EXPERIMENTAL STUDY ON CHLORIDE MIGRATION COEFFICIENTS OF SCC WITH BINARY AND TERNARY MIXTURES OF FLY ASH AND LIMESTONE FILLER

Pedro Raposeiro da Silva[1], Jorge de Brito[2]

1. Polytechnic Institute of Lisbon, Portugal
2. ICIST Technical University of Lisbon, Portugal

ABSTRACT. The durability of concrete is strongly associated with its ability to resist chloride ingress. Today, the corresponding migration coefficient appears associated to the standardization of concrete specification not only in Portugal, through the specifications of the National Laboratory of Civil Engineering (LNEC), but also at the European level with the DuraCrete Project (probabilistic performance based durability design of concrete structures), for example.

From the different testing methods available, the Rapid Chloride Migration (RCM), even though with some well-known limitations, emerges as the simplest and fastest test and has an acceptable precision considering the level of repetitiveness. Therefore, this was the method used in this work.

Based on that test, this article intends to evaluate the chloride migration coefficient, from non-steady-state migration experiments (according to the LNEC specification E 463 based on the norm NT BUILD 492), of SCC produced with binary and ternary combinations of fly ash (FA) and limestone filler (LF).

For that purpose, a total of 13 self-compacting mixes were produced: one with cement only (C); three with C+FA in 30%, 60% and 70% substitution; three with C+LF in 30%, 60% and 70% substitution; four with C+FA+LF in combinations of 10-20%, 20-10%, 20-40% and 40-20% substitution; and finally two mixes according to the LNEC specifications E 464 in reference to the standard NP EN 206-1.

Keywords: Self-compacting concrete**,** fly ash, limestone filler, durability, chloride migration coefficient.

Pedro Silva is an Assistant Professor at the Polytechnic Institute of Lisbon, Lisbon, Portugal. He received his MSc in construction from Instituto Superior Técnico (IST), Portugal.

Jorge de Brito is a Full Professor at IST and Head of the ICIST Research Centre. He received his MSc and PhD in civil engineering from IST. His research interests include the deterioration, rehabilitation, and management of concrete structures, and sustainable construction.

INTRODUCTION

Concrete, as it is known nowadays, has been used for thousands of years. Concrete is constituted by a composite of coarse aggregate kept together by a paste of hydraulic binder, which was already used by the Romans in the construction of part of their structures, some of which survived to the present days.

With the invention of normal Portland cement (NPC) in the first half of the 19th century, modern concrete appeared. It became, in modern times, the most important construction material in the world. Nevertheless, and despite the popularity of its use, concrete is associated with several anomalies observed in infra-structures currently in use, usually linked to problems related to the mixes, poor casting at the construction site or inadequate or even inexistent maintenance, which may lead to permanent deterioration of the structures and to the consequent loss of in-service conditions.

In that context, Professor Okamura from the Tokyo University initiates, in 1986, the development of a concrete (self-compactable) that would not require human intervention in the casting phase [1]. In the beginning of the 90s, in Japan, this technology was already developed to the point of being used both in bridge construction or buildings infrastructures. That concrete can fill the moulds completely, passing through densely reinforced areas, without particles flocculation or segregation, simply by the effect of its own weight and without resorting to any compacting method. The use of SCC in Europe initiates in the 90s, very much through the influence of the pre-casting industry but also with the use of ready-mixing in bridges and buildings among other infrastructures.

The use of SCC answers the need for improvement in the structures durability, independently of the quality of the construction work and therefore the labour force intervention at the casting stage, since it is a material that goes without any compacting method. Due to the changes necessary to obtain the required self-compactability (with fluidity and segregation and bleeding resistance), that is, necessary to eliminate the vibration process, the impact of SCC use is essentially related to the production process and with the placing. The main changes are related to the constituent materials, namely:

- Decrease of the relation between the quantities of course aggregate and mortar;
- Consequent increase of the mortar volume (more ultra-fine material like cement and additions);
- Adequate control of the aggregates' maximum dimension;
- Use of chemical admixture of the superplasticizers' and/or viscosity modifying agents' type.

One should also highlight the changes, at the productivity level, of the structure's execution process, the improvement of the working conditions as well as the conditions around the working site (reduction of the level of noise), the potential improvement of its properties in the hardened state (e.g. mechanical strength, durability and the final aspect of the finished surface).

Regardless of the impacts mentioned and despite the fact that the requirements of the SCC, regarding the hardened state properties, are the same as those of the conventional concrete (CC), the quantities used in the mix, as well as the proportions in which the different components combine are different. Therefore, it is fair to say that its properties in the hardened state regarding durability can vary and are still a little uncertain [2][3].

Like what happens with CC, to obtain a higher durability, SCC will have to make it more difficult for the aggressive agents to penetrate it. The corrosion process of reinforcing steel induced by the penetration of chlorides can be one of the determining factors for durability, mainly in situations of exposure to sea water or de-icing salts, making the knowledge of that process extremely important. Nevertheless, the penetration of chlorides is a complex process that involves several phenomena such as diffusion, capillary absorption and permeation (that may occur in isolation or simultaneously) [4][5]. That said, the concrete durability study, namely the effect of the chloride penetration, has an increased importance not only from the point of view of the concrete structures' service life conditions through the corresponding maintenance and reparation costs but also from the dimensioning point of view and the capacity to predict its useful life span (prediction models of the long-term concrete behaviour in function of the chlorides action).

There are several methods (laboratorial and *in-situ*) to determine the depth of the chloride penetration, its concentration or the corresponding diffusion coefficient. *In-situ* measurements allow for the preparation of maintenance and reparation of structures in use. However, for the prediction at the design phase, it is necessary to resort to theoretical models normally based on results obtained from experimental mixes in laboratory. For these cases, there are also different types of laboratory testing methods with more or less lengthy procedures, of which the Rapid Chloride Migration test (RCM) is the most commonly used. Initially developed by Tang and Nilsson [6], then transformed into norm through the NT Build 492 [7] and in Portugal through the specification E 463 [8], it is also mentioned in the European DuraCrete project [9] (through the use of its diffusion coefficient in the service life model for concrete) as well as, more recently, in the European project chlorotest [10].

Despite some controversy associated with the use of this method [4][5][11][12][13][14], essentially due to the differences observed between the theoretical models (which were its foundation) related to the chloride ions concentration profile caused by an electrical potential and the experimental profiles obtained, it continues to be a much used laboratory testing method allowing for the comparison of the results obtained not only with the SCC produced but also with those of other authors.

Therefore, this paper intends to evaluate the influence of the use of FA and LF in the chlorides diffusion coefficient in binary and ternary SCC mixtures at three ages (28, 91 and 182 days) resorting to the rapid chloride migration test according to the NT Build 492 norm [7] and the E 463 [8] specification.

For that purpose, a total of 13 self-compacting mixes were produced: one with cement only (C); three with C+FA in 30%, 60% and 70% substitution; three with C+LF in 30%, 60% and 70% substitution; four with C+FA+LF in substitution combinations of 10-20%, 20-10%, 20-40% and 40-20%; and finally two mixes according to the LNEC specifications E 464 [15] in reference to the standard NP EN 206-1 [25].

EXPERIMENTAL PROGRAMME

Materials

The materials used in this study were selected taking into consideration their availability in Portugal and the concrete under analysis (SCC). The following materials were therefore used:

- One type of cement complying with NP EN 197-1 [16] (NPC type I-42.5 R with specific gravity of 3.14);
- Two mineral additions: fly ash (FA) complying with NP EN 450-1 [17] and NP EN 450-2 [18] with specific gravity of 2.30 and limestone filler (LF) complying with LNEC specification E 466 [19] with specific gravity of 2.72;
- Two limestone-based coarse aggregates complying with NP EN 12620 [20], Gravel 1 with specific gravity of 2.59, D_{max} of 11 mm and water absorption of 1.46% and Gravel 2 with specific gravity of 2.64, D_{max} of 20 mm and water absorption of 0.78%;
- Two siliceous sands complying with NP EN 12620 [20], one coarse (0/4) with specific gravity of 2.55, fineness modulus of 3.70 and water absorption of 1.10% and one fine (0/1) with specific gravity of 2.58, fineness modulus of 2.03 and water absorption of 0.70%;
- A third-generation concrete high-range/strong water-reducing admixture complying with NP EN 934-1 [21] and NP EN 934-2 [22] (a modified polycarboxylic high-range water-reducing admixture in liquid form with a density of 1.07);
- Tap water complying with NP EN 1008 [23].

Concrete Mixes Used

With the goal of including the different variations of the quantities used for the mixes and the corresponding analysis of the binary and ternary mixtures of FA and LF, 11 SCC mixes were produced according to the NP EN 206-9 [24] and 2 reference concretes according to the NP EN 206-1 [25]. This data is showed in Table 1.

The mix quantities used were obtained according to the method presented by Nepomuceno [26] and already used in several publications [27]. Summarising, the method mentioned proposes a new methodology for calculation of the SCC mix quantities based on the methods of Okamura et al. [28] and of JSCE [29] through the introduction of new parameters that will be more adequate for the control, not only of the SCC's mechanical resistance but also of other properties in the fresh state. The referred method is properly explained in the author's PhD thesis [26]. Several practical applications of it also exist, namely the verification of its applicability in the work presented by Silva and de Brito [27].

Regarding the establishment of the mix quantities presented in Table 1, one should mention the procedure to determine the proportions between the aggregates used, as well as the establishment of the different mix parameters considered. In that way, the proportions between the coarse aggregates (coarse aggregate 1 + coarse aggregate 2) and between the sands (sand 0/1 + sand 0/4) were established with the goal of obtaining the maximum compacity possible through the analysis of the reference mixes as well as the corresponding fine aggregate modules. In this way, it was intended to minimize the empty spaces between the particles and optimize the proportions among them.

As for the fixation of the parameters of the studied mixes' proportions in way to be able to only evaluate the change in the unitary substitution percentages of the cement by the mineral additives, it depended on the following conditions:

- the volume ratio between the mortar and coarse aggregate content (V_m/V_g=2.625), as well as the absolute volumes of coarse aggregate (Vg=0.268 m^3/m^3) and mortar (Vm=0.702 m^3/m^3), were maintained constant;

- for the purpose of the calculations, a value of the void volumes (V_v=0.03 m^3/m^3) was considered constant;
- the volume ratio between the total powder content, cement and mineral additions, and fine aggregates in the mixture (V_p/V_s=0.80), was maintained constant;
- the volume ratio between the water and fine material content in the mixture (V_w/V_p), as well as the percentile ratio in mass between the high-range water reducing admixture (S_p) and fine material content in the (S_p/p%), will vary depending on the need for water and S_p of each mixture in order to obtain the self-compacity parameters.

Table 1 Mixes design and basic properties of SCC and reference concretes

Mix proportions		SCC1.100C	SCC2.30LF	SCC2.60LF	SCC2.70LF	SCC3.30FA	SCC3.60FA	SCC3.70FA	SCC4.10FA20LF	SCC4.20FA10LF	SCC5.20FA40LF	SCC5.40FA20LF	BR.XS1■2	BR.XS3
CEM I 42,5 R	[kg/m³]	707	512	297	222	503	290	218	506	506	297	293	256	272
Fly ash	[kg/m³]	---	---	---	---	158	318	373	53	106	109	215	64	68
Limestone filler	[kg/m³]	---	190	386	449	---	---	---	125	63	257	127	---	---
Superplasticizer	[kg/m³]	7	5	3	3	5	4	3	5	5	3	3	2	2
Water	[l/m³]	189	175	168	170	183	180	178	180	180	168	175	176	153
Fine aggregate $_{0/1}$	[kg/m³]	436	450	457	456	443	447	448	446	446	457	451	549	562
Fine aggregate $_{0/4}$	[kg/m³]	287	297	301	300	292	294	295	294	294	301	297	362	370
Corse aggregate $_1$	[kg/m³]	417	417	417	417	417	417	417	417	417	417	417	511	523
Corse aggregate $_2$	[kg/m³]	283	283	283	283	283	283	283	283	283	283	283	347	355
W/C	[-]	0,27	0,34	0,57	0,76	0,36	0,62	0,82	0,36	0,36	0,57	0,60	0,69	0,56
W/CM	[-]	0,27	0,34	0,57	0,76	0,28	0,30	0,30	0,32	0,29	0,41	0,35	0,55	0,45
W/FM	[-]	0,27	0,25	0,25	0,25	0,28	0,30	0,30	0,26	0,27	0,25	0,28	0,55	0,45
Basic properties														
Slump Flow	[mm]	770	675	678	620	648	613	595	775	738	685	645	slump210	slump200
V-funnel	[s]	9,3	10,3	9,1	9,9	7,3	8,4	8,6	9,3	10,8	9,1	10,0	---	---
L-box	[-]	0,9	0,9	0,9	0,8	0,8	0,8	0,8	0,9	0,9	0,9	0,8	---	---
Air	[%]	2,5	2,9	4,0	4,4	3,0	4,6	4,6	2,4	2,4	2,6	2,7	---	---
$f_{cm,7d}$	[MPa]	64,6	66,7	38,5	26,4	58,8	34,4	21,6	60,7	62,7	32,6	31,6	---	---
$f_{cm,28d}$	[MPa]	83,6	70,1	42,3	30,5	68,4	54,0	35,3	63,4	70,9	47,8	49,1	47,0	49,6
$f_{cm,91d}$	[MPa]	85,5	70,0	42,8	32,6	71,7	62,5	48,9	70,4	75,8	57,9	56,9	---	---
$f_{cm,182d}$	[MPa]	88,2	74,1	49,2	35,5	69,5	59,9	49,6	71,1	74,7	59,9	55,9	---	---

To establish the parameters V_w/V_p and S_p/p%, experimental mixes of self-compacting mortars produced according to the work presented by Nepomuceno [26] and by Silva and de Brito [27] were used.

The composition of 2 mixes produced according to the specifications in E 464 [15] is shown in Table 1 with references BR.XS1&2 and BR.XS3. With the two mixes presented and described according to the specification mentioned, the intention is to verify the framework for the remaining SCC mixes studied considering the environmental exposure classes, namely in the case of chloride action, as well as evaluate the suitability of the mixes' proportions parameters presented in E 464 [15] in the particular case of the SCC in order to fulfil the timing of a 50 year service life of a project.

The reference mixes were established according to Table 7 of the E 464 [15], namely in terms of the maximum W/C ratio, minimum cement content and minimum strength class. The calculation of mortars' quantities followed, as far as possible, the methodology used for the remaining mixes, having maintained the aggregates proportions. The cement type I 42.5 R was used as supplied by the producer, while the type IV/A for the reference mixes was combined respecting what is prescribed in the NP EN 197-1 [16], according to the following percentages per mass unit: 80% CEM I 42,5 R + 20% FA.

Test Method and Sample Preparation

As mentioned above, the test procedure used to determine the chloride diffusion coefficient was the one described in the NT Build 492 norm [7] and the E 463 specification [8].

For that purpose, cylindrical moulds with 100 mm in diameter and 200 mm in height were used. From those moulds, 3 ϕ100 x 50 mm moulds were cut (eliminating approximately 20 to 25 mm from each end). After the adequate time of humid cure (climate room at 20 ºC ± 2 ºC and more than 90 % RH), the moulds cut were pre-conditioned in vacuum and immerged in a saturated calcium hydroxide ($Ca(OH)_2$) solution in distilled water.

Afterwards, the ϕ100 x 50 mm moulds were connected to a rubber sleeve in order to contain the anodic solution, without chlorides, of sodium hydroxide in distilled water (NaOH 0,3N).

The rubber sleeve, with the mould properly sealed according to the illustration in Figure 1, is inserted in the sodium chloride catholyte solution (at 10% in NaCl mass in tap water).

Then, through the stainless steel plaques situated on the mould's tops according to the representation in Figure 1, an electric potential (according to the specification in point 6.4.4 of the NT Build 492 [7] or E 463 [8]) is applied, that will force, by migration, the transportation of the chloride ions through the mould.

After a certain test period, the mould is broken by being axially split and the rectangular sections obtained are sprayed with a silver nitrate solution ($AgNO_3$ 0.1 N). From the visible white silver chloride precipitation, the penetration depth is measured.

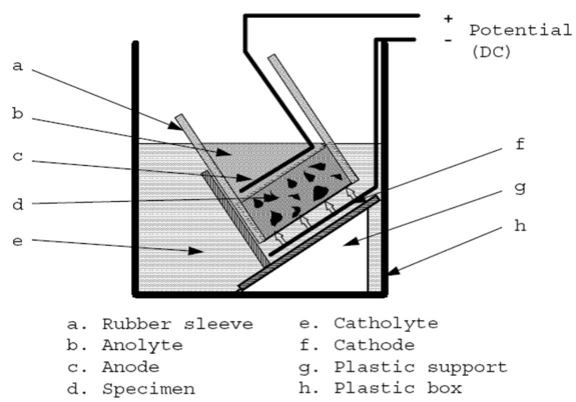

Figure 1 Migration test setup [7][8]

Figure 2 Slip open concrete specimen sprayed with $AgNO_3$

Based on the penetration depth measurement performed as well as in other parameters, it is possible to calculate the chloride (D_{nssm}) diffusion coefficient in non stationary regime from the equation (1):

$$D_{nssm} = \frac{RT}{zFE}\left(\frac{x_d - \alpha\sqrt{x_d}}{t}\right) \quad \text{with} \quad E = \frac{U-2}{L} \quad \text{and} \quad \alpha = 2\sqrt{\frac{RT}{zFE}}\,\mathrm{erf}^{-1}\left(1 - \frac{2c_d}{c_0}\right) \tag{1}$$

D_{nssm} = non-steady-state migration coefficient (m²/s);
z = absolute value of ion valence, for chloride, z=1;
F = Faraday constant (9,648 × 10^4 J/(V·mol));
U = absolute value of applied voltage (V);
R = gas constant (8,314 J/(K·mol);
T = average value of the initial and final temperatures in the anolyte solution (K);
L = thickness of the specimen (m);
x_d = average value of penetration depths (m);
t = test duration (s);
erf^{-1} = inverse of error function;
c_d = chloride concentration at which the colour changes (~ 0.07 N for CEM I concrete);
c0 = chloride concentration in the catholyte solution (~ 2 N).

Since $\mathrm{erf}^{-1}\left(1 - \frac{2x0,07}{2}\right) = 1,28$, the following simplified equation (2) can be used:

$$D_{nssm} = \frac{0,0239\ (273+T)L}{(U-2)t}\left(x_d - 0,0238\sqrt{\frac{(273+T)Lx_d}{U-2}}\right) \tag{2}$$

D_{nssm} = non-steady-state migration coefficient (x 10^{-12} m²/s);
U = absolute value of the applied voltage (V);
T = average value of the initial and final temperatures in the anolyte solution (°C);
L = thickness of the specimen (mm);
x_d = average value of the penetration depths (mm);
t = test duration (hours).

TEST RESULTS AND DISCUSSION

Table 2 shows the average values of the results obtained for chlorides D_{nssm} at the three ages studied (28, 91 and 182 days), their standard deviation (S) and the corresponding variation coefficient (CV), as well as some data to aid the interpretation of the data provided. For each of the studied mixes and for each age, three moulds of ϕ100 x 50 mm were tested. The average values are also shown graphically in Figure 3, to facilitate its reading and interpretation.

Table 2 Results of non-steady-state migration coefficient

Mixture	specimen age	Test conditions		Penetration depth			Non-steady-state migration coefficient		
		Applied voltage	Test duration	$x_{d\ average}$	S	CV	D_{nssm}	S	CV
	[days]	[V]	[hour]	[mm]		[%]	[$X10^{-12}m^2/s$]	[$X10^{-12}m^2/s$]	[%]
SCC1.100C	28	30	24	16,75	1,16	6,94	7,51	0,34	4,53
	91	30	24	14,71	0,51	3,43	6,52	0,50	7,66
	182	30	24	12,11	0,45	3,75	5,37	0,56	10,42
SCC2.30LF	28	30	24	27,50	0,30	1,10	12,70	0,21	1,67
	91	30	24	18,32	0,25	1,38	8,53	0,13	1,49
	182	15	24	9,93	1,45	14,60	8,21	1,34	16,27
SCC2.60LF	28	10	24	20,60	0,61	2,95	29,02	1,23	4,25
	91	10	24	18,17	1,68	9,22	22,45	2,36	10,53
	182	10	24	16,18	0,15	0,94	21,74	0,27	1,24
SCC2.70LF	28	10	24	33,29	0,40	1,21	48,51	0,49	1,02
	91	10	24	29,05	2,31	7,95	42,51	4,35	10,23
	182	10	24	25,63	0,28	1,08	37,49	0,43	1,15
SCC3.30FA	28	30	24	15,52	0,36	2,32	7,07	0,23	3,31
	91	30	24	10,43	0,20	1,94	4,50	0,10	2,23
	182	30	24	3,90	0,68	17,29	1,46	0,32	21,53
SCC3.60FA	28	30	24	25,76	1,01	3,93	12,10	0,53	4,37
	91	30	24	6,43	0,61	9,43	2,62	0,25	9,51
	182	30	24	5,86	0,65	11,18	2,33	0,32	13,80
SCC3.70FA	28	20	24	33,57	0,61	1,81	23,96	0,88	3,68
	91	25	24	14,39	1,36	9,47	7,36	1,05	14,32
	182	30	24	15,32	0,45	2,97	6,99	0,33	4,77
SCC4.10FA20LF	28	30	24	23,64	0,30	1,28	11,26	0,12	1,10
	91	30	24	14,18	1,46	10,33	6,20	0,70	11,20
	182	15	24	7,71	0,10	1,31	6,08	0,11	1,84
SCC4.20FA10LF	28	30	24	15,59	0,42	2,72	7,31	0,19	2,64
	91	30	24	8,12	1,11	13,70	3,32	0,47	14,28
	182	30	24	7,50	---	---	3,07	---	---
SCC5.20FA40LF	28	25	24	25,40	0,44	1,72	14,72	0,11	0,73
	91	30	24	18,24	1,11	6,08	8,41	0,63	7,45
	182	30	24	11,93	---	---	5,14	---	---
SCC5.40FA20LF	28	30	24	23,79	1,86	7,83	8,76	0,72	8,20
	91	30	24	13,02	0,68	5,18	5,66	0,32	5,57
	182	30	24	8,39	0,35	4,21	3,46	0,12	3,40
BR.XS1&2	28	10	24	13,68	1,26	9,23	18,61	1,84	9,89
	182	20	24	11,04	0,76	6,87	6,80	0,44	6,42
BR.XS3	28	10	24	12,52	0,48	3,80	16,60	0,76	4,57
	182	20	24	10,18	1,87	18,36	6,39	1,33	20,79

In a first analysis of the results obtained, it is seen that chlorides penetration resistance is strongly conditioned by the use of mineral admixtures in the SCC production and by their type. This can be observed in the values for SCC3 with FA, which are significantly lower when compared to those for SCC2 with LF.

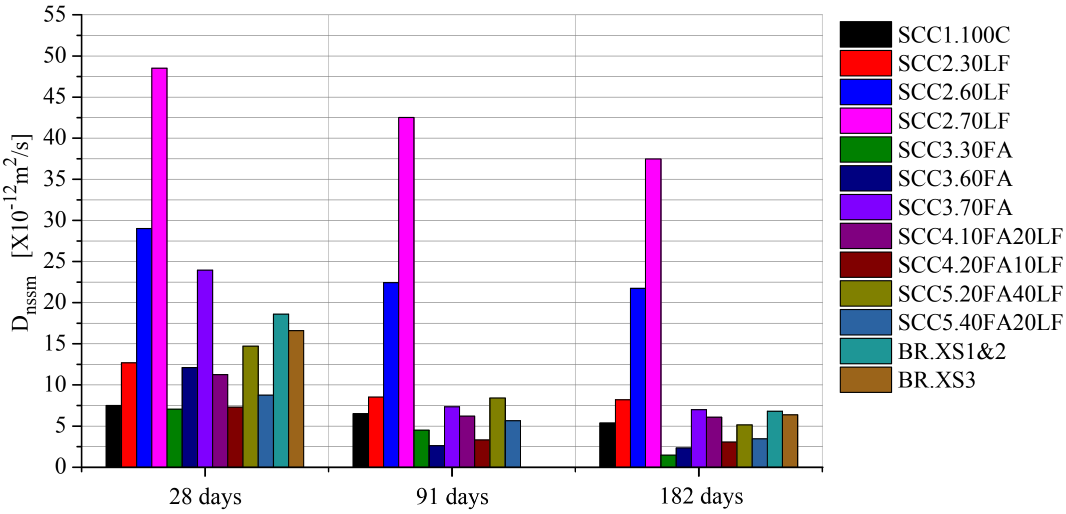

Figure 3 Results of non-steady-state migration coefficient

These results confirm the ones obtained, for example, by Zhu and Bartos [2][30] and Audenaert et al. [4]. Comparing the results obtained with those of the authors mentioned, one should highlight that the use of FA may result in a higher resistance to chlorides penetration when compared to the concrete produced only with CEM I or to concrete produced with C + LF. Zhu and Bartos [2][30] state that the increase of resistance to chloride penetration due to the incorporation of FA observed may be the result of the chloride ions passage by diffusion being more difficult or even blocked, since the FA particles, which are more round, significantly contribute to a higher compacity of the particles, both of the SCC pasta matrix and of the ITZ itself around the coarser aggregates.

For the mixes analysed, and considering the practically constant pasta volume, it is possible to observe a D_{nssm} decrease with the increase in the cement quantity and the decrease in LF (Figure 4), which can be explained by the decrease in the corresponding porosity.

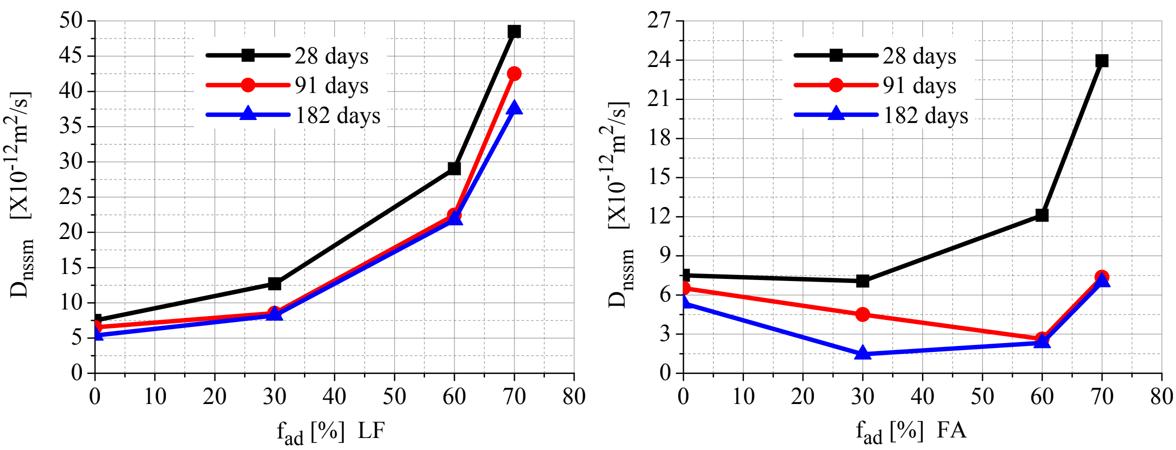

Figure 4 Influence of type and amount of powder in binary mixtures

Regarding the D_{nssm} variation with the age and the percentage of substitution (f_{ad}), it is observed in Figure 4 that those differences are minimal and decrease significantly with age, i.e. for all the values of f_{ad}, the variation from 91 days to 182 days is minimal.

The same is not true for the SCC3 with FA. For these mixes, a small decrease is observed in the value of D_{nssm} with the increase of f_{ad} to 60% at the age of 91 days. That value tends to stabilize, mainly for values of f_{ad} of 60% at the age of 182 days. For f_{ad} of 70 %, the value of D_{nssm} tends to increase despite being still significantly below the value obtained for the SCC2 with LF.

Despite the fact that, in this work, the influence of the variation in volume of the fine materials (cement and additions) in D_{nssm} was not evaluated, one should mention the work of Audenaert et al. [4], which describes the value of the referred coefficient increasing with the volume of fine material, for constant W/C ratio. Audenaert et al. [4] also mention that the use of LF finely grounded can cause an improvement in D_{nssm}.

Interpreting the data in figure 3, it is seen that the results obtained show a consistent coherence when compared to the variation of the D_{nssm} with the ages' tests as well as with the f_{ad} used. One should also mention its coherence with the results obtained by the other authors mentioned. The best behaviour is that of the mix with 30% of FA (SCC3 30FA) at all ages when compared to all the mixes produced (except for SCC2 60FA which at 91 days shows a slightly lower D_{nssm}).

From the joint analysis of Table 2 and Figures 3 and 5, it is observed that the ternary mixtures show a very satisfactory behaviour when compared to the remaining mixtures. One should highlight the behaviour shown at the first ages by the SCC5 40FA20LF with a D_{nssm} lower by 27.6% than the SCC3 60FA (both with total f_{ad} of 60%). That difference vanishes in the more advanced ages, maintaining, nevertheless, reduced values for the migration coefficients for both SCC. The ternary mix SCC4 20FA10LF (with total f_{ad} of 30%) shows, at 28 days, a value for D_{nssm} very close to that of SCC3 30FA, with a difference between them of approximately 3.3%. At 182 days of age, the difference mentioned increases to approximately 50%, remaining, nevertheless, with still the lowest value of the ternary mixtures at that age.

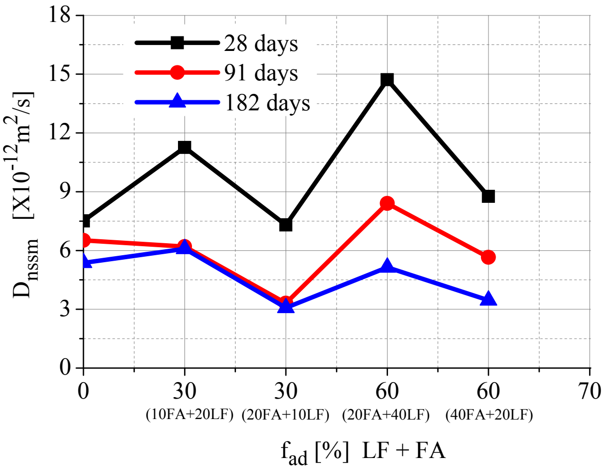

Figure 5 Influence of type and amount of powder in ternary mixtures

It is also observed that, in general, the ternary mixtures, in terms of their behaviour towards chlorides' penetration, follow the same trend as the binary mixtures, i.e. the addition of FA represents a significant advantage relatively to LF. The behaviour of the SCC4 20FA10LF mixture should be highlighted as the best of the ternary at all ages, even when compared to the remaining mixtures with a D_{nssm} only higher to that of the mixtures of FA with f_{ad} of 30% at all ages and of 60% at 91 and 182 days.

Regarding the mixes corresponding to the composition limits established for the XS environmental exposure classes of the E 464 specification [15] in reference to the NP EN 206-1 [25] and shown in Table 2 and Figure 3, one can say that the value of their D_{nssm} is in the range of the values obtained, under identical circumstances, for this type of concrete by other authors such as McNally et al. [32]. Comparing the results just mentioned with those obtained for the SCC produced, it can be stated that, with the exception of SCC2 with LF and of SCC3 70FA, all the SCC produced are within the specified limits, both for the XS1 and 2 classes and for the XS3. One has to highlight that, like for the SCC mixes, the migration coefficients decreased significantly with age.

Several authors, namely Marušić et al. [31] and McNally et al. [32], argue that the definition of the environmental exposure classes related to the chlorides' penetration through the concrete's composition parameters is not sufficient to guarantee their resistance to chlorides. The establishment of those limits should be made based on the precise values of the migration coefficient. The same authors also put forward some doubts about the establishment of the testing age, given the big change of the coefficient mentioned with the age change, as can be observed in the results shown in the work.

CONCLUDING REMARKS

Based on the results showed, the following conclusions can be drawn.

The chloride migration coefficient is strongly influenced by the quantity and type of additions used, as well as by the age of the tested concrete.

The use of FA in partial substitution of the NCP reduces the chloride migration coefficient essentially due to the improvement of the concrete's permeability. If, in a way, the use of FA causes an increase in the concrete's porosity in the hardened state at younger ages, it also causes a reduction in the average pores diameter with consequences such as a decrease in the concrete's permeability and a denser ITZ, making it less susceptible to the penetration of chlorides.

The migration coefficient increases considerably with the partial substitution of cement with LF. According to the results obtained with the ternary mixtures and consulting some work produced on the use of LF, namely Ramezanianpour et al. [33], it is argued that the optimal substitution percentage ranges between 10% and 15%.

The ternary mixtures show very satisfactory results when compared to the remaining mixtures. The behaviour of the mixture with f_{ad} of 20% FA and 10% of LF should be highlighted. The incorporation of FA in the ternary mixtures turned to be very beneficial to the behaviour of those concretes towards the penetration of chlorides.

With the exception of the mixes with LF and with 70% of FA, all SCC produced show lower values than those of the reference concrete produced according to LNEC's specification.

ACKNOWLEDGMENTS

The authors acknowledge the support of the Polytechnic Institute of Lisbon and the Lisbon Superior Engineering Institute through the *Programa de apoio à formação avançada de docentes* *do Ensino Superior Politécnico* (PROTEC) for facilitating this work under the context of the PhD scholarship with the reference SFRH/PROTEC/67426/2010. The support of the Foundation for Science and Technology (FCT) and of the ICIST research centre is also acknowledged.

REFERENCES

[1] LWIN M M, The state-of-the-knowledge of SCC - report, Office of Bridge Technology, Washington D.C., 2006, 9 p.

[2] ZHU W AND BARTOS J M, Permeation properties of self-compacting concrete, Cement and Concrete Research Vol 33, Issue 6, 2003, pp. 921-926.

[3] BOEL V, AUDENAERT K, SCHUTTER G, HEIRMAN G, VANDEWALLE L, DESMET B AND VANTOMME J, Transport properties of self-compacting concrete with limestone filler or fly ash, Materials and structures Vol 40, number 5, 2007, pp. 507-16.

[4] AUDENAERT K, YUAN Q AND SCHUTTER G DE, On the time dependency of the chloride migration coefficient in concrete, Construction and Building Materials, Vol 24, Issue 3, 2010, pp. 396-402.

[5] SPIESZ P AND BROUWERS H J H, Analysis of the theoretical model of the Rapid Chloride Migration test, 8th fib PhD Symposium in Kgs. Lyngby, Denmark, 2010.

[6] TANG L AND NILSSON L, Rapid determination of the chloride diffusivity in concrete by applying an electrical field, ACI Materials Journal Vol 89, Number 1, 1992, pp. 49-53.

[7] NT BUILD 492 (Nordtest Method), Concrete, mortar and cement-based repair materials, Chloride migration coefficient from non-steady-state migration experiments, Nordtest, Finland, 1999, 8 p.

[8] LNEC E 463, 2004, Concrete, determination of diffusion coefficient of chlorides from non-steady-state migration test (in Portuguese), National Laboratory for Civil Engineering, Lisbon, Portugal, 8 p.

[9] DURACRETE, Probabilistic Performance based Durability Design of Concrete Structures, DuraCrete Final Technical Report, Document BE95-1347/R17, 2000.

[10] CHLOROTEST, Resistance of concrete to chloride ingress – From laboratory tests to in-field performance, Guideline for practical use of methods for testing the resistance of concrete to chloride ingress, EU-Project (5th FP GROWTH) G6RD-CT-2002-00855.

[11] SPIESZ P AND BROUWERS H J H, Influence of electrical field applied in chloride migration tests on the properties of concrete, International congress on durability of concrete, Trondheim, Norway, 2012.

[12] STANISH K, HOOTONB R D AND THOMASC M D A, A novel method for describing chloride ion transport due to an electrical gradient in concrete: Part 1. Theoretical description, Cement and Concrete Research Vol 34, Issue 1, 2004, pp. 43-49.

[13] STANISH K, HOOTONB R D AND THOMASC M D A, A novel method for describing chloride ion transport due to an electrical gradient in concrete: Part 2. Experimental study, Cement and Concrete Research Vol 34, Issue 1, 2004, pp. 51-57.

[14] GLASS G K AND BUENFELD N R, The influence of chloride binding on the chloride corrosion risk in reinforced concrete, Corrosion Science Vol 42, 2000, pp. 329-344.

[15] LNEC E 464, 2007, Concrete, Prescriptive methodology for a design working life of 50 and of 100 years under the environmental exposure (in Portuguese), National Laboratory for Civil Engineering, Lisbon, Portugal, 15 p.

[16] NP EN 197-1, 2001/A3, 2008, Cement, Part 1: Composition, specifications and conformity criteria for common cements (in Portuguese). Lisbon, Portugal. IPQ. 8 p.

[17] NP EN 450-1, 2005 + A1, 2008, Fly ash for concrete, Part 1: Definition, specifications and conformity criteria (in Portuguese). Lisbon, Portugal. IPQ. 35 p.

[18] NP EN 450-2, 2006, Fly ash for concrete, Part 2: Conformity evaluation (in Portuguese). Lisbon, Portugal. IPQ. 29 p.

[19] LNEC E 466, 2005, Limestone fillers for hydraulic binders (in Portuguese), National Laboratory for Civil Engineering, Lisbon, Portugal. National Laboratory for Civil Engineering. 2 p.

[20] NP EN 12620, 2002 + A1, 2010, Aggregates for concrete (in Portuguese). Lisbon, Portugal. IPQ. 61 p.

[21] NP EN 934-1, 2008, Admixtures for concrete, mortar and grout. Part 1: Common requirements (in Portuguese). Lisbon, Portugal. IPQ. 13 p.

[22] NP EN 934-2, 2009, Admixtures for concrete, mortar and grout. Part 2: Concrete admixtures - Definitions, requirements, conformity, marking and labelling (in Portuguese). Lisbon, Portugal. IPQ. 28 p.

[23] NP EN 1008, 2003, Mixing water for concrete - Specification for sampling, testing and assessing the suitability of water, including water recovered from processes in the concrete industry, as mixing water for concrete. Lisbon, Portugal. IPQ. 22 p (in Portuguese).

[24] NP EN 206-9, 2010, Concrete, Part 9: Additional rules for self-compacting concrete (SCC) (in Portuguese). Lisbon, Portugal. IPQ. 35 p.

[25] NP EN 206-1, 2007, concrete, Part 1: Specification, performance, production and conformity (in Portuguese). Lisbon, Portugal. IPQ. 84 p.

[26] NEPOMUCENO M, Methodology for Self-Compacting Concretes Design (in Portuguese), PhD thesis in Civil Engineering, Beira Interior University, Covilhã, Portugal, 2005, 734 pp.

[27] SILVA P M, BRITO J D E AND COSTA J M, Viability of two new mix design methodologies for SCC, ACI Materials Journal, Vol 108, Number 6, 2011, pp. 579-588.

[28] OKAMURA H; OZAWA K AND OUCHI M, Self-Compacting Concrete, fib Structural Concrete, V. 1, No. 1, 2000, pp. 3-17.

[29] DOMONE P, Mix Design (Background Document) in Self-Compacting Concrete: State-of-the-Art Report, RILEM Technical Committee 174-SCC, RILEM Publications S.A.R.L., 2000, pp. 49-65.

[30] ZHU W AND BARTOS J M, Aspects of Durability of self-Compacting Concrete, 9th International Conference on the Durability of Building Materials and Components, Brisbane, Australia, 2002, paper 249.

[31] MARUŠIĆ E, AKRAP N, DRAGOVIĆ T, ČUJIĆ NIKIĆ I AND JURAŠIN M, Concrete Exposure Classes concerning Corrosion Induced by Chlorides - Criterions - Experimental Results and Possible Misleads, Codes in Structural Engineering - Developments and Needs for International Practice, Hirt, M A, Radić J, Mandić A (ed.), Zagreb, SECON - CSSE, 2010, pp 1105-1112, ISBN: 978-953-7621-05-6.

[32] MCNALLY C, RICHARDSON M G, EVANS C AND CALLANAN T, Chloride diffusion coefficient determination for specifications, Dhir R K (ed.) Proceedings of the 6th International Congress on Global Construction, University of Dundee, UK, 2005, ISBN: 978-0-7277-33877-0.

[33] RAMEZANIANPOUR A, GHIASVAND E, NICKSERESHT I, MAHDIKHANI M AND MOODI F, Influence of various amounts of limestone powder on performance of Portland limestone cement concretes, Cement and Concrete Composites, Vol 31, Issue 10, 2009, pp. 715-720.