCE OF CONCRETE

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ABSTRACT

Extensive research and practical experience have shown that partial replacement of cement by metakaolin improves concrete durability as a result of the refinement of the pore structure. While literature confirms much research on the performance of concrete with metakaolin, it is scarce concerning the performance with regards to chloride penetration, and the effect on the service life of reinforced concrete structures.

In this study, several concrete mixes were cast with varying cement type and content and were evaluated for their chloride penetration performance. Reference mixes where made with CEM I 42,5R and CEM IV/A 42,5 type cements. Two cement contents levels where defined: 330 kg/m^3 and 440 kg/m^3 based on mix designs currently used in the ready-mix industry for C20/25 and C30/37 concretes. Cement was replaced with metakaolin with levels varying from 10 - 20%. All concretes where tested for fresh properties, compressive strength, electrical resistivity and chloride diffusion characteristics (migration and ponding), and mercury intrusion porosimetry.

The results demonstrate the improved resistance to chloride penetration of concretes with metakaolin additions. A beneficial effect on strength and durability properties of metakaolin was also observed. In addition, service life design calculations of reinforced concrete structures in marine environment based on the performance indicators obtained show a significant increase in the time to fulfil the serviceability limit state of corrosion initiation.

Key-words: Durability, metakaolin, chloride, electrical resistivity, service life, additions.

INTRODUCTION

The benefits of cementitious materials and natural pozzolans as partial replacement of Portland cement are well established for durability of concrete. Metakaolin can be used as a concrete addition, replacing partially cement due to its pozzolanic properties.
Metakaolin is produced from calcining kaolin clay at a specific temperature range (500-900 ºC) to make it reactive, with the general form Al_2O_3-SiO_2 [1-3]. Extensive research and practical

experience have shown that partial replacement of cement by metakaolin improves concrete strength and durability as a result of the refinement of the pore structure. Besides the performance benefits of using metakaolin in concrete, there are also ecological benefits, which make metakaolin concrete a more sustainable alternative to OPC concrete. The production of metakaolin does not release CO_2 as does that of OPC as a result of the de-carbonation of limestone, and, lower temperatures are required to produce metakaolin, hence lower energy required. While much research on the mechanical and durability performance of concrete with metakaolin has been performed, it is scarce with regards to chloride penetration, and the consequences for service life design. Kim et al. [4] shows the identical, performance of metakaolin with silica fume (SF) measuring the total charge passed (ASTM C 1202 [5]). Using the same test method, Poon et al. [6] shows that the total charged passed decreased for increasing metakaolin contents and for varying water/binder ratios. Studies by Boddy et al. [7] show that circa 8% metakaolin in concrete can reduce diffusion coefficients by 50%, where as 12% metakaolin can reduce apparent diffusion coefficient (DA) by 30%. Zeljkovic et al. [8] also studied the total charge passed and DA with similar results. Nokken et al. [9] work shows similar tendencies, with 8% metakaolin having identical performance as that of 4% SF. Courard et al. [10] measured diffusion coefficients of mortars, obtaining lower values with increasing metakaolin contents.

EXPERIMENTAL

The pozzolanic effect of metakaolin additions in concrete is studied in this research with the use of two reference cements: CEM I 42,5R and CEM IV/A (V) 42,5. These references cements where chosen so as to be able to study the pozzolanic effect with OPC as well as the combined effect of pozzolanic cement with pozzolanic additions. Two cement contents levels where chosen based on mix designs currently used in the ready-mix industry for C20/25 and C30/37 concretes: 330 kg/m^3 and 440 kg/m^3, respectively. Cement was replaced with metakaolin with levels varying from 10-20%. All concretes where tested for fresh properties, compressive strength, electrical resistivity and chloride diffusion characteristics (migration and ponding), and mercury intrusion porosimetry.

Materials

Two cements where used in the production of concrete specimens: CEM I 42,5R (Secil) and CEM IV/A (V) 42,5 (Secil) in accordance to the NP EN 197-1 [11]. A commercially available metakaolin (Optipozz) used was - Class N according to the ASTM C 618 [12]. In Table 1 the chemical and physical characteristics of the cements and metakaolin used are presented.

As aggregates, two crushed granite coarse aggregates and a river sand used where. The coarse aggregates with sizes 5-15 mm and 15-30 mm have specific gravities of 2.63 g/cm^3 and 2.67 g/cm3, respectively. The water absorption is 1.60 % and 1.38 %, respectively. The river sand had specific gravities of 2.63 g/cm^3 and absorption of 1.04 %.

Concrete mixtures

Mix design was based on maintaining a constant water/binder (w/b) ratio. Two series with a 0.45 w/b ratio and 440 kg/m^3 of binder, and one series with a 0.60 w/b ratio and 330 kg/m^3 of binder (only CEM I 42,5R). Each series was comprised of a references mixture with no metakaolin, and three additional mixtures with 10%, 15% and 20% of cement replacement with metakaolin. Details of the concrete mixtures and their workability are presented in Table 2. Concrete

workability was kept within the S2/S3 class of the NP EN 206-1 [13].

Table 1 – Properties of cements and metakaolin

Parameters	CEM I 42,5R	CEM IV/A (V) 42,5	Metakaolin
SiO_2 (%)	19.55	38.06	51.5
Al_2O_3 (%)	4.24	4.67	44.5
K_2O (%)	-	-	0.21
Na_2O (%)	-	-	0.11
Fe_2O_3 (%)	3.34	3.80	0.45
CaO (%)	62.61	43.97	0.02
SO_3 (%)	3.26	3.00	-
MgO (%)	2.51	2.51	0.12
Cl^- (%)	0.03	0.03	-
Loss on ignition (%)	2.96	2.53	< 0.8
Specific gravity	3.12	2.84	2.20
Specific Surface (cm^2/g)	4071	4369	-

Table 2 – Concrete compositions and workability

Series	w/b	Water (l/m^3)	Binder (kg/m^3)		Aggregate (kg/m^3)			Slump (mm)
			Cement	MK	Course 1	Course 2	Sand	
330-0 (REF)	0.60	198	300	0	405	835	710	90
330-10		198	297	33				130
330-15		198	280.5	49.5				140
330-20		198	264	66				145
440-0 (REF)	0.45	200	440	0	420	820	600	90
440-10		200	396	44				120
440-15		200	374	66				125
440-20		200	352	88				130
440FA-0 (REF)	0.45	200	440	0	420	820	600	95
440FA -10		200	396	44				90
440FA-15		200	374	66				85

The three concrete series where produce in a vertical axis mixer with a 120 litre capacity. Cubic specimens of 100 mm and 150 mm in dimension and cylinders of 100 mm in diameter and 200 mm in height where cast in steel moulds and compacted using a vibrating table. 24 hours after casting the specimens where removed from the moulds and permanently cured in water tanks at 20 ± 3 ºC until testing. Testing was performed at 7, 14, 28, 90 and 180 days.

Compressive strength

The compressive strength of the concrete was evaluated 150 mm cubes. The tests were performed on an ELE compressive machine with 3000 kN capacity, at the rate of 0.3 N/mm^2s. Each result represents an average of 3 specimens. The compressive strength tests were performed according to the NP EN 12390-3 [14].

Electrical resistivity

The electrical resistivity (ER) of the concrete was determined using a four-probe resistivity-meter (RM MK II - alternating trapezoidal current wave with frequency of 13 Hz) on 150 mm cubic concrete specimens. Measurements where performed with 40 mm electrode spacing. The apparent electrical resistivity determined by the equipment is obtained from Eq. (1) considered valid for a homogeneous semi-finite volume of the material.

$$\rho_A = 2\pi a V / I \qquad (1)$$

Where ρ_A is the electrical resistivity (Ωm), a the electrode spacing (m), V the voltage drop (V), and I the current (A). According to LMC testing procedure for ER of concrete [15], cubic specimens are measured on three adjacent surfaces with two measurements per surface perpendicular to each other.

Non-steady state chloride migration

The non-steady state chloride migration coefficient was determined on cylindrical specimens of 100 mm diameter and 50 mm height according to the LNEC E463 [16]. Each results represents an average of 3 specimens. The electrical potential and duration of testing are defined according to the initial current measured across the concrete specimen for a reference electrical potential of 30 V. After testing, specimens are split in half and silver nitrate is sprayed onto the surface. Based on the measurement of chloride penetration the non-steady state chloride migration coefficient (D_{NSS}) is determined.

Chloride immersion

The chloride immersion test was performed on 100 mm cubic specimens according to the LNEC E390 [16]. Concrete specimens are immersed in a 3% NaCl solution for 90 days after which powder samples are taken at 5 mm interval in depth from the surface. The chloride profiles are determined after chloride titration of the powdered samples has been performed. Each results represents an average of 3 specimens. Curve fitting of Fick's 2nd Law of diffusion result in the determination of the apparent diffusion coefficient (D_A) and the surface concentration of chlorides (C_S).

Mercury intrusion porosimetry

The porosimetry testing was performed with an Auto Pore IV scanning mercury porosimeter having a pressure range from sub-ambient to 33,000 psi. The contact angle and the surface tension of mercury considered were 130° and 0.485 N/m [18], respectively. Prior to test specimens were oven-dried at 105°C for 24 hours. To obtain representative pore-size distribution curve for the concrete samples, the results of two porosimetry data were averaged. The mercury porosimetry graphs showing the distribution of pore diameters are shown below. The y-axis is the log differential intrusion in ml/g, or dV/dlogD, where V is the volume of mercury intruded into the pores of the sample. As you can see, this is the derivative of intruded volume with respect to the logarithm of pore diameter. The derivative with respect to log D is used instead of the derivative with respect to D to amplify the dV/dD values. Thus, the derivative plot enables clearly identifying points of inflection, which shows us where clusters of pores of a particular diameter occur.

RESULTS & DISCUSSION

Compressive strength

The results of the compressive strength tests are presented in Table 3.

Table 3 – Compressive strength and electrical resisitivty results

Series	Average compressive strength (MPa) (CoV)					Average electrical resisitivty (Ωm) (CoV)			
	7 days	14 days	28 days	90 days	180 days	7 days	28 days	90 days	180 days
330-0 (REF)	18.87 (1.70)	22.17 (1.71)	23.87 (2.15)	28.07 (3.92)	29.07 (0.79)	30.03 (4.11)	39.53 (4.64)	49.48 (5.76)	50.80 (5.12)
330-10	17.00 (1.18)	22.20 (0.78)	26.60 (0.38)	31.10 (5.58)	31.83 (1.73)	25.58 (5.54)	73.13 (4.22)	74.05 (6.13)	74.89 (5.46)
330-15	14.93 (1.55)	20.97 (2.20)	25.03 (2.01)	31.53 (1.20)	33.10 (1.98)	21.67 (7.07)	65.36 (5.99)	65.68 (6.67)	66.37 (7.58)
330-20	12.37 (0.93)	18.77 (0.62)	23.40 (2.38)	29.63 (2.91)	33.60 (0.52)	20.30 (6.71)	62.46 (4.82)	63.18 (4.68)	65.93 (5.04)
440-0 (REF)	30.53 (6.27)	33.73 (4.75)	40.62 (1.37)	44.03 (0.35)	44.77 (0.68)	38.27 (5.91)	54.84 (4.80)	71.58 (5.82)	72.53 (5.97)
440-10	30.23 (4.80)	35.87 (0.85)	40.90 (1.29)	44.80 (2.72)	45.40 (2.20)	32.58 (5.34)	95.51 (4.53)	95.93 (4.50)	96.68 (7.57)
440-15	32.67 (2.64)	40.43 (4.49)	47.97 (0.94)	53.67 (2.70)	54.57 (2.21)	39.34 (5.34)	124.75 (3.81)	127.10 (3.07)	127.98 (3.76)
440-20	24.73 (1.24)	32.07 (3.76)	39.73 (0.63)	46.77 (1.82)	47.63 (1.49)	30.16 (5.72)	85.99 (5.93)	107.61 (3.75)	112.53 (4.23)
440FA-0 (REF)	22.43 (5.32)	27.05 (3.92)	29.67 (2.91)	38.53 (2.02)	43.27 (2.02)	34.47 (5.27)	58.51 (4.74)	98.82 (5.10)	205.03 (4.80)
440FA -10	24.47 (5.44)	32.57 (3.95)	37.90 (1.99)	45.63 (2.64)	48.03 (0.52)	50.05 (5.32)	185.18 (4.12)	227.00 (5.56)	276.75 (4.96)
440FA-15	20.63 (4.23)	30.53 (3.84)	36.37 (0.69)	43.53 (2.74)	50.23 (0.46)	35.16 (4.77)	137.88 (5.11)	184.91 (5.59)	248.67 (5.78)

An analysis of the result in Table 3 reveals the well-known beneficial effect of metakaolin on compressive strength due to the refinement of the pore structure as a result of the pozzolanic reaction (i.e. the reaction of the metakaolin with the cement hydrates).
From approximately 14 days onwards the reference compositions present the lowest compressive strength. All levels of replacement showed improvement at 28 days. Significant improvement is observed from 15% replacement for series 440 CEM IV and CEM I (± 20%). For the 330 series the increase in strength is approximately 10-15% between 28 and 180 days. For the 440 CEM I series, the 15% replacement reveals interesting results from 14 days maintaining a 20% increase in strength up to 180 days. For the 440 CEM IV series, the 10 and 15% replacements also reveal interesting results from 14 days maintaining a 15 -20% increase in strength up to 180 days.

Electrical resistivity

While 7 day electrical resistivity values are often lower than those of the reference cement, at 14 days the tendency is clearly revered, with the concretes with metakaolin addition having significantly higher electrical resistivity values. This shows how quickly the metakaolin starts to react with the cement hydrates and contribute to improving the pore structure. An analysis of the result in Table 3 shows for the 330 and 440 series, 25 – 50% and 25 – 75 % increase in ER is observed at 28 days, respectively. From this date onwards no significant variation is observed. For the 440 CEM IV series, a constant improvement up to 180 days is observed. At 28 days, ER is between 100 – 200% higher, however at 180 days the reference composition has reduced the difference to approximately 30% as the lower pozzolanic content takes a longer time to react and contribute positively to the performance. Comparing the result for 440 between cements, clearly

the CEM IV has a better performance than CEM I concrete (with and without additions).

Non-steady state chloride migration

In Table 4 the chloride migration coefficient is presented (average of 3 specimens). For the 330 series mix, from 28 days onward no significant improvement in the migration coefficient (D_{RCM}) is observed. For the same period, the mixes with metakaolin have a D_{RCM} of approximately half that of the reference concrete. For the 440 CEM I series, the overall performance has improved with D half that of the 330 series. Again, the reference mix presents the worst performance, with 28 day onwards values approximately double that of the mixes with metakaolin. With an increase in metakaolin content there is a tendency to improve D_{RCM}, except for 20% levels of replacement where D_{RCM} values are slightly higher. For the 440 CEM IV series, the overall scenario is identical, except that of the reference mix which at 180 days catches-up with the mixes with metakaolin. 28 day mixes for both 440 series present D_{RCM} less than 10e-2 m^2/s (considered good performance). As in the electrical resistivity results, the reference mix from the 440 series with pozzolanic cement tends to improve its performance by reducing the difference in value at 28 days to a much closer one by 180 days. It is at the early ages when concrete is most vulnerable to penetration that the rapid improvement of concrete performance is always desired.

Table 4 – Results of the non-steady state migration and immersion test

Series	D_{RCM} (e^{-12} m^2/s)				Diffusion coefficient (e^{-12} m^2/s) / Surface Chloride concentration (%/mass binder)		
	7 days	28 days	90 days	180 days	D_A	C_S	Depth of 0.6% Cl
330-0 (REF)	53.99 (6.05	31.28 (2.69)	30.66 (3.74)	29.41 (4.00)	12.00	5.24	≈ 21
330-10	47.77 (7.01)	15.84 (2.35)	13.43 (6.49)	13.38 (9.74)	3.52	7.98	≈ 12
330-15	59.13 (4.04)	17.05 (9.17)	14.31 (11.01)	14.22 (4.15)	3.95	8.73	≈ 10
330-20	51.06 (4.91)	23.10 (4.09)	15.15 (2.89)	14.86 (3.07)	2.78	6.99	≈ 8
440-0 (REF)	25.11 (4.50)	15.49 (3.02)	13.18 (4.98)	13.15 (7.75)	4.82	5.34	≈ 12
440-10	26.69 (8.16)	8.52 (3.17)	8.32 (5.93)	8.14 (2.48)	3.62	4.65	≈ 10
440-15	24.15 (1.23)	7.03 (10.63)	6.64 (9.93)	5.77 (12.18)	2.32	6.59	≈ 7
440-20	27.35 (8.78)	10.49 (2.91)	7.34 (3.84)	6.26 (9.11)	1.35	11.86	≈ 7
440FA-0 (REF)	41.79 (3.24)	21.45 (5.63)	11.41 (8.02)	5.69 (4.44)	5.27	4.85	≈ 12
440FA -10	23.75 (6.33)	7.82 (2.15)	4.64 (13.30)	4.58 (4.00)	1.97	9.16	≈ 7
440FA-15	22.61 (2.04)	10.30 (18.25)	5.81 (19.62)	5.43 (8.76)	1.82	9.55	≈ 7

Chloride immersion

The chloride profiles measured from the specimens subject to the immersion test are presented in Figures 1-4. In Figure 1, the chloride profiles of the reference cements are presented together. The results of the curve fitting of Fick's 2nd Law of diffusion to the chloride profiles (D_A and Cs) are presented in Table 4. The results for the 330 series are more than half of the other mixes and no significant difference is noted between 10-20% replacements. For 440 series the values are even smaller for CEM IV and Da decreases as metakaolin increases.

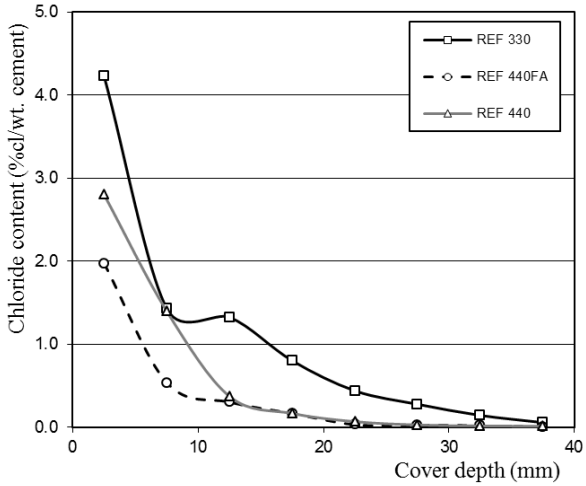

Figure 1 – Chloride profiles for the reference concretes without metakaolin.

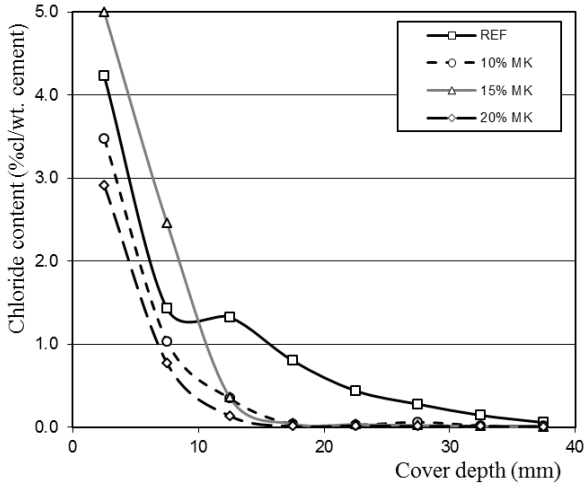

Figure 2 – Chloride profiles for the concrete mixes with total binder content of 330 kg/m3 and CEM I 42,5 reference cement.

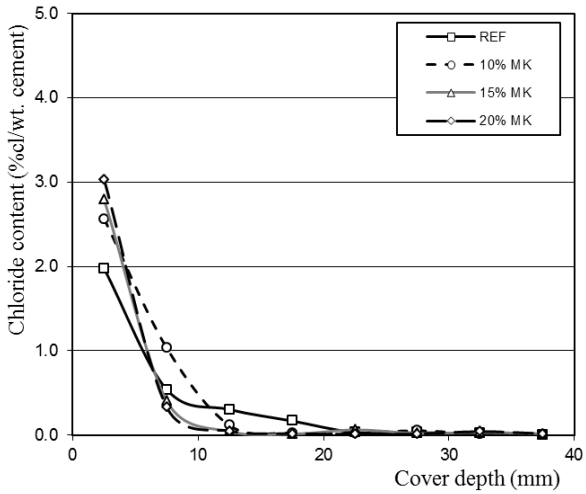

Figure 3 – Chloride profiles for the concrete mixes with total binder content of 440 kg/m^3 and CEM I 42,5 reference cement.

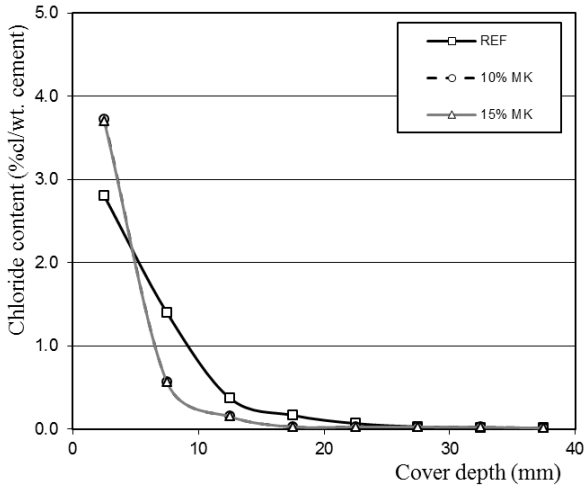

Figure 4 – Chloride profiles for the concrete mixes with total binder content of 330 kg/m^3 and CEM IV/A (V) 42,5 reference cement.

Observing the chloride profiles the beneficial effect of metakaolin is verified. With both CEM I series, the highest % of metakaolin (20%) resulted in the lowest early age chloride penetration. The reference after 3 months ponding, presented the highest depth for the critical chloride concentration considered (0.6 %/wt. cement). With increase in metakaolin content the depth of the critical chloride concentration decreases.

Mercury intrusion porosimetry

Figure 5 shows mercury porosimetry graphs for the reference concrete mixes with total binder content of 330 kg/m^3 and 440 kg/m^3 for CEM I 42,5. The pore-size distribution curves are of similar shape, as expected. Both curves show a cluster of pore-size diameters in the range of 0.02 to 0.5 microns. However, the porosity data for REF 330 concrete give a total intrusion volume of 0.11 mL/g (or 1.1 x 10^{-7} m^3/g), while the total intrusion volume for REF 440 concrete is only 0.05 mL/g (or 0.5 x 10^{-7} m^3/g). So, total intrusion volume of REF 440 is about half of REF 330 but both showing a cluster of pore-size diameters around 0,1 microns (from 0.02 to 0.5 microns). In Figure 6 mercury porosimetry graphs are presented comparing reference concrete with total

binder content of 330 kg/m^3 and concrete mixes with 10%, 15% and 20% metakaolin replacement. It shows that total intrusion volume for concrete with 15% and 20% metakaolin replacement is slightly higher than reference concrete, except for 10% metakaolin replacement. However, the pore-size diameters of concrete with metakaolin replacement are in the range of 0.01 to 0.2 microns, which clearly confirms the refinement of concrete structure; ie. the porosity within range of 0.2 to 0.5 microns has been annulled while small size pores (from 0.01 to 0.02 microns) have increased.
Similar results, although not so obvious, were also found for the concrete mixes produced with 440 kg/m^3 binder content and having metakaolin replacement.

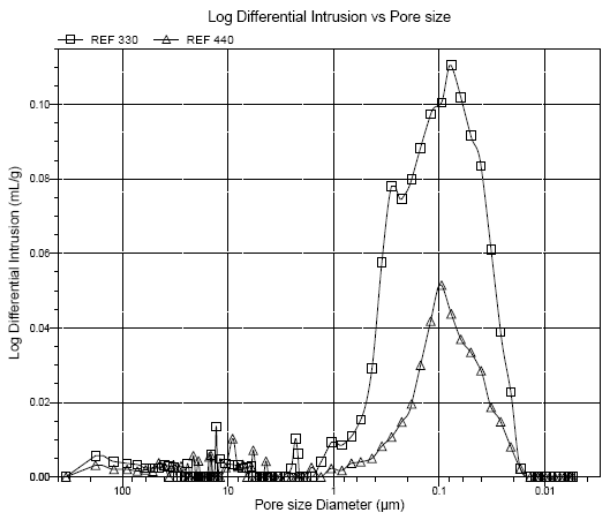

Figure 5 – Log differential intrusion versus pore size for the reference concrete mixes with total binder content of 330 kg/m3 and 440 kg/m3 for CEM I 42,5.

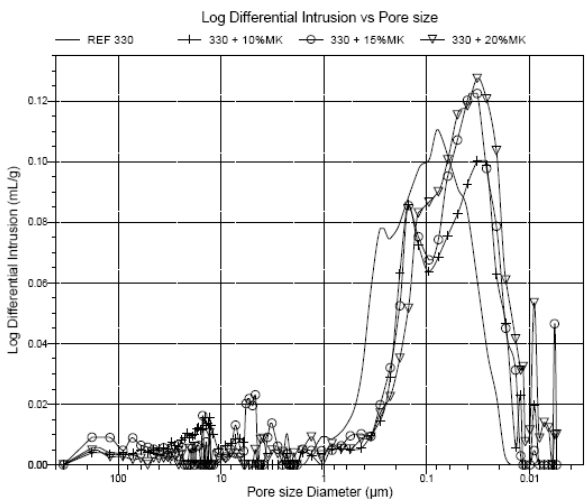

Figure 6 – Log differential intrusion versus pore size for the concrete mixes with total binder content of 330 kg/m3 and CEM I 42,5 reference cement.

SERVICE LIFE DESIGN

Here, the results of SLD calculation are presented briefly, with the intention of demonstrating the beneficial effect metakaolin has on long term durability. For this purpose, a service life design software was used to calculate the performance of concrete mixes in marine environment [19]. The model for chloride penetration of concrete is that which is presented in the *fib* Model Code for Service Life Design – Bulletin 34 [20].
A serviceability limit state of corrosion initiation was considered in the calculation. The limit state is considered to have failed when the chloride content at the depth of the reinforcement has exceeded a critical chloride content. The calculation is performed by Monte Carlo simulation with 10^6 simulations for each individual year. In Table 5 the parameters and values used in the calculation are presented. The service life design calculation was performed for the reference concretes and the mixes with 10% metakaolin replacement.

Table 5 – Results of the non-steady state migration and immersion test

Series	D_{RCM} (e^{-12} m^2/s)				Diffusion coefficient (e^{-12} m^2/s) / Surface Chloride concentration (%/mass binder)		
	7 days	28 days	90 days	180 days	D_A	C_S	Depth of 0.6% Cl
330-0 (REF)	53.99 (6.05	31.28 (2.69)	30.66 (3.74)	29.41 (4.00)	12.00	5.24	≈ 21
330-10	47.77 (7.01)	15.84 (2.35)	13.43 (6.49)	13.38 (9.74)	3.52	7.98	≈ 12
330-15	59.13 (4.04)	17.05 (9.17)	14.31 (11.01)	14.22 (4.15)	3.95	8.73	≈ 10
330-20	51.06 (4.91)	23.10 (4.09)	15.15 (2.89)	14.86 (3.07)	2.78	6.99	≈ 8
440-0 (REF)	25.11 (4.50)	15.49 (3.02)	13.18 (4.98)	13.15 (7.75)	4.82	5.34	≈ 12
440-10	26.69 (8.16)	8.52 (3.17)	8.32 (5.93)	8.14 (2.48)	3.62	4.65	≈ 10
440-15	24.15 (1.23)	7.03 (10.63)	6.64 (9.93)	5.77 (12.18)	2.32	6.59	≈ 7
440-20	27.35 (8.78)	10.49 (2.91)	7.34 (3.84)	6.26 (9.11)	1.35	11.86	≈ 7

In Figures 7 and 8 the probability of failure, i.e. the probability of exceeding the serviceability limit state of corrosion initiation, for a 50 year service life period is presented for the reference concrete mixes and the mixes with 10 % replacement, respectively.

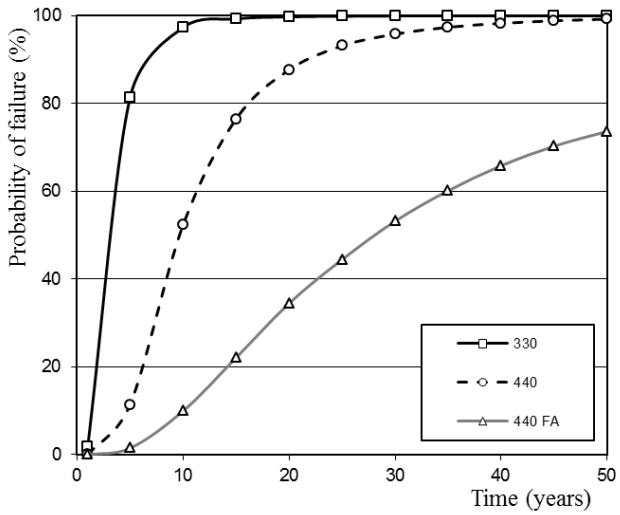

Figure 7 – Probability of corrosion initiation as a function of time for the reference concretes without metakaolin.

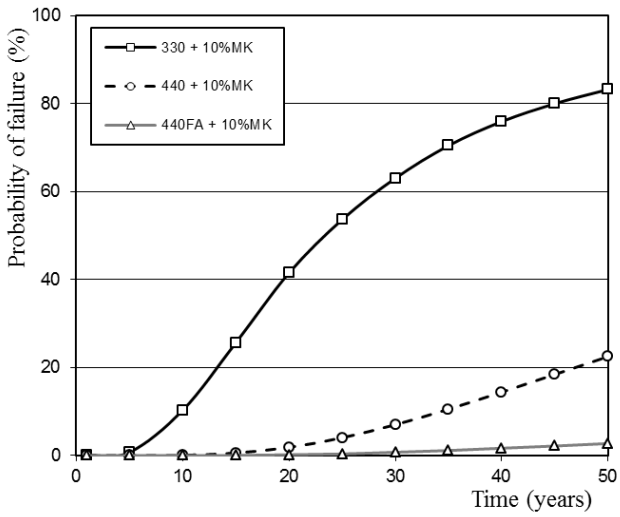

Figure 8 – Probability of corrosion initiation as a function of time for the concretes mixes with 10% metakaolin addition.

From Figures 7 and 8 the beneficial effect on service life performance is clear, with an increase in the time to exceed the serviceability limit state of corrosion initiation (considered at 10% for this analysis sake). Despite the improvement of the concrete mixes with metakaolin, only the 440 series either fulfill or are close to fulfilling the limit state requirements (Figure 6).

CONCLUSIONS

In this study, several concrete mixes were cast with varying cement type and metakaolin contents and were evaluated for their chloride penetration performance. Despite the limited number of testing, from the results of the study it is possible to conclude the following:

· Until 20 % metakaolin replacement of CEM I and CEM IV type cements improves the overall performance of concrete, in specific with regards the chloride penetration, without compromising the compressive strength.

· Chloride profiles show a delay in the penetration of chlorides due to the beneficial effect of metakaolin addition. This can be related to the refinement of the pore structure, as shown by the mercury intrusion tests performed.

· No significant difference is distinguished between 10 – 20% metakaolin replacements.

· With regards to durability indicators, the D_{RMC} (migration coefficient) for concrete with metakaolin additions is roughly half that of the reference concrete for both cement types.

· Service life design calculations based on the *fib* – Bulletin 34 model show that concrete with partial replacement of cement by metakaolin performs better. The time to reach the serviceability limit state of corrosion initiation is increased.

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