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Calculation of Chloride Penetration Profile in Concrete Structures

*G. Roa-Rodriguez**, W. Aperador*, A. Delgado.*

Departament of Engineering, Universidad Militar Nueva Granada, Carrera 11 No. 101-80, Fax:+57(1) 6343200, Bogotá, Colombia.
*E-mail: g.ing.materiales@gmail.com
**E-mail: guillermoroa.rrg@gmail.com

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This article shows the development and implementation of a software that calculate the chloride penetration profile in concrete obtained using traditional Portland cements and cementitious mixtures from the addition of pozzolanic materials such as silica fume, metakaolin, fly ash, etc. The software calculates the penetration profile taking into account parameters such as the water-cement ratio, initial chlorides concentration, and the pozzolan content in the mixture.

Keywords: Chloride concentration, Concrete, Pozzolan, Software, Penetration Profile.

1. INTRODUCTION

In steel embedded within concrete, the main electrochemical reactions take place in the limited volume of aqueous solution present in the pores of the concrete surrounding the metal. As a result of this process, the steel loses mass, and its cross section decreases. However this is not one of the obvious risks associated with steel corrosion in concrete, instead it is about solid products of corrosion. These products are deposited in the gap between the concrete and steel, due to being in a very small place, this process generates efforts that can break the concrete coat causing a progressive deterioration of it [1].

One of the most common reasons that cause corrosion in reinforcements is the chlorides penetration through the net of pores when these are located in marine environments or when in the mixture such ions are incorporated. Chloride ions are capable of causing localized corrosion therefore lead to a premature and unexpected failure of the structure [2].

Normally, concrete is an excellent protection for steel reinforcements inside the structure, but exposure to various environmental conditions during its service life may accelerate the destruction process. A well-known cause of steel corrosion is chloride penetration; many factors govern the phenomenon of chloride penetration into concrete, such as the type of cementitious material, the water - cement ratio, curing time, period of exposure to chlorides and other physical factors. Generally, the ingress of chlorides rate, depends on the diffusion coefficient of chlorides, which varies with the exposure time.

The evaluation of the transport properties into concrete (chloride's diffusion), results essential in order to project the life time of concrete structures. The interest is concentrated in the critical threshold of chlorides concentration that cannot be overpassed in the reinforcement surface, to avoid the corrosion phenomena [3].

Given the importance that chlorides penetration have acquired, this paper exposes in general terms, the software development to calculate the chloride penetration profile in different concrete mixtures, which by the entry of specific parameters of the concrete composition (water – cement ratio, initial concentration of chlorides, and the content of pozzolan in the mixture) allows to estimate the deterioration degree. With the present development, it is not necessary to perform a laboratory test on the cores taken from the study site to determine the penetration value.

2. MATHEMATICAL MODELING OF CHLORIDE PENETRATION INTO CONCRETE

Chloride ions might be present in the concrete in three different ways: bound, adsorbed and dissolved in water that is retained in the pores, which forms the pore solution. Chloride ions that are harmful to the reinforcing steel are those which are dissolved or are free, but due to the balances that occur, it is possible that chloride ions which are adsorbed, be incorporated into the solution and become hazardous [4][5][6].

Chemical reactions that produce chlorides bound occur in the concrete between the chloride ions and the cement paste. The major reaction occurs between free chloride ions and tricalcium aluminate (C_3A), which form aluminum chlorides. Free chloride ions, also react with the silicate gels $3CaO \cdot 2SiO_2 \cdot 3H_2O$ (C-S-H) and calcium hydroxides and magnesium hydroxides ($Ca(OH)_2$y $Mg(OH)_2$ respectively) in the cement paste. The physical and chemical adsorption of chloride ions in the pores of concrete walls, produce joints chlorides as well.

When free chloride ions penetrate the pore system of the concrete structure, some of the ions are fixed to solid concrete structure. The transient chemical reaction affects the flow of free ions in the pore solution [7].

Diffusion through a porous medium such as concrete is a phenomenon of chloride ion transport, is the principal mechanism of chloride penetration into concrete. Its study is based on obtaining three main parameters: the concentration of chloride, the diffusion coefficient and the concentration of chlorides in the concrete surface. According to Fick's second law of diffusion, it is assumed a unidimensional transport process [8][9].

$$\frac{\partial C}{\partial t} = D_a \frac{\delta^2 C}{\delta x^2} \qquad (1)$$

Assuming $C(x,0) = 0, C(0,t) = C_S$, and the diffusion coefficient D_a as constant, analytical solution is obtained from equation 1 (equation 2) [8][10]:

$$C_x = C_s\left[1 - erf\left(\frac{x}{2\sqrt{D_a t}}\right)\right] \therefore D_a = apparent\ diffusion\ coefficient \tag{2}$$

Although equation 1 and its analytical solution (equation 2) adequately describe the behavior of the concentration of chlorides in the concrete structure, the assumption of having a constant diffusion coefficient, D_a, restricts the use of the equation.

A model that can accurately estimate the profile of chloride penetration into concrete for a long term, it should incorporate, rather than a constant coefficient, a variable diffusion coefficient respect to time D_c [11].

Mangata P. [12] has taken into account several measurements carried out on cores exposed to the action of the chlorides, where the diffusion coefficient was measured, these measurements showed that the coefficient depends on the time. The relationship between time and was approximately in the study using an empirical relationship (Equation 3).

$$D_c = D_i t^{-m} \tag{3}$$

Where D_i is the effective diffusion coefficient, t is time (measured in seconds), and m an empirical constant. Thus, equation 3 can be replaced in equation 1 as follows (Equation 4) [12]:

$$\frac{\partial C}{\partial t} = D_i t^{-m} \frac{\delta^2 C}{\delta x^2} \tag{3}$$

The analytical solution of Equation 3 can be expressed by the equation 4 [12][7]:

$$C_x = C_s\left[1 - erf\left(\frac{x}{2\sqrt{\frac{D_i t^{(1-m)}}{1-m}}}\right)\right] \tag{4}$$

Where *t* is expressed in seconds. The equation 4 can be transformed to terms of years (Equation 5):

$$C_x = C_s\left[1 - erf\left(\frac{x}{2\sqrt{\frac{31536000 \cdot D_i t^{(1-m)}}{1-m}}}\right)\right] \tag{5}$$

The empirical constant *m*, can be estimated by interpolation in terms of cementitious material and water-cement ratio. Thus, the values of *m* can be obtained through equation 6 [6-12]:

$$m = \delta(F) + \varphi \tag{6}$$

Where δ and φ, are empirical coefficients given in terms of the water-cement ratio *W/C* (equations 7 and 8) [6-13]:

$$\delta = -0.0015(W/C) + 0.0034 \tag{7}$$

$$\varphi = -0.175(W/C) + 0.840 \tag{8}$$

By substituting equations 7 and 8 in equation 6 gets:

$$m = [-0.0015 \cdot (W/C) + 0.0034](F) + [-0.175 \cdot (W/C) + 0.840] \tag{9}$$

Where F is the concentration of cement (%). The equation 9 is valid for calculating the empirical constant m for cementitious concentrations not higher than 50% by weight of cementitious and relations W/C in the range of $(0.45 - 0.65)$ [7][14-15].

Finally, the error function of Equation 5 is calculated by the polynomial as described in equation 10:

$$erf = 0.0095 \cdot x^6 - 0.1057 \cdot x^5 + 0.4416 \cdot x^4 - 0.7686 \cdot x^3 + 0.1625 \cdot x^2 + 1.1024 \cdot x + 0.0007 \tag{10}$$

2.1. Concrete samples, specimen preparation and Carrying out the experiment

As cement, fly ash type F (FA) was used from the power plant Termozipa, the chemical composition is recorded in Table 1. The ignition loss was 4.23% of the total mass which is determined by calcination of the sample at 1000 ° C, value associated with unburnt carbon residues. In addition, we evaluated the percentage of reactive silica of fly ash following the procedure described in the standard UNE 80-225-93, obtaining a value of 41.23% by mass. The other cementing was Portland cement type I, commonly used in construction. The aggregates used are gravel at a maximum size of 17 mm, specific gravity 3.12, and absorption of 1.6%; and river sand with specific surface area of 2380 $\frac{kg}{m^3}$ and absorption of 3.0%. From these materials were elaborated concrete of 400 kg of cementitious per cubic meter of concrete and water-cementitious ratio of 0.65 [15-16].

Table 1. Chemical composition of fly ash

Composite	Fly ash (percentage by weight)
SiO_2	56,6
Al_2O_3	23,1
Fe_2O_3	4,6
CaO	5,7
MgO	0,9
Na_2O	0,8
K_2O	1,4
P_2O_5	0,7
TiO_2	1
MnO	0,01
SO_3	0,50
SiO_2/Al_2O_3	2,7

For the study, samples were formed using concrete Portland (OPC) as the reference mixture, and also mixes of concrete alkali activated slag, adding fly ash (FA) with percentages of 15%, 20% and 35%, which were exposed in an atmosphere with different concentrations of chlorides (Table 2). Samples were taken at the end of 2 years and 4 years.

Table 2. Physical characteristics and initial conditions for the samples subjected to chloride attack

Mixtures	W/C	Initial concentration of chlorides (%)	
100%	0.65	2 years	4 years
		4	5.6
15%FA	0.65	5.3	6.9
25%FA	0.65	5.5	6.3
35%FA	0.65	4.8	5.7

The tests for determining the presence of chloride ion in the concrete, and their respective penetration were performed according to ASTM C1543-02 on specimens cured for 91 days. Cylindrical specimens were used (50 Ø × 100 mm). The specimens were immersed in a saturated solution of calcium hydroxide $Ca(OH)_2$ in distilled water, contained in a closed vessel. They remained until reaching constant weight, ± 0.1% by mass. Subsequently the samples were immersed for a period of 2 years and 4 years in a solution of 3.5% NaCl in distilled water. The concentration of the NaCl solution was kept constant during the time span of the assay, practicing the necessary adjustments every week.

Table 3. Measurements taken on specimens Portland 100% and initial conditions

Sample Type	Measuring depth (mm)	Sample concentration at 2 years (% by weight of cement)	Sample concentration at 4 years (% by weight of cement)
Portland 100% ($C_{o2years} = 4\%$ $C_{o\,4\,years} = 5.6\%$)	0	3,67	5,60
	5	3,23	4,96
	10	2,78	4,33
	15	2,35	3,73
	20	1,94	3,16
	25	1,58	2,64
	30	1,26	2,17
	35	0,99	1,76
	40	0,76	1,40
	45	0,57	1,09
	50	0,42	0,84
	55	0,30	0,63
	60	0,21	0,47

At the end of the period of two years and four years for each set of specimens, these were removed from the solution and measurements were taken. Samples were extracted from the dried material reaching the 60 mm deep, taking them at intervals of approximately 5 mm (Tables 3 to 6) in order to describe the profile of penetration of chlorides (Fig. 1 to 4). Samples were extracted using a drill press.

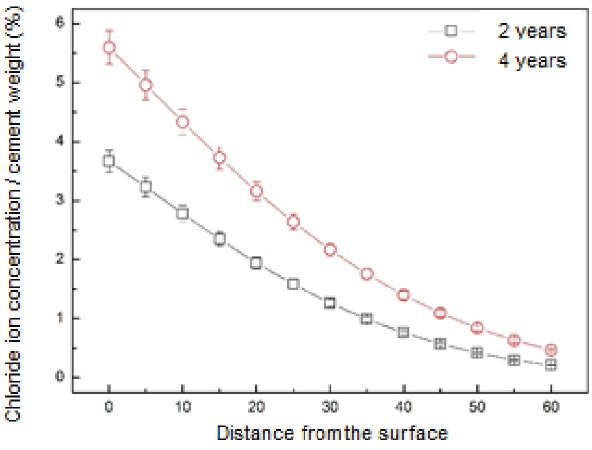


Figure 1. Chloride penetration profile Portland 100% (samples taken at 2 years and 4 years)

Table 4. Measurements taken on specimens Portland FA 25% and initial conditions

Sample Type	Measuring depth (mm)	Sample concentration at 2 years (% by weight of cement)	Sample concentration at 4 years (% by weight of cement)
Portland Fly Ash 25% ($C_{o2years} = 5.5\%$ $C_{o\,4\,years} = 6.3\%$)	0	5,41	6,22
	5	4,39	5,60
	10	3,41	4,45
	15	2,54	3,41
	20	1,82	2,52
	25	1,24	1,79
	30	0,81	1,22
	35	0,50	0,80
	40	0,29	0,50
	45	0,16	0,29
	50	0,08	0,16
	55	0,03	0,08
	60	0,00	0,04

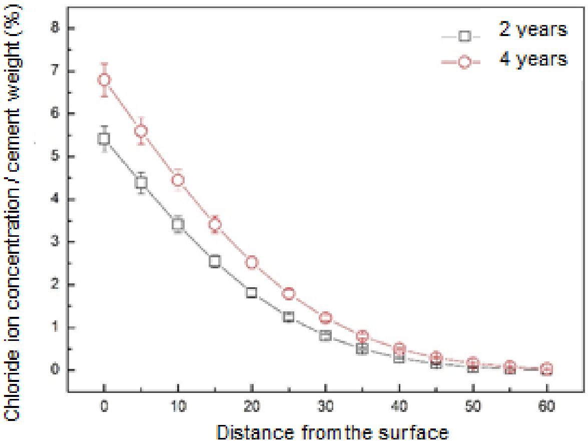


Figure 2. Chloride penetration profile Portland FA 25% (samples taken at 2 years and 4 years)

Table 5. Measurements taken on specimens Portland FA 15% and initial conditions

Sample Type	Measuring depth (mm)	Sample concentration at 2 years (% by weight of cement)	Sample concentration at 4 years (% by weight of cement)
Portland Fly Ash 15% ($C_{o2years} = 5.3\%$ $C_{o\,4\,years} = 6.5\%$)	0	5,01	6,30
	5	4,07	5,19
	10	3,36	4,30
	15	2,66	3,49
	20	2,43	2,74
	25	1,48	2,10
	30	1,28	1,99
	35	0,90	1,15
	40	0,50	1,01
	45	0,32	0,57
	50	0,19	0,36
	55	0,11	0,29
	60	0,06	0,17

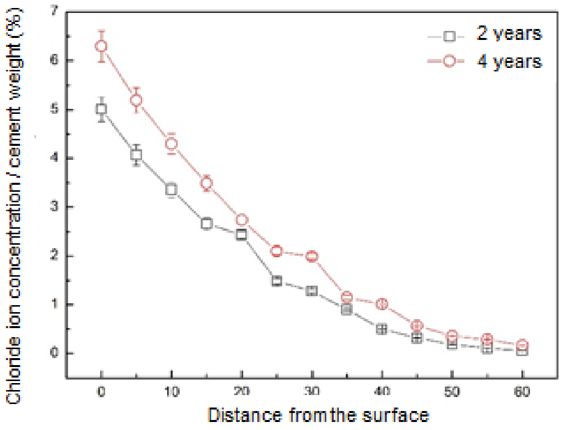


Figure 3. Chloride penetration profile Portland FA 15% (samples taken at 2 years and 4 years).

Tabla 6. Measurements taken on specimens Portland FA 35% and initial conditions.

Sample Type	Measuring depth (mm)	Sample concentration at 2 years (% by weight of cement)	Sample concentration at 4 years (% by weight of cement)
Portland Fly Ash 35% ($C_{o2years} = 4.8\%$ $C_{o\,4\,years} = 5.7\%$)	0	4,38	5,20
	5	3,41	4,12
	10	2,51	3,11
	15	1,74	2,23
	20	1,14	1,51
	25	0,70	0,97
	30	0,40	0,59
	35	0,21	0,33
	40	0,10	0,18
	45	0,04	0,08
	50	0,01	0,03
	55	0,00	0,00
	60	0,00	0,00

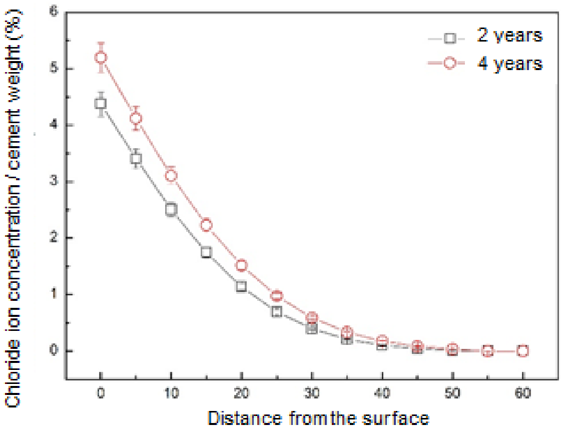


Figure 4. Chloride penetration profile Portland FA 35% (samples taken at 2 years and 4 years).

3. RESULTS

With the mathematical model describing the diffusion of chloride ions within the concrete, described in the previous section, the equation 5 was programmed with the purpose of estimate the depth and the penetration profile of chloride.

The software was programmed under development platform Sharp Develop, which is a free integrated development environment for C #. Use the free supplement for generating 2D graphics zedgraph.dll.

The application has 3 screens:

- Platform Load Screen (fig. 5).
- Startup screen (fig. 6).
- Working Screen (fig. 7).

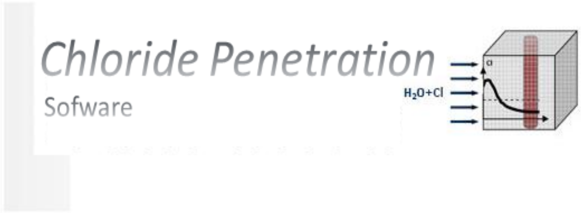
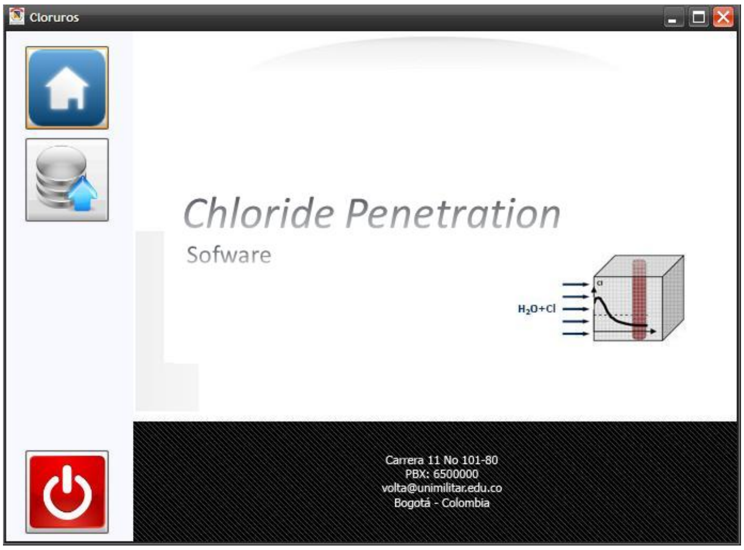
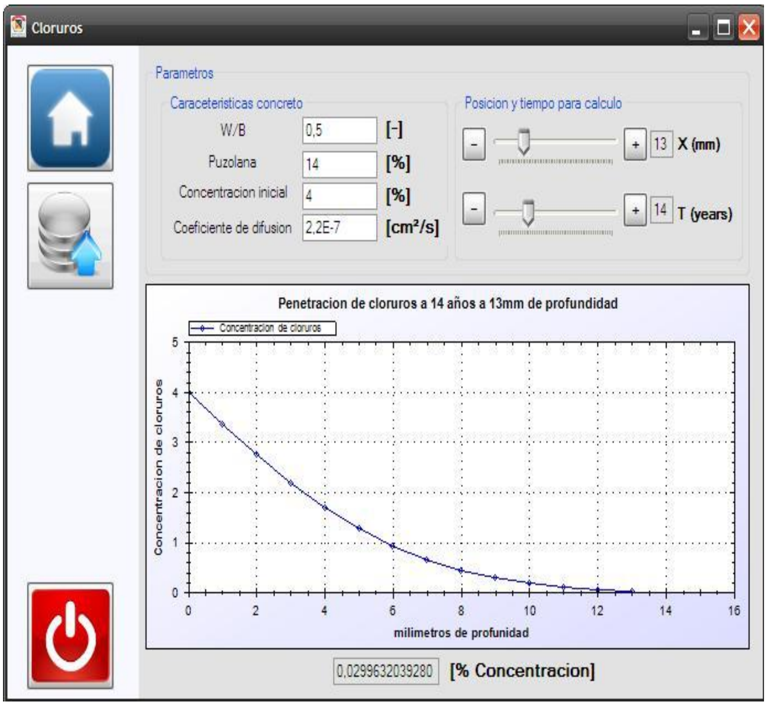


Figure 5. Platform Load Screen.



Carrera 11 No 101-80
PBX: 6500000
volta@unimilitar.edu.co
Bogotá - Colombia

Figure 6. Startup screen.



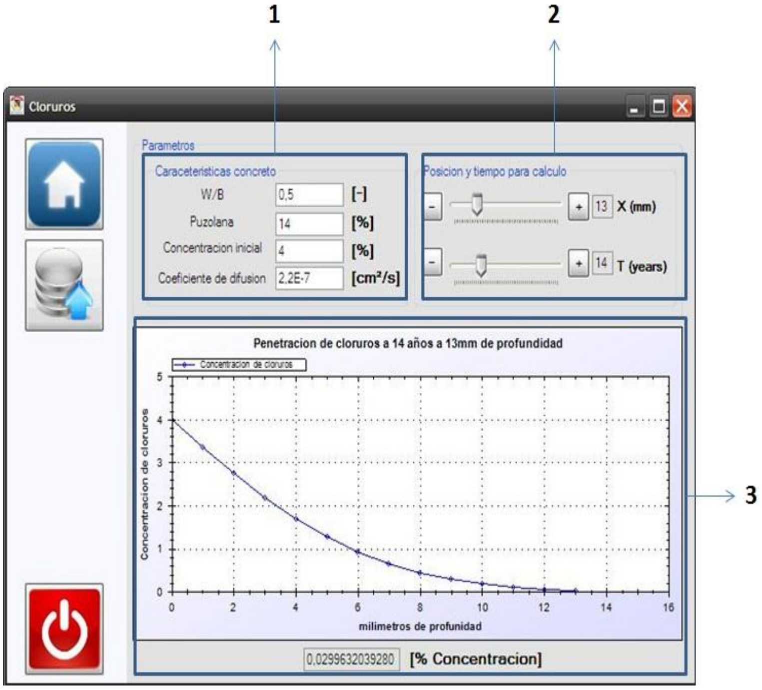
W/B 0,5 [-]
Puzolana 14 [%]
Concentracion inicial 4 [%]
Coeficiente de difusion 2,2E-7 [cm²/s]

13 X (mm)
14 T (years)

0,0299632039280 [% Concentracion]

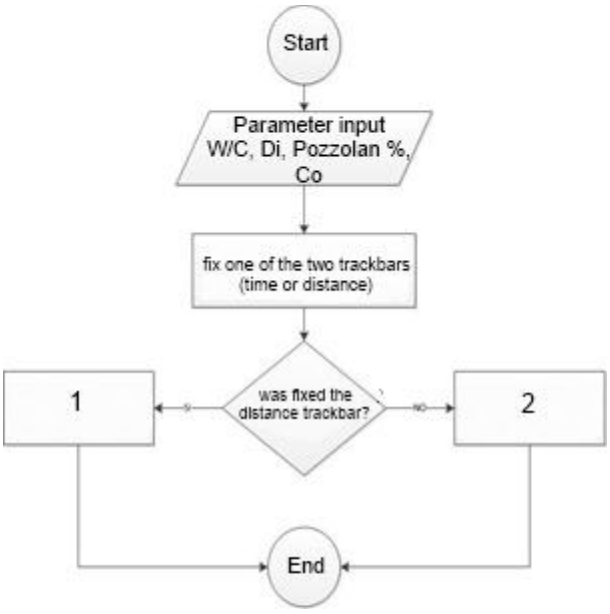
Figure 7. Working Screen

Within the working screen is housed the application, this screen is composed of 3 zones (fig. 8):



W/B 0,5 [-]
Puzolana 14 [%]
Concentracion inicial 4 [%]
Coeficiente de difusion 2,2E-7 [cm²/s]
13 X (mm)
14 T (years)
0,0299632039280 [% Concentracion]

Figure 8. Zones of the working screen



1	2
Calculation of chloride penetration respect to time	Calculation of chloride penetration through the structure at a given time

Figure 9. Programming flowchart.

1. Parameters zone: In this area the user enters the parameters required by the program with which to perform the calculation (water-cement ratio, pozzolan concentration, chloride concentration at the surface, and the diffusion coefficient).

2. Calculation depth and time settings zone: In this area are located the trackbars of time and distance, which as they move, allow the calculation of the chloride concentration at a specific distance time-dependent, or identifying the chloride concentration in a fixed time depth dependent.
3. Display area: This area identifies graphically and numerically the chloride concentration in the structure (Penetration profile).

The software to calculate the chloride penetration profile, requires the user to enter the required parameters, then fix one of the two trackbars (time or distance) and finally vary the interest trackbar (time or distance) for calculation (Fig. 9).

3.1. Comparison measurements with estimates obtained by the software

The parameters from the concrete samples exposed to the assay were entered in the developed software (section 2.1). The application showed the chlorides penetration profile, with which was performed the contrast of the experimental measurements (tables 7 to 10).

Table 7. Comparison measurements Portland cement 100%.

Type of specimen	Depth (mm)	Sample concentration at 2 years (% by weight of cement)	Sample concentration at 4 years (% by weight of cement)	Concentration at 2 years (Software) (% by weight of cement)	Concentration at 4 years (Software) (% by weight of cement)	Error % (concentration to 2 years)	Error% (concentration to 4 years)
Portland 100% ($C_{o2years} = 4\%$ $C_{o\,4\,years} = 5.6\%$)	0	3,67	5,14	3,97	5,60	8,17	8,95
	5	3,23	4,64	3,50	4,96	8,36	6,90
	10	2,78	4,01	3,01	4,33	8,27	7,98
	15	2,35	3,43	2,54	3,73	8,09	8,75
	20	1,94	2,89	2,10	3,16	8,25	9,34
	25	1,58	2,29	1,71	2,64	8,23	15,28
	30	1,26	1,94	1,37	2,17	8,73	11,86
	35	0,99	1,51	1,07	1,76	8,08	16,56
	40	0,76	1,28	0,82	1,40	7,89	9,37
	45	0,57	0,95	0,62	1,09	8,77	14,74
	50	0,42	0,74	0,45	0,84	7,14	13,51
	55	0,30	0,71	0,33	0,63	10,00	11,27
	60	0,21	0,52	0,23	0,47	9,52	9,62

As shown in the tables above, the weighted error obtained was 8.73%, as a result of all tests conducted. Figure 10 shows a comparison between the assay performed on specimens of Portland cement FA 15% at 2 years, and the penetration profile obtained by the software.

Table 8. Comparison measurements FA 25% Portland cement.

Type of specimen	Depth (mm)	Sample concentration at 2 years (% by weight of cement)	Sample concentration at 4 years (% by weight of cement)	Concentration at 2 years (Software) (% by weight of cement)	Concentration at 4 years (Software) (% by weight of cement)	Error % (concentration to 2 years)	Error% (concentration to 4 years)
Portland Fly Ash 25% ($C_{o2years} = 5.5\%$ $C_{o\,4\,years} = 6.3\%$)	0	5,41	6,22	5,50	6,30	1,59	1,21
	5	4,39	5,60	4,46	5,19	1,50	7,34
	10	3,41	4,45	3,46	4,12	1,58	7,33
	15	2,54	3,41	2,58	3,16	1,69	7,30
	20	1,82	2,52	1,85	2,34	1,37	7,30
	25	1,24	1,79	1,26	1,66	1,53	7,21
	30	0,81	1,22	0,82	1,13	0,99	7,05
	35	0,50	0,80	0,50	0,74	0,80	7,50
	40	0,29	0,50	0,29	0,46	1,03	7,80
	45	0,16	0,29	0,16	0,27	0,00	5,86
	50	0,08	0,16	0,08	0,15	1,25	5,00
	55	0,03	0,08	0,03	0,08	0,00	2,50
	60	0,00	0,04	0,01	0,03	1,63	7,33

Table 9. Comparison measurements FA 15% Portland cement.

Type of specimen	Depth (mm)	Sample concentration at 2 years (% by weight of cement)	Sample concentration at 4 years (% by weight of cement)	Concentration at 2 years (Software) (% by weight of cement)	Concentration at 4 years (Software) (% by weight of cement)	Error % (concentration to 2 years)	Error% (concentration to 4 years)
Portland Fly Ash 15% ($C_{o2years} = 5.3\%$ $C_{o\,4\,years} = 6.5\%$)	0	5,01	6,30	5,30	6,90	5,32	8,70
	5	4,07	5,19	4,45	5,87	9,34	13,20
	10	3,36	4,30	3,62	4,88	7,67	13,40
	15	2,66	3,49	2,86	3,95	7,59	13,03
	20	2,43	2,74	2,19	3,11	9,95	13,74
	25	1,48	2,10	1,63	2,39	9,97	13,69
	30	1,28	1,99	1,17	1,79	8,48	10,07
	35	0,90	1,15	0,81	1,30	10,11	12,98
	40	0,50	1,01	0,54	0,91	8,59	9,70
	45	0,32	0,57	0,35	0,62	9,50	8,38
	50	0,19	0,36	0,21	0,41	9,33	12,71
	55	0,11	0,29	0,12	0,26	11,71	9,47
	60	0,06	0,17	0,07	0,15	13,56	10,59

Table 10. Comparison measurements FA 35% Portland cement.

Type of specimen	Depth (mm)	Sample concentration at 2 years (% by weight of cement)	Sample concentration at 4 years (% by weight of cement)	Concentration at 2 years (Software) (% by weight of cement)	Concentration at 4 years (Software) (% by weight of cement)	Error % (concentration to 2 years)	Error% (concentration to 4 years)
Portland Fly Ash 35% ($C_{o2years}$ = 4.8% $C_{o\,4\,years}$ = 5.7%)	0	4,38	5,20	4,80	5,70	8,67	3,70
	5	3,41	4,12	3,74	4,52	9,59	3,11
	10	2,51	3,11	2,75	3,40	9,48	2,08
	15	1,74	2,23	1,91	2,44	9,66	0,81
	20	1,14	1,51	1,25	1,66	9,39	0,76
	25	0,70	0,97	0,76	1,07	9,00	2,71
	30	0,40	0,59	0,44	0,65	8,75	5,00
	35	0,21	0,33	0,23	0,37	9,05	7,81
	40	0,10	0,18	0,11	0,19	10,00	10,94
	45	0,04	0,08	0,05	0,09	15,00	15,41
	50	0,01	0,03	0,01	0,04	10,00	16,94
	55	0,00	0,00	0,00	0,00	1	9,61
	60	0,00	0,00	0,00	0,00	1	1

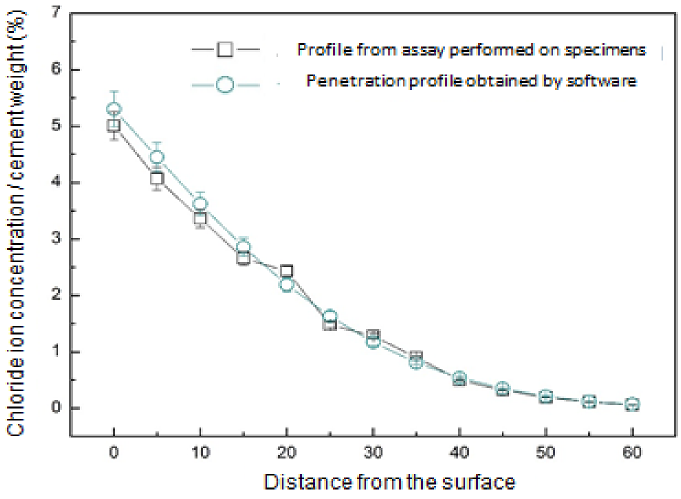


Figure 10. Comparison between chloride penetration profile obtained experimentally and that obtained by software to Portland FA 15% specimens tested during 2 years.

4. CONCLUSIONS

Through this study, it was corroborated that susceptibility which present the penetration of chlorides in the concrete is related according to the amount of pozzolanic materials used in their production. It also showed the importance of the water / cement factor which influences the capacity of penetration of chlorides in the structure.

The software to calculate the chloride penetration profiles, allows estimate the concentration of chlorides through the interior of the structure by entering characteristic parameters of the composition of the concrete. The big benefit which is obtained when estimating using the software, is that it is not necessary to perform a laboratory test on the cores taken from the study site to determine the exact compositions, but simply by an approximation to these values and making variations on them, can be made a determination of the behavior of the penetration profile in the interior of the structure, avoiding to some extent the intervention on the study site.

Using the application developed in the study, Estimates of chloride penetration profiles were performed, entering the calculation different parameters of the material, aggression was observed, which gives the low use of fly ash to the concentration of chloride inside the structure; profiles were corroborated experimentally.

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