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CHLORIDE PENETRATION INTO MORTAR FOR NON-DESTRUCTIVE DETERMINATION OF THE CHLORIDE BINDING ISOTHERM

J.-P. Bigas

1. Introduction

To evaluate the service life concrete structure exposed to marine environment, it will be important to predict the penetration of chloride ions into concrete. The Fick's second law gives the chloride concentration C as a function of the distance x from the exposed surface and as a function of the time t , assuming a constant D , intrinsic chloride diffusion coefficient in a semi-infinite porous medium:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

Equation (1) is valid only if there is no interaction between chloride and solid phases. In fact, when binding process (chemical and physical) occurs, the chloride penetration is slower. Then, the determination of D should be reduced to:

1. the measurement of the effective diffusion coefficient D_e ,
2. the quantification of the binding process.

The differential equation describing the migration of chloride into concrete [1] should be written as:

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \quad (2)$$

with $D_a = \frac{D\tau}{\alpha} = \frac{D_e}{\alpha}$ defined as the apparent diffusion coefficient, taking into account the binding phenomenon between the liquid phase and the solid phase [2, 3]. The capacity factor α is expressed as $\alpha = \tau + (1-\tau)\rho_s K_d$. Assuming an instantaneous exchange driven by a linear binding isotherm K_d is the binding capacity as $C_s = K_d C$ with C_s as bound chloride, τ as concrete porosity and ρ_s its density.

In fact, the apparent diffusion coefficient D_a which takes into account chloride binding, is not a constant because the binding isotherm is non-linear. Classical determinations [4] of binding isotherm are done on crushed materials, neglecting the real microstructure of the concrete, particularly the microcracks. Our original approach [6, 7], which takes into account the bulk microstructure of the material, is based on an utilisation of the data obtained with classical diffusion tests.

2. Materials and methods

These tests were realised on mortars samples (Table 1). The 28 day characteristics for the mortar cured in water at 20°C are: compressive strength = 40 MPa, density $\rho_s = 2400 \text{ kg/m}^3$, water porosity $\tau_{\text{water}} = 0.16$ and mercury porosity $\tau = 0.14$.

Table 1. Mix proportions

Materials	
CPA-CEM I	519 kg/m ³
Siliceous sand (0.6/1.2 mm)	1067 kg/m ³
Siliceous sand (1.2/25 mm)	457 kg/m ³
Water	255 l/m ³

After curing, slices were removed from 11*22 cm cylinders and placed in diffusion cells. The diffusion area is $7.088 \cdot 10^{-3} \text{ m}^2$, and the volume of both compartment of this cells is $3.73 \cdot 10^{-4} \text{ m}^3$. Each cell was filled with an alkaline solution of KOH (4.65 g/l) and NaOH (1 g/l) at pH 13.

Different concentration gradients (Table 2) are obtained using different initial concentration C_o in chloride and using different thickness of slices.

Table 2. Experimental program. The X sign indicates the tested variables

	$C_o = 169.6 \text{ g/l}$	$C_o = 20.2 \text{ g/l}$	$C_o = 10.0 \text{ g/l}$	$C_o = 5.0 \text{ g/l}$	$C_o = 1.0 \text{ g/l}$
L=1 cm	X	X	X	X	X
L=1.5 cm		X	X		

The downstream solution was removed at regular term (twice a month) to maintain the $C=0$ condition at $x=L$. At each term the chloride content was determined by a potentiometric method.

3. Modelling

For linear binding, the resolution of Fick's second law, shows an asymptotic increase of the quantities of diffused chloride with time when steady state occurs (Fig 1). The time lag t_i , is defined as the abscissa of the asymptote [1]:

$$t_i = \frac{\alpha L^2}{6D_e} \quad (3)$$

D_e , is assumed to be independent of C_o , and calculated from the slope of the asymptote.

Without binding, the factor capacity α is represented by the porosity, the time lag is:

$$t_i = \frac{\tau L^2}{6D_e} = \frac{L^2}{6D} \quad (4)$$

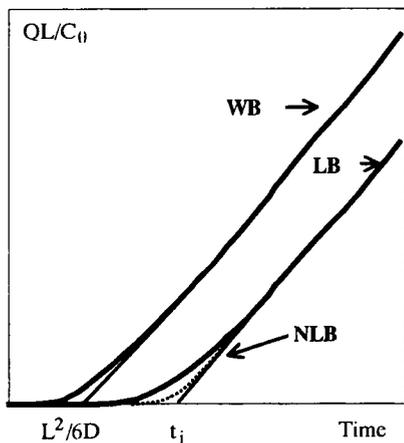


Fig 1. Diffusion curves; WB diffusion without binding, LB diffusion with linear binding, NLB diffusion with non-linear binding

The steady state regime, characterised by a linear concentration profile in the liquide phase between the upstream and the downstream cells, is independent of the non-linearity or the linearity of the isotherm. In the case of non-linear binding, we can write:

$$\frac{QL}{C_o} = D_e t - \alpha_{eq} \frac{L^2}{6} \quad (5)$$

where α_{eq} is the equivalent capacity factor of the diffusion with linear binding which have the same asymptotic flow as the diffusion with non-linear binding. The abscissa of the intercept of the asymptote is:

$$t_i = \frac{\alpha_{eq} L^2}{6D_e} = \frac{L^2}{6D} + \frac{L^2}{6D_e} (1-\tau) \rho_s K_{deq}, \quad (6)$$

where K_{deq} is the equivalent binding capacity of the equivalent linear isotherm.

Definition of an equivalent linear isotherm and of an equivalent capacity factor

Let us assume that the non-linear binding is described by a Freundlich isotherm $C_s = aC^y$ with $0 \leq y \leq 1$. The basis of our modelling is to make the non-linear Freundlich binding isotherm similar to an equivalent linear isotherm.

The equivalent linear isotherm, associated to α_{eq} , is defined as the one, which gives at $C_o/2$, the same bound chloride concentration as the non-linear isotherm (Fig 2).

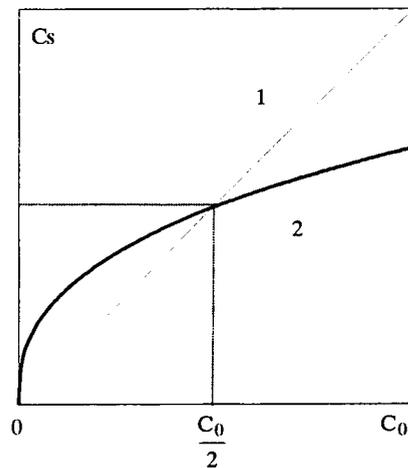


Fig 2. Chloride binding isotherms: Curve 1 is the linear equivalent isotherm and curve 2 is the Freundlich isotherm

4. Experimental results

For each diffusion test driven for a given concentration or a given thickness, we obtain the data for t_i , D_e and α_{eq} (Table 3) by a graphic determination from the diffusion curves.

Table 3. Experimental data for t_i , D_e , et α_{eq}

C_o (g/l)	L (10^{-2} m ²)	t_i ; (d)	D_e exp (10^{-12} m ² /s)	α_{eq} exp
169.6	1	35	1.15	0.210
20.2	1	64	1.93	0.639
20.2	1.4	131	2.04	0.706
10.0	1	86	2.43	1.081
10.0	1.44	175	2.45	1.075
5.0	0.95	112	2.63	1.690
1.0	0.96	200	2.93	3.290

On the basis of these experimental results, we make a numerical simulation [7] resolving the Fick's second law in the case of binding driven by an equivalent linear isotherm (in this case $y=1$). Then we obtain the corrected values of D_e and α_{eq} . Also the decrease in the concentration in the upstream cells can be calculated for a given term (Table 4).

Table 4. Adjusted data obtained by numerical simulation with the equivalent linear isotherm

C_o (g/l)	L (10^{-2} m)	D_e (10^{-12} m ² /s)	α_{eq}	K_{deg} (10^{-3} m ³ /kg)	$\frac{C_o - \Delta C_o}{C_o}$
169.6	1	1.18	0.215	0.037	0.949
20.2	1	2.04	0.676	0.26	0.897
20.2	1.4	2.19	0.763	0.30	0.859
10.0	1	2.75	1.226	0.53	0.799
10.0	1.44	2.77	1.212	0.51	0.792
5.0	0.95	3.07	1.985	0.89	0.753
1.0	0.96	3.62	4.072	1.95	0.633

Two main observations should be made; firstly, the effective diffusion coefficient is a function of the chloride concentration and secondly the equivalent capacity factor is a function of the chloride concentration.

5. Determination of the Freundlich isotherm parameters

The definition of the equivalent linear isotherm specify that the retention rates are the same for $C_o/2$ considering linear or Freundlich isotherm.

So we can write:

$$K_{deg} \left(\frac{C_o}{2} \right) = a \left(\frac{C_o}{2} \right)^y, \text{ then } K_{deg} = a \left(\frac{C_o}{2} \right)^{y-1} \text{ and}$$

$$\alpha_{eq} = \tau + (1-\tau) \rho_s a \left(\frac{C_o}{2} \right)^{y-1}. \quad (7)$$

Based on experiments, each diffusion test give us several couples of data $(C_o; \alpha_{eq})$ and from the equation (7) the equivalent capacity factor α_{eq} can be consider as a linear function of $\left(\frac{C_o}{2} \right)^{y-1}$. A linear regression procedure is then carried out to determine the Freundlich parameters "y" and "a". In this procedure y is considered as a parameter varying from 0 to 1.

Experimentals data of α_{eq} are plotted (Fig 3) in function of $\left(\frac{C_o}{2} \right)^{y-1}$ and for each values of y, we determine the regression straight line and the standard deviation.

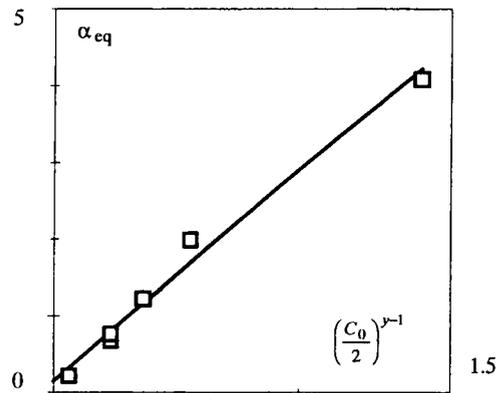


Fig 3. α_{eq} vs $\left(\frac{C_o}{2} \right)^{y-1}$ for $y=0.38$

The value of y chosen is the one which gives us the minimum standard deviation (Fig 4) associated to a realistic value of the porosity.

Next it is possible to determine the porosity τ and the coefficient "a" of the Freundlich equation calcula-

ted from the slope $[(1-\tau)\rho_s a]$ of the regression straight line.

From our experimental studies, we obtain a minimum standard deviation and a porosity value of 0.14 for $y = 0.38$.

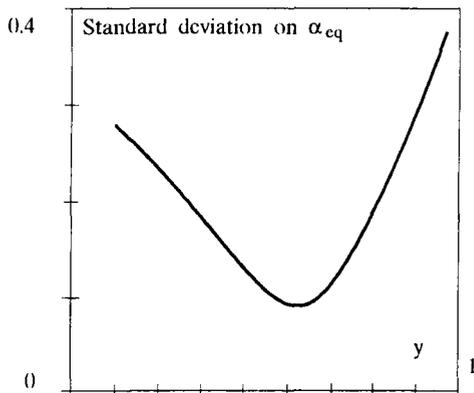


Fig 4. Standard deviation on α_{eq} vs y

The straight line equation is:

$$\alpha_{eq} = 0.149 + 2.73 \left(\frac{C_o}{2} \right)^{-0.62},$$

so we get $a = 1.34 \cdot 10^{-3}$.

For our mortar, the non-linear binding isotherm expressed as a Freundlich isotherm is:

$$C_s = 1.34 \cdot 10^{-3} C^{0.38}.$$

6. Conclusion

Seven classical chloride diffusion tests on mortar made with CPA-CEM I 42.5 cement have shown the dependence between the chloride concentration C_o and the quantity of chloride bound by the solid phase. The non-linearity of chloride binding for the bulk material could be expressed by a Freundlich isotherm. A method based on equivalent linear isotherms has been presented.

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CHLORIDO SKVARBA Į SKIEDIKLĮ KAIP NEARDOMASIS BŪDAS CHLORIDO RIŠAMAJAI IZOTERMAI NUSTATYTI

J. P. Bigas

S a n t r a u k a

Chlorido įsiskverbimo į betono struktūrą koeficientą galima būtų nustatyti išmatavus efektyviosios difuzijos koeficientą, nustatčius nelinijinį chlorido ir betono rišimąsi. Siūlomas naujas būdas rišimosi procesui modeliuoti – Freundlichio izoterma, apskaičiavus jos lygtį iš kelių tradicinių difuzijos bandymų pastoviosios būklės sąlygomis.

Siūlomo būdo pranašumas (palyginti su klasikiniiais bandymų metodais, kai rišimosi izotermos gaunamos iš trupintų bandinių) yra tas, kad taikoma nelinijinio rišimosi izotermos lygtis betono mikrostruktūrai natūraliomis eksploatacijos sąlygomis. Šiuo atveju galima studijuoti mikrostruktūros poveikį chlorido jonų rišimuisi.

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