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Modelling the carbonation of cementitious matrixes by means of the unreacted-core model, UR-CORE

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ABSTRACT

This paper presents a model for the carbonation of cementitious matrixes (UR-CORE). The model is based on the principles of the "unreacted-core" systems, typical of chemical engineering processes, in which the reacted product remains in the solid as a layer of inert ash, adapted for the specific case of carbonation. Development of the model has been undertaken in three steps: 1) Establishment of the controlling step in the global carbonation rate, by using data of fractional conversion of different phases of the cementitious matrixes, obtained by the authors through neutron diffraction data experiments, and reported in [M. Castellote, C. Andrade, X. Turrillas, J. Campo, G. Cuello, Accelerated carbonation of cement pastes in situ monitored by neutron diffraction, Cem. Concr. Res. (2008), doi:10.1016/j.cemconres.2008.07.002]. 2) Then, the model has been adapted and applied to the cementitious materials using different concentrations of CO_2, with the introduction of the needed assumptions and factors. 3) Finally, the model has been validated with laboratory data at different concentrations (taken from literature) and for long term natural exposure of concretes. As a result, the model seems to be reliable enough to be applied to cementitious materials, being able to extrapolate the results from accelerated tests in any conditions to predict the rate of carbonation in natural exposure, being restricted, at present stage, to conditions with a constant relative humidity.

1. Introduction

The alkalinity of the concrete pore solution induces the chemical passivity of the steel of reinforcement. However, this alkalinity is neutralized by the penetration of the carbon dioxide gas from the environment. The neutralization is produced as a more or less flat front that advances inwards from the concrete surface and induces corrosion of the reinforcement when it arrives at its surface. Carbonation of concrete has been studied for years by researches of cement chemistry [1–29], looking at the modifications that it produces in the structure and properties of the concrete in the course of time [2,4,7,11–13,22,30–34,36–40,44].

Carbonation is assumed to be mainly a diffusive phenomenon where the carbonation front moves at a rate proportional to the square root of time [5,41–43,60,61]. This diffusive process has been modelled though different solutions of Fick's second law [45,46]. Some of them are based in other transport parameters different than the diffusion coefficient [47,48]. The models proposed can be based on an apparent diffusivity including the reaction process [45], or can express and account explicitly for the reaction of the carbon dioxide with the cement phases [49–52].

Despite all these research, there is the need to develop models that, based in accelerated tests in order to shorten the time of testing, could predict long term performance with accuracy, as no experimental evidence has been found in literature on short term results giving reliable long term performance. In general, an overestimation of the predicted results at long term [53] has been found, which is due mainly to the fact that the resulting microstructure of pastes carbonated using high CO_2 concentration is different that those of air-carbonated pastes [2,13,21–23,53,54], and also the resulting amount of carbonated material increases when increasing the CO_2 concentration [54,55].

In the present paper, a model is presented, whose basis is taken from the chemical engineering world, to calculate the progression of the fluid–solid reactions. The selected model for being applied to the case of carbonation is named "unreacted-core model". The conceptual fundamentals for this model have proved to represent the actual behaviour closely, in most cases in which the reacted product remains in the solid as a layer of inert "ash", as it is the case of carbonation.

The model, labelled here as UR-CORE, has been applied to data of concretes from which natural carbonation depths at different ages have been recorded, and for concretes submitted to accelerated conditions but having also natural results of carbonation at long term [53].

The results indicate that the controlling step is that of diffusion of the CO_2 through the carbonated part of the sample, fitting very well the theoretical equation for the three types of cement tested, which simplifies very much the modelling of the process, and confirms the

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validity of the use of the law of the square root of time [5,41–43] to describe the advance of the front in a given condition, even though the carbonation depth deviates from a square root of time law when the material is submitted to drying–wetting cycles [46]. The main advantage of the model is that enables the prediction of the advance of the carbonation front in natural conditions from results of accelerated tests. At this stage, this model is restricted to environmental conditions with a constant relative humidity.

2. Experimental

2.1. Carbonation model

Carbonation of a cementitious matrix can be considered as a heterogeneous reaction system in which several solid phases of the sample reacts with the CO_2 (gas) in parallel according to the following scheme:

$$x\mathrm{CH(s)} + \mathrm{CO_2(g)} \rightarrow \mathrm{CaCO_3(s)} + \mathrm{H_2O}$$

$$y\mathrm{Ettr(s)} + \mathrm{CO_2(g)} \rightarrow u\mathrm{CaCO_3(s)} + v\mathrm{H_2O} + w$$

$$z\mathrm{C{-}S{-}H(s)} + \mathrm{CO_2(g)} \rightarrow r\mathrm{CaCO_3(s)} + s\mathrm{SiO_2} + t\mathrm{H_2O}$$

However, as most real processes, this is a quite complex system, that can differ considerably from the stoichiometric equations. In fact, in this type of heterogeneous systems, the overall rate expression becomes complicated because of interaction between physical and chemical processes. This means that models describing these type of processes have to consider the transport of the different phases (gas) and not only the rate of the chemical reaction rate.

There are various mathematical models, in the field of the chemical reactions engineering, for the description of the gas–solid reactions. Among them, simplified models of the type “unreacted-core” have proved to represent the actual behaviour closely, in most cases in which the reacted product remains in the solid as a layer of inert “ash”, as it is the case of carbonation. The conceptual basis for these models is presented schematically in Fig. 1, where the concentration of the solid reactant in function of the radial position is given for different times of carbonation. For the sake of clarity, the reacted and unreacted parts of the sample have been depicted as no coloured, and shaded zones as if being treated with a phenolphthalein indicator.

It is necessary to be aware that it has been proved, by TG profiles, that there is a transitional zone rather than a sharp interface [5,35,36,56,57] in the carbonation front. The existence of the transitional zone could be explained by the fact that the chemical reactions are not at equilibrium (not instantaneous) [58]. However, testing the carbonation front using chemical indicators (phenolphthalein) is also satisfactory for standard depth of carbonation tests and probably gives the best indication as far as the overall depassivation of the steel is concerned [5].

Therefore, the main premise of an unreacted-core model is considered to be accomplished by the advance of the carbonation front, and thus it can be applied. The overall rate expression is then formulated by considering the successive steps involved in the gas–solid process, that in the classical theory of chemical engineering, are the following ones:

a) Diffusion through the gas film: diffusion of gaseous reactant, CO_2, from the bulk of the first phase (gas phase) to the interface between the two phases (gas–solid).
b) Penetration and diffusion of the gas through the “reacted shell” to the surface of the “core” not yet reacted (diffusion of CO_2 through the external carbonated part of the sample).
c) Chemical reaction between the reactants.
d) Diffusion of the products formed that do not precipitate to form the “reacted shell” (water vapour/liquid released in the carbonation reaction) from the surface of the unreacted-core towards the external surface. In addition, diffusion of ions like Ca^{2+}, OH^-, etc., is also possible from the unreacted area to the carbonated zone.
e) Diffusion of these non-solid products (water vapour/liquid) through the gas film.

These steps have been schematically represented in Fig. 2 (a–b), in which the transitional zone in the surface of the unreacted-core has also been depicted, as a smooth change in the concentration from steps b to c and c to d. In Fig. 2a, the generic profile of the concentration of the reactant gas (CO_2) have been depicted for the steps a), b) and c). In Fig. 2b, the evolution in the concentration of the water formed through the carbonation has also been depicted (steps c), d) and e)).

Considering the resistance of all these steps in the equation of rate of carbonation, and therefore all these different values for the concentration of the CO_2, solid reactants and water, would make the problem very difficult to solve. In addition, the resistance of the different steps

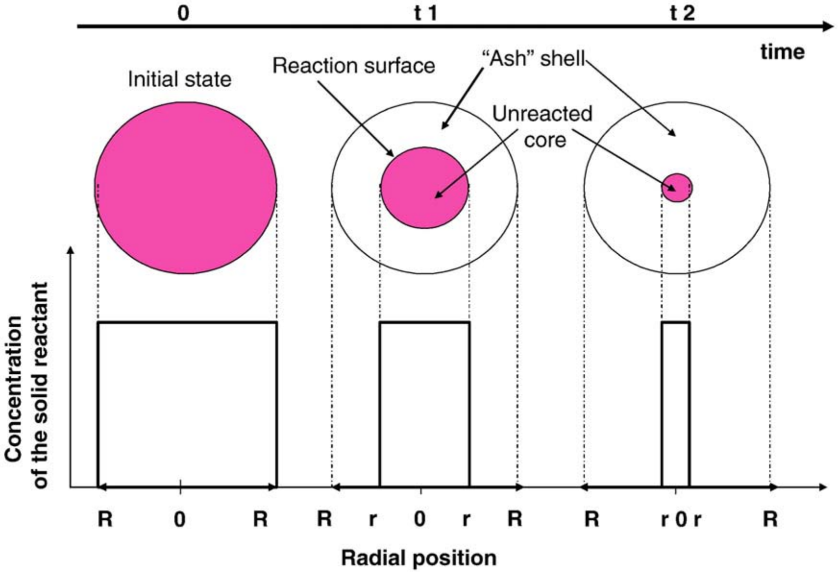
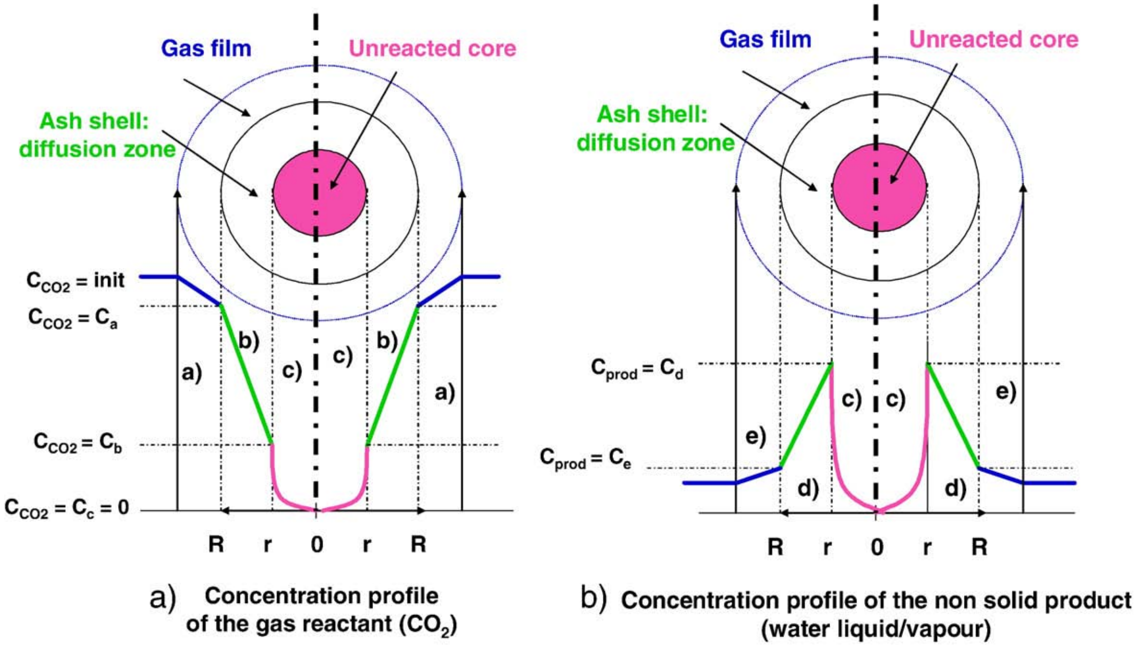


Fig. 1. Conceptual basis of the unreacted-core-model: Concentration of the solid reactant in function of the radial position, for different times of carbonation.



a) Concentration profile of the gas reactant (CO_2)

b) Concentration profile of the non solid product (water liquid/vapour)

Fig. 2. (a–b): Schematic representation of the successive steps involved in the unreacted-core model. a) Evolution of the profile of the reactant gas (CO_2) for the different steps (a, b and c). b) Concentration profile of the non- solid product formed (steps c), d) and e)).

normally is quite different and therefore the slowest one is the controlling step that determines the rate of the global process. Let's then analyze the different steps in the carbonation process.

In the case of carbonation of cementitious matrixes, the steps of the diffusion through the gas film (steps a) and e)) can be directly neglected. Concerning step d), most of the products of the carbonation process are solid phases. The only fluid product is the water formed, whose release depends on the relative humidity of the environment where carbonation is taking place, which is known to strongly influence the global speed. If the assumption of constant HR is assumed (as in the case of experiments with control of humidity), this step may be not studied, as is the case of the approach presented in this paper. However, this is an important point to be incorporated in the model, as it is clearly depicted by the influence of drying–wetting cycles on carbonation [46]. In addition, deuterated and ordinary specimens submitted to carbonation at 3% CO_2 in a laboratory chamber, exactly in the same conditions, have proved that carbonation takes place quicker for the ordinary samples [54,55]. As the chemical behaviour is the same for both samples, this has been attributed to the slower physical processes of the denser deuterated water. More research is being carried out to clarify this point.

Therefore, the steps to be taken into account are: step b) diffusion of CO_2 through the carbonated part and c) Chemical reaction. These steps have been expressed as differential material balances, in which the diffusion through the "reacted layer" is modelled by the first Fick's law (steady-state assumption) and the chemical reaction is considered of first order with respect to CO_2. The integrated equations conversion-time for a cylindrical sample, for both possibilities of controlling step are shown in Table 1 [59]. The set of Eq. (1), in the left, are applied when the controlling step is the diffusion of CO_2 through the carbonated part, and the set of Eq. (2) when it is the chemical reaction.

From the equations presented in Table 1, it can be deduced that the same input data are needed for both types of controlling steps, in the global process. From these data, if the controlling step were the diffusion of CO_2 through the carbonated layer, the model would make it possible to obtain the diffusion coefficient of CO_2 that, using the set of Eq. (1), enables predicting other situations. On the other hand, if the controlling step were the chemical reaction, the model would make it possible obtaining the reaction rate constant to be used into the set of Eq. (2).

2.2. Experimental data

In the application of the model, for the carbonation of cementitious matrixes, three steps have been carried out.

a) Finding out the controlling step in the global carbonation rate, through fitting the set of Eqs. (1) and (2). to experimental results.
b) Adaptation of the model to the specific case of cementitious matrixes.
c) Validation of the model, by comparing the predictions made with experimental data.

For the sake of clarity, in Table 2 a summary of the experimental data used in this paper with the references of the original papers, is presented. For undertaken step a), and finding out the controlling step in the global rate of carbonation, data of fractional conversion for the

Table 1
Integrated equations "conversion-time" of the model for a cylindrical sample, depending on the controlling step of the global rate of carbonation

Rate controlled by	
Step b) Diffusion of CO_2 through the carbonated part	Step c) Chemical reaction
Set of equation (1)	Set of equation (2)
$X_s = 1-\left(\frac{r}{R}\right)^2$ (1.1)	$X_s = 1-\left(\frac{r}{R}\right)^2$ (2.1)
$\frac{t}{\tau} = X_s + (1-X_s)\ln(1-X_s)$ (1.2)	$\frac{t}{\tau} = 1-(1-X_s)^{1/2}$ (2.2)
$\tau = \frac{\rho_s R^2}{4bDC_{CO2}}$ (1.3)	$\tau = \frac{\rho_s R}{bk_s C_{CO2}}$ (2.3)

Where: X_s: Fractional conversion of the solid reactant, s, at time t. ρ_s: Molar fraction of the reactant, s, in the solid (mol/cm^3). t: Time of experiment (s). τ: Time for complete conversion of the reactant s (s). D: Effective diffusion coefficient of CO_2 through the carbonated layer (cm^2/s). b: Stoichiometric coefficient for the reaction: $b\,S(s)+CO_2 \rightarrow \ldots$ k_s: Reaction rate constant (cm/s). C_{CO2}: Concentration of CO_2 in the gas phase (mol/cm^3). r: Radius of unreacted-core (cm). R: Radius of the cylinder (cm).

different phases are needed. These data have been obtained by the authors through the in-situ monitoring, by neutron diffraction, of accelerated carbonation of cement pastes, at 100% CO_2 concentration, and reported in [55] (series A in Table 2). These experiments have provided the monitoring of the major features of the carbonation tests, i.e. the phases existence domains and their growing and decaying: carbonation implies the simultaneous reduction of Portlandite, Ettringite and C–S–H gel while Calcite increases progressively. The samples consisted of deuterated cement pastes (w/c: 0.5) with three different types of binders. The first binder was plain OPC cement type I/45A/SR-MR, having a 5% of addition of lime. The second one, mix OPC-FA, that was prepared using the same cement substituted in a 35% by fly ash. The third type, mix OPC-MS, was used again the same cement with a substitution of a 10% by micro-silica [55].

Adaptation of the model to the specific problem of cementitious matrixes has been made by using data got through:

1) The in-situ neutron diffraction experiments (series A in Table 2),
2) From complementary data, of twin samples fully carbonated at the laboratory and cast with ordinary water [55] (series C in Table 2).
3) Data of pastes made with the binder OPC, carbonated at different CO_2 concentrations (natural exposure, 3%, 10% and 100%, as reported in [54] (series D in Table 2).

For validation of the model, also three types of experimental data have been used:

1) The first one, for the same sample (OPC binder) that that used for the in-situ neutron diffraction experiments, but using a different concentration of CO_2. (series B in Table 2).
2) The second set consisted of concrete specimens that were cast and submitted to carbonation, in natural exposure, during 11.75 years. They consisted of cylindrical concrete samples (only one type of binder) with dimensions of 150 mm Φ and 300 mm height, that were cast with CEM I/42.5/Sulphate resistant (the same cement than used for pastes reported in [55]) without additions, made of 400 kg cement /m^3 and w/c ratio of 0.45. After curing, they were exposed outdoors in sheltered conditions. At the ages of 4, 7, 9 and 11.75 years, the state of carbonation was analysed according to the phenolphthalein tests. (series E in Table 2)
3) The last case for the model validation has used data from literature [53] (series F in Table 2). Mix proportions for two different compositions of concrete (type A and B, series I in [53]) were submitted to two very different conditions for the carbonation tests [53]: 5 days at 100% CO_2 and 2 years at natural exposure. Both concretes were cast with CEM I 52.5 EN 197-1:2000 having 250 and 350 kg/m^3 of cement, with w/c ratio of 0.69 and 0.49 respectively for types A and B).

From the data obtained from the accelerated conditions, the model has been applied to determine the depth of carbonation in natural conditions after the two years and compared with the experimental data given. (series F in Table 2).

3. Results and discussion

As mentioned, even though several models have been proposed in literature to predict the advance of the carbonation front in cementitious matrixes, the validity of the accelerated tests to extrapolate results in natural conditions continues to be very doubtful, not having found in literature any validated model able to use data of tests, in any condition, for predicting the rate of carbonation in any other situation. This is the objective of the development of the UR-CORE model of the carbonation rate presented in this paper. The three steps described in Section 2.2. are developed next.

3.1. Finding out the controlling step in the global carbonation rate

According to the unreacted-core model proposed, the overall rate expression has to be formulated by considering a series of successive steps. However, in order to have a solvable problem, it is necessary to simplify the physical phenomena and identify the slowest step that is the controlling one, that will determine the rate of the global process.

As explained in the experimental section, in the case of application to the carbonation of cementitious matrixes, the steps identified that could control the process, are the steps labelled, in the general model, as b) diffusion of CO_2 through the carbonated part, and c) chemical reaction, whose integrated equations are given respectively as the set of Eqs. (1) and (2) in Table 1. In Fig. 3, for the case of carbonation of cementitious materials, the profiles of concentration of CO_2 in the sample for the two different controlling steps are schematized.

As explained in the experimental section, the in-situ neutron diffraction results [55] provide the kinetic data of fractional conversion for the different phases, making it possible, for the first time, to

Table 2
Summary of the data used in this paper, with the references, of the original papers

Series	Type of sample	Cement type	Casting water*	Experiment**	$[CO_2]$%	Time of carbonation (days)	Final state***	Ref.
A	Paste	OPC	D	IS-ND	100	0.375	PC	[55]
		OPC-FA				0.382		
		OPC-MS				0.538		
B		OPC		LC	3%	103		–
C	Paste	OPC	O	–	–	–	NC	[55]
		OPC-FA						
		OPC-MS						
		OPC	O	LC	100	103	CC	
		OPC-FA						
		OPC-MS						
D	Paste	OPC	O	NE	~0.03	103	PC	[54]
				LC	3		CC	
					10			
					100			
E	Concrete	OPC-1	O	NE	~0.03	4, 7, 9 and, 11.75 years	PC	–
F	Concrete	A- OPC	O	LC	100	5	PC	[53]
		B- OPC		LC				
		A- OPC		NE	~0.03	2 years		
		B- OPC		NE				

*D: Deuterated water; O: Ordinary water.
**IS-ND: In-situ Neutron Diffraction, LC: Laboratory chamber, NE: Natural exposure.
***NC: No Carbonated; PC: Partially Carbonated; CC: Completely Carbonated.

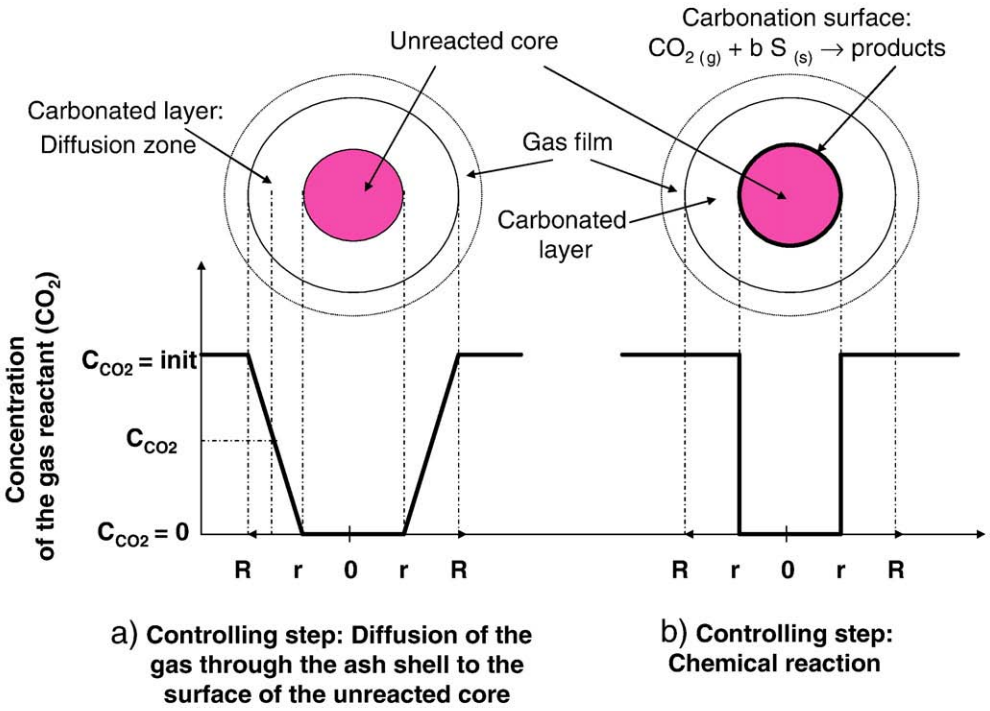


Fig. 3. Profiles of concentration of CO_2 in the sample for the two different controlling steps.

discriminate the controlling step by comparing the experimental results with the corresponding theoretical equations. For the sake of clarity, the comparison has been done in a graphical way: The theoretical equations have been depicted in Fig. 4a, where the differences in the behaviour of the process depending on the controlling step (see Table 1 for meaning of the symbols) are clearly seen.

The experimental conversion data, for Portlandite, CH, [55], have been drawn on these theoretical equations (Fig. 4b, c and d) for OPC, OPC-FA and OPC-MS respectively. As the times for complete conversion of the reactants were not known, the tau (τ) has been iterated until obtaining the best fit into the different curves conversion-time.

From Fig. 4, it can be deduced that the controlling step is that of diffusion of the CO_2 through the carbonated part of the sample, fitting very well the theoretical equation with the experimental results for the three types of cement. As explained in [55], it has been possible to get the fractional conversion data for Portlandite and Ettringite, for the

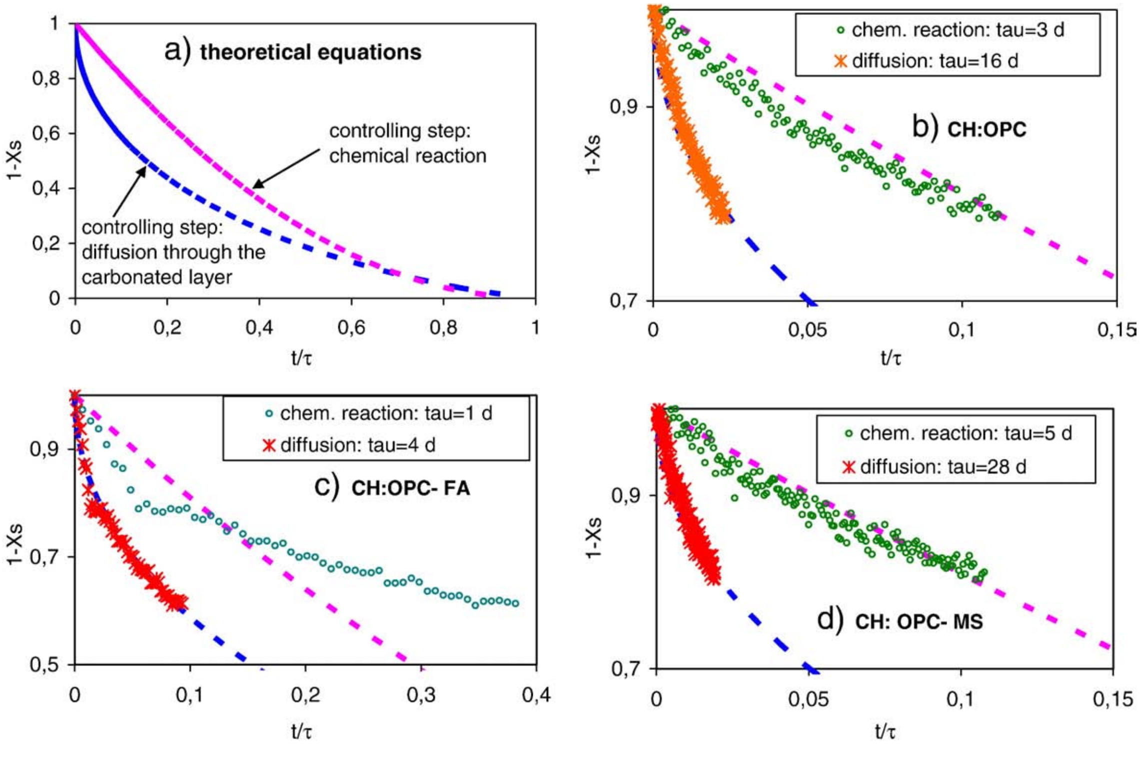


Fig. 4. a) Graphical presentation of equations given in Table 1. b–c–d) fitting of the experimental data obtained through in-situ neutron diffraction monitoring during carbonation, for Portlandite, CH, for OPC, OPC-FA and OPC-MS respectively [55].

three binders tested, and C–S–H gel only for OPC. The trends in Fig. 4, for Portlandite, is the same for the other two phases whose fractional conversion with the time are given in [55]: Ettringite and C–S–H (only for OPC).

However, in the case of the chemical reaction, it can be deduced that the experimental data do not fit the theoretical curve. At low conversions, the experimental values are under the theoretical curve, and there is a point (around 0.1 of t/τ) in which the data tend to go up to it. This tendency, not fitting the theory, is very clear for mix OPC-FA but looking carefully, it can be observed that is the same for the three mixes.

In [35], as in other studies, it was stated that under normal environmental conditions of CO_2 and relative humidity, carbonation was controlled by gas diffusion through the empty pores in the surface layer. Here, it has been demonstrated, using a different model, that the controlling step in the carbonation rate is the diffusion of the CO_2 through the external carbonated part of the sample. Therefore, the simplified use of the simple law of the square root of time [5,41–43,60,61] to describe the advance of the front in given conditions is demonstrated as adequate.

Therefore, from now, it has been demonstrated that the set of equations to be applied in the case of carbonation is the set 1 of equations given in Table 1.

3.2. Adaptation and application of the model to cementitious materials

Adaptation of the model to cementitious materials implies the knowledge of every parameter involved in the set of Eqs. (1).

Concerning Eq. (1.1), it correlates the fractional conversion, X_s, with the radius of the non-carbonated zone, r, for a sample (cylindrical shape) of radius R, after an experiment, or time exposed to carbonation, t.

$$X_s = 1-\left(\frac{r}{R}\right)^2 \tag{1.1}$$

Therefore, if the fractional conversion is known, the layers of carbonated and uncarbonated zone are automatically known. On the contrary, if the carbonated layer is known (through the phenolphthalein tests), the fractional conversion can be calculated. Having the fractional conversion and the time of carbonation, t, it is possible to obtain, through Eq. (1.2), the time for full carbonation of the sample, τ.

$$\frac{t}{\tau} = X_s + (1-X_s)\ln(1-X_s) \tag{1.2}$$

Once τ has been calculated, Eq. (1.3) allows the calculation of the diffusion coefficient, provided that "ρ_s" (molar fraction of the reactant in the solid, mol/cm^3) and "b" (stoichiometric coefficient for the reaction: 1 $CO_2 + b\ S(s) + \rightarrow \ldots$.) are known.

$$\tau = \frac{\rho_S R^2}{4bDC_{CO2}} \tag{1.3}$$

Once the diffusion coefficient has been calculated, the process can be applied for other conditions (C_{CO2} and time of exposure).

If there was only one phase carbonating in the cement paste with a definite stoichiometry, "ρ_s" and "b" would be directly known. However, as most real processes, cement paste is a quite complex system, in which different phases are carbonating at the same time (Portandite, Ettringite, C–S–H (crystalline and amorphous fractions), anhydrous phases [54]), and some of them do not have defined stoichiometric equations. Therefore, it is necessary to define the simplified values of "ρ_s" and "b" to be used in the model, which is undertaken next.

3.2.1. Preliminary considerations

In [55], as said, individual data of fractional conversion, for each phase (Portlandite and Ettringite (for the three binders tested), and C–S–H (only for OPC)) were obtained through the neutron diffraction data. Therefore, from Eq. (1.2) it has been possible to determine the time for complete conversion of each phase, τ. The results are depicted in Fig. 5a, from which it is possible to deduce that even though for the same sample of cement paste, the time for full carbonation for the different phases is different. However, it is also noticeable that there is the same proportionality between each phase in the different samples, in agreement with the qualitative deductions obtained in [55] from fitting of the trend curves to empirical equations of exponential decay of first order. That is to say, for example, (time to full carbonation of Ettringite / time to full carbonation of Portlandite)~(0. 13/1), for every binder tested. This has been depicted in Fig. 5b.

This deduction may appear to be contradictory, with the controlling step of the process of the diffusion of CO_2 through the external carbonated part of the sample, however it is not. The different τ are not attributed to different chemical reaction rates, but they are attributed to the different molar fraction of each phase reactant, "ρ_s", and the different stoichiometric coefficient, "b", being the D a common parameter for the different individual isolated phases (Eq. (1.3)).

For testing this assumption, lets take the individual phase of Portlandite ($Ca(OH)_2$), with the data of series A (Table 2), as all the parameters involved in the Eq. (1.3) are known: The concentration of the CO_2 gas used in the experiment is a known data; in the case of Portlandite, $b_{\text{porlandite}} = 1$, and the $\rho_{\text{porlandite}}$ can be easily calculated from the data of TG and MIP (% Portlandite and bulk density in the uncarbonated sample) [55]. Therefore, the individual diffusion coefficient can be calculated.

Now, lets apply the model individually for Ettringite, $(Ca_6(Al(OH)_6)_2(SO_4)_3(H_2O)_{26})$, whose $b_{\text{ettringite}}$ is $= 1/6$. Using the D obtained with the data for Portlandite, the "$\rho_{\text{ettringite}}$" can be calculated (Eq. (1.3)). The physical sense of the value obtained will be checked by comparing it

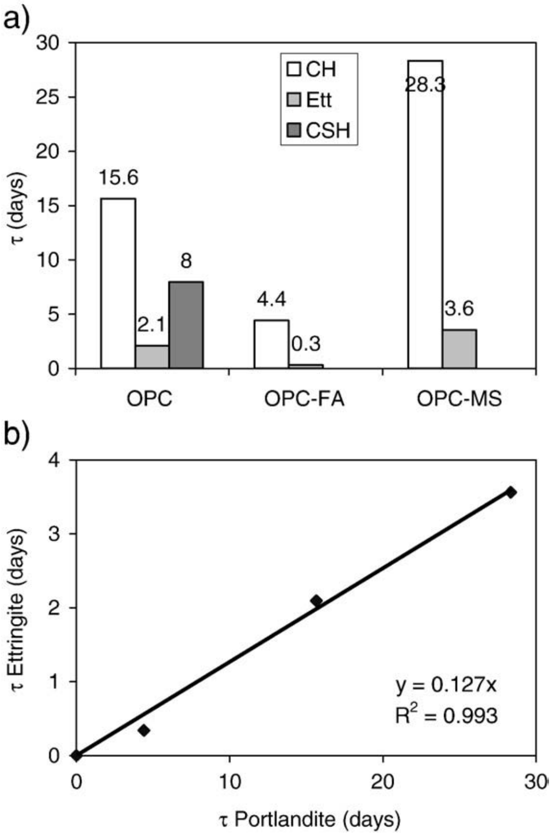


Fig. 5. (a–b): a) Times calculated for complete conversion of each phase for the different mixes. b) linear relationship of the τ obtained for Portlandite and Ettringite for the different samples tested in [55].

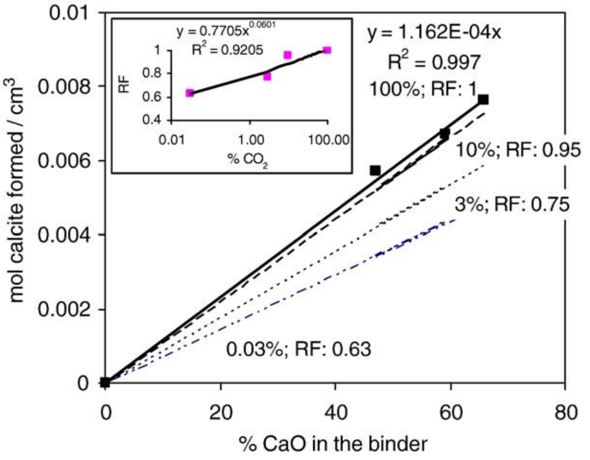


Fig. 6. Relationship between the percentage of CaO in the binder and the mol/cm^3 of calcite formed when fully carbonating at 100% CO_2 (data from [55]), and reductions factors, RF to be applied when carbonating at other CO_2 concentrations (data from OPC in [54]). In the detail, graph of the correlation between the RF and concentrations of CO_2.

with the maximum amount of Ettringite that could be formed, calculated stoichiometrically from the amount of Al in the cement.

The so calculated "$\rho_{\text{ettringite}}$" for OPC has been of 7.35 E−5, very close to the calculated maximum amount of 7.73 E−5, by stoichiometric calculations from the amount of Al in the cement, which validates the hypothesis which is required to apply the model.

However, from a practical point of view, when applying the model to the cementitious materials the following points have to be taken into account:

3.2.2. Determination of "ρ_s" to be used in the model

Usually, the amount of the different phases able to carbonate in the original sample is not known. Therefore, it is necessary to find a simplified value for "ρ_s" to be introduced in the model. The proposal made here is using the amount of calcite formed when the sample is fully carbonated.

With the data given in [55] for the fully carbonated samples, a linear relationship between the percentage of CaO in the binder and the mol/cm^3 of calcite formed when fully carbonating at 100% CO_2 has been found. It is given in Fig. 6. The existence of a relation between these parameters have been also reported elsewhere [45–47], having found different relationships by different authors.

On one hand, in [54], it was reported by the authors that when carbonating using different CO_2 concentrations, the total amount of calcite formed was different. Therefore, there should be a different relationship between the percentage of CaO in the binder and the mol/cm^3 of calcite formed for each concentration of CO_2 used. To undertake this fact, the concept of "reductions factors", RF, has been introduced to be used in the model. The RF is a factor smaller than the unity (RF = 1 for concentration of CO_2 at 100%) when carbonating at other CO_2 concentrations different from 100% CO_2.

From the data given in [54], the values of the RF for natural carbonation (~0.03%), 3% and 10% of CO_2, have been obtained, and the values obtained are given also in Fig. 6. (In a detail in the graph, the correlation between the RF and concentrations of CO_2). The use of the RF is absolutely necessary to transport results from one concentration of CO_2 to other different concentration. The correlation found for getting RF in function of the concentration of CO_2 is given as Eq. (3), and has been obtained using data of OPC samples. Data of RF using different binders is being undertaken in order to find if these RF are of general use of if it is necessary to apply different equations of RF to different binders.

$$\mathrm{RF} = 0.7705[\%\ \mathrm{CO_2}]^{0.0601} \tag{3}$$

There is another factor to be introduced in order to define the molar fraction of reactants, (mol/cm^3) if the samples are not cement paste, as the amount able to react in a defined volume diminishes if using mortar and concrete. Therefore, in these cases, it is necessary to introduce the factor CFP (Correcting Factor to Paste), for correcting the amount of paste in the sample, provided the mix proportion of the mortar or concrete is known. The use of this factor will be illustrated in the section of validation with concretes.

On the other hand, it has to be taken into account that all these experiments have been carried out under Relative Humidity (%RH) controlled to the 65%; that is to say, in the same humidity conditions. Therefore, as said before, the relative humidity is an important parameter to be introduced in the model, as it could imply even a different amount of calcite formed depending on the environment. The introduction of this parameter in the model is being studied as present.

3.2.3. Determination of "b" to be used in the model

As said, several phases carbonating in the cement paste do not have a definite stoichiometry (for example C–S–H), so, the global stoichiometric parameter "b" is not known. Therefore, it is necessary to find a simplified value for "b" to be introduced in the model. The proposal made here is using b = 1, as it is the value for Portlandite, and some other

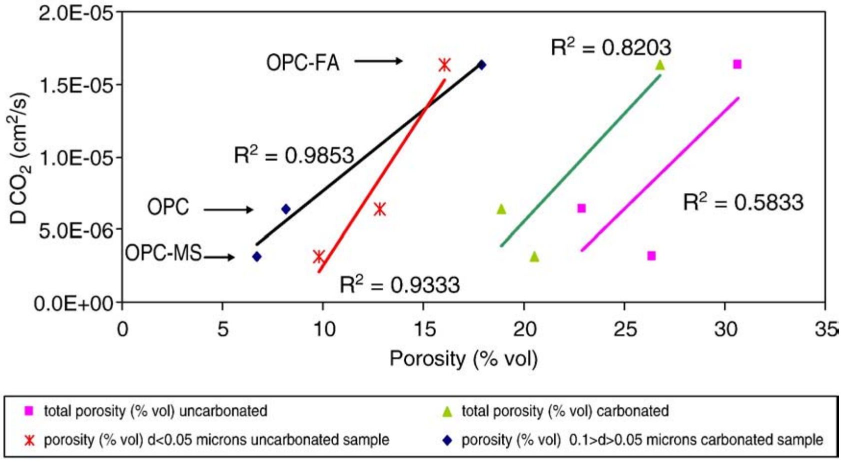


Fig. 7. Summary of the relationships between the D, obtained by applying the model, for the different samples, and its relation with the porosity of the carbonated and uncarbonated samples [55] (series C).

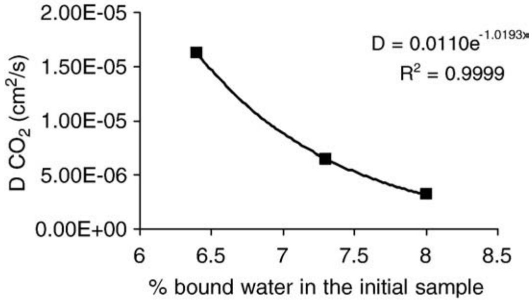


Fig. 8. Relationship between the *D* obtained for the different samples, obtained by applying the model, and the percentage of bound water in the uncarbonated samples [55].

phases could higher values and (C–S–H), and some other smaller values (Ettringite).

3.2.4. Validity of "ρ_s" and "b" proposed to be used in the model

In order to check the validity of using for "ρ_s" the amount of calcite formed when the sample is fully carbonated, and $b=1$, the diffusion coefficient knowing the actual data (averaged conversion, averaged b and actual ρ_s,) given in [55] for the OPC samples, has been calculated (D=5.1E−6 cm^2/s). This coefficient has been compared with that obtained using the proposed approximation for "ρ_s" and "b", which has resulted to be of D=6.4E−6 cm^2/s. The comparison of these values indicates that both results are quite close, and of the same order of magnitude as those given in [62]. Therefore, the simplified values proposed are accepted and it follows that:

$$\rho_s/b = (\text{mol calcite at fully carbonation at } 100\,\%\,\mathrm{CO_2/cm^3}) \times \mathrm{RF} \times \mathrm{CFP} \qquad (4)$$

Therefore, Eq. (1.3) can be written as:

$$\tau = \frac{2.905E^{-5}\cdot(\%\,\mathrm{CaO_{binder}})\cdot \mathrm{RF}\cdot \mathrm{CPF}\cdot R^2}{D\cdot C_{\mathrm{CO2}}} \qquad (1.3^*)$$

Finally, it has to be pointed out that these correlations and the reduction factors obtained here need now to be refined, if necessary, and validated with data taken from other authors.

3.2.5. Estimation of D from other microstructure parameters

If previous data for carbonation are not allowable, *D* might be estimated indirectly from other microstructure parameters and use the data got in the model for predictions.

In Fig. 7, a summary of the relationship between the *D* obtained by applying the model, for the fully carbonated samples, and its relation with the porosity of the carbonated and uncarbonated samples [55] is presented. From Fig. 7, it can be deduced that there is not a direct relationship between the *D* and the total porosity neither for the carbonated samples nor for the uncarbonated one. The only relationship found between the diffusion coefficient and the porosity (vol.%) has been, for the carbonated samples, in the range of pores between the 0.1 and 0.05 µm (R^2=0.9853). This confirms the controlling step through the carbonated layer, and makes a bit difficult to be able to predict a diffusion coefficient just from porosity data. For the uncarbonated sample, the most approximated relationship found has been for the range of pores smaller than 0.05 µm (R^2=0.9333).

However, considering that one of the conclusions given in [55] is that the main diminution in porosity with carbonation is related to the bound water (105 °C–425 °C), it has been considered that there should be a

Table 3
Application of the model with the assumptions postulated to the OPC specimen carbonated at 3% CO_2

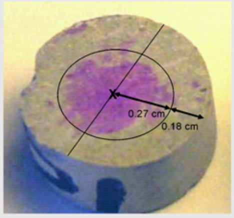
Data		
t (days)	103	
b	1	
ρs	From % CaO RF = 0.75 CFP=1	
D (cm²/s)	6.4 E-6	
Concentration CO_2	3%	
R (cm)	0.45	
Results		
Fractional conversion	**0.63**	
r (cm)	**0.27**	

Table 4
Values of the carbonated depth front for the OPC concrete specimens (series E) at the different times of exposure tested

Time of exposure (years)	4	7	9	11.75
Phenolphthalein front (mm)	2.4	3.25	3.84	4.41

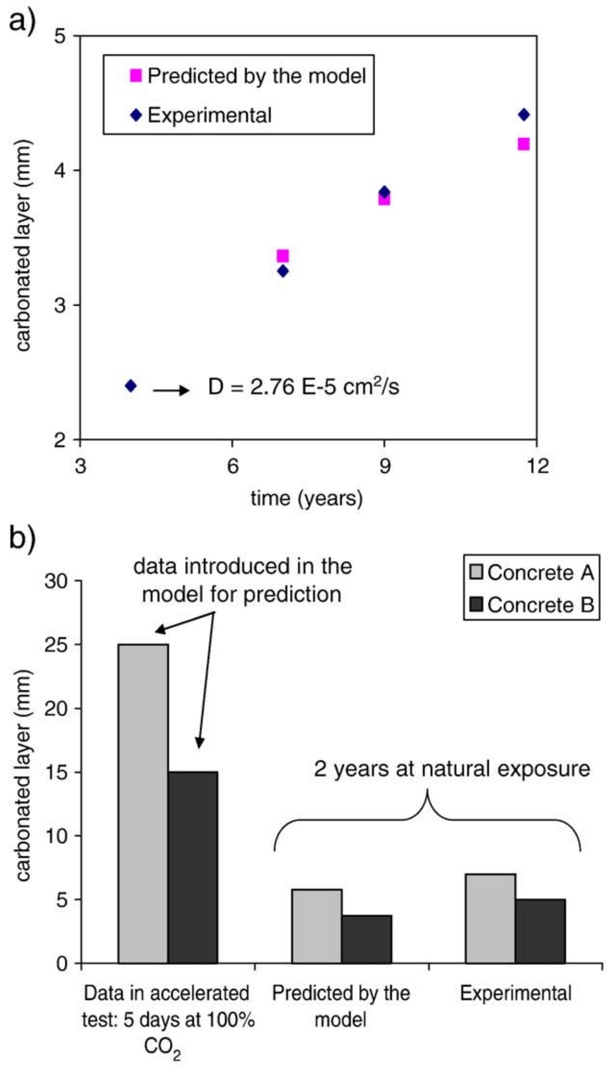


Fig. 9. (a–b): Validation of the model for concrete samples. Comparison between the experimental and the predicted data for two different cases. a) series E: in the same conditions (natural exposure at long term) and b) series F: data from accelerated experiment and prediction for natural conditions (data from [53]).

close relationship between the diffusion coefficient and the percentage of bound water in the samples. The results, for the three different cement pastes are given in Fig. 8, from which it can be deduced an exponential relationship with a R^2 of 0.9999. This relationship has to be validated for many other matrixes, with different amount of aggregates, before obtaining directly the *D* from the results from a TG analysis with the aim of making predictions.

3.3. Validation of the model

As explained in the experimental section, for validation of the model, two types of experimental data have been used: The first one, for the same sample (OPC binder) that that used for the in-situ neutron diffraction experiments, but using a different concentration of CO_2. (series B in Table 2). The second set consisted of two different cases of concrete specimens.

3.3.1. Validation of the use of different CO_2 concentrations values

In order to check the validity of the reductions factors with other concentration of CO_2, the model has been checked with the same deuterated OPC paste specimen than used in [55] for getting the fractional conversion data, but carbonated at the 3% in a chamber in the lab for 103 days. (series B in Table 3). Therefore, according to data in Fig. 6, RF = 0.75. Provided that the sample is made of cement paste, the factor correcting the amount of paste in the sample, CFP equals the unity; CPF = 1. Having the diffusion coefficient of 6.4 E−6 (cm^2/s) (as calculated in Section 3.2.4), use of the model (Eqs. (1.1), (1.2), and (1.3*)) give the results for the fractional conversion and uncarbonated layer presented in Table 3.

In Table 3, a summary of the data to be introduced in the model, the results obtained and the photograph showing the front of carbonation are given that indicates quite good agreement with the experimental evidence.

3.3.2. Validation with different samples

Finally, the model has been tested with data from concrete specimens, in order to validate also the extrapolation from paste to concrete. In order to obtain the right ρ_s (mol/cm^3) it is necessary to calculate the factor correcting the amount of paste in the sample, CFP, provided the mix proportion of the concrete is known. Provided that the density of the paste fraction for each concrete was not known, a generic value for the density of the paste fraction of 1.7 g/cm^3 has been used for all the cases.

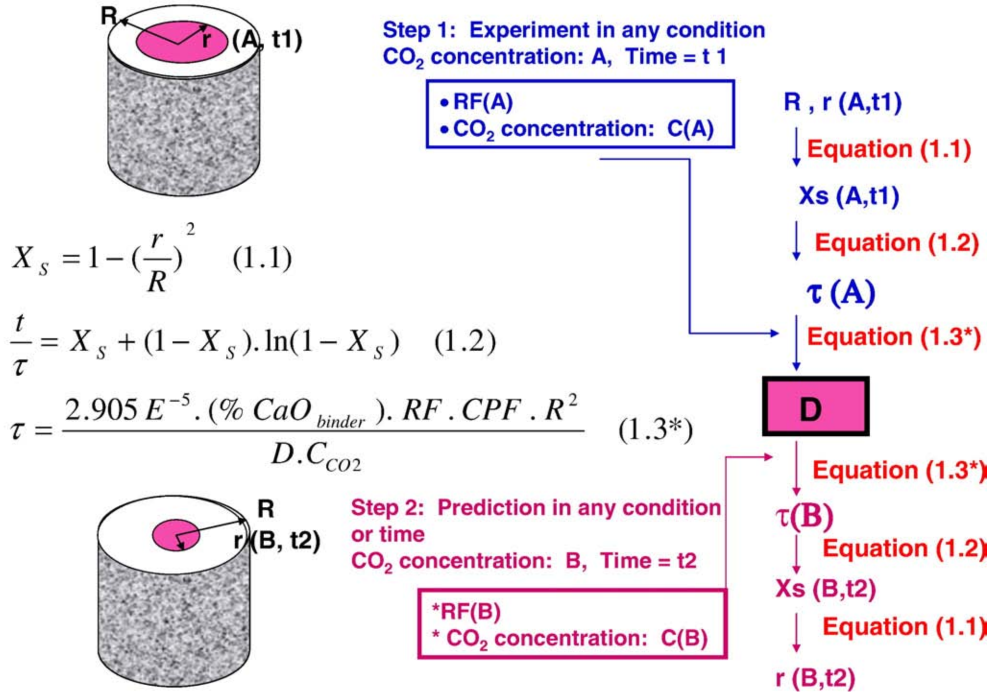
As already explained, the model has been tested for two different cases:

1) From the data of series E). At the ages of 4, 7, 9 and 11.75 years, the state of carbonation was analysed according to the phenolphthalein tests by cutting two different slices of the central part of the specimens and measuring the depth of the phenolphthalein front. The average of the values obtained at the different times of exposure tested are given in Table 4.

Given the carbonation depth at the first time of carbonation, the predictions for the future in the same conditions have been made. Therefore, the data corresponding to 4 years has been used as the input data for the model, that has allowed to determine the diffusion coefficient, *D*, and therefore, from them, using the model to make the extrapolation and predict the carbonated amount for the rest of the years. For this concrete, a CFP of 0.34 cm^3 paste/cm^3 sample has been obtained. The *D* calculated has been of D_{CO2} = 2.76E−5 cm^2/s, and the predicted results are given in Fig. 9a, where it can be seen that the correspondence between the experimental data and the predicted ones at the three different ages is very good.

2) The second case for validation uses data from literature [53] (series F). Mix proportions for two different compositions of concrete (type A and B, series I in [53]) and two very different conditions for the carbonation tests are given: 5 days at 100% CO_2 and 2 years at natural exposure. From the data obtained from the accelerated condition, the model has been applied to determine the depth of carbonation in natural conditions after two years.

For these two concretes, the calculated CFP's have been of 0.25 and 0.31 cm^3 paste/cm^3 sample, and D_{CO2} of 2.11E−4 cm^2/s and 1.10E−4 cm^2/s for concretes A and B respectively. These coefficients are lower but of the same order of magnitude than that obtained by application of the models [45,46] (calculated in [53]).



$$X_S = 1 - \left(\frac{r}{R}\right)^2 \quad (1.1)$$

$$\frac{t}{\tau} = X_S + (1 - X_S).\ln(1 - X_S) \quad (1.2)$$

$$\tau = \frac{2.905\,E^{-5}.(\%\,CaO_{binder}).\,RF\,.\,CPF\,.\,R^2}{D.C_{CO2}} \quad (1.3^*)$$

Fig. 10. Schematic presentation of the application of the developed model, UR-CORE, with the corresponding equations, for cylindrical geometry.

The results for the validation are given in Fig. 9b, where it can be seen that even though the conditions of the two different conditions are the extreme ones, the experimental data and the predicted ones for both concretes are very good.

4. Model and procedure proposed

The carbonation model proposed, UR-CORE, based on the principles of the unreacted-core systems of reaction but applied to the special characteristics of the cement based materials, seems to be reliable enough, being able to extrapolate the results from accelerated tests to predict natural conditions, and from one age to further ages.

For applying this model, it is necessary to obtain the *D* of CO_2 through the carbonated layer of the matrix, that then will be used to extrapolate to any other conditions and times. This coefficient can be obtained in two different ways:

1: From data of a carbonation experiment with the same material, using any concentration of CO_2, by application of the model.
2: From the percentage of bound water in the sample (from a TG analysis).

The first procedure is more recommended at present, until the relationship between *D* and bound water have been confirmed in a generalized manner with other cement types.

In the adaptation of the generic model to the cementitious materials, two different factors have been defined and introduced:

1: The "Reductions Factors", RF, to consider the different amount of calcite formed when carbonating at other CO_2 concentrations different from 100% CO_2.
2: The "Correcting Factor to Paste", CFP. If using mortar and concrete it is necessary to introduce for correcting the amount of paste in the sample, as the amount able to react in a defined volume diminishes.

A schematic presentation of the UR-CORE steps, using the data obtained in a carbonation experiment, with the corresponding equations for cylindrical geometry, and the assumptions and adopted from this research, is given in Fig. 10. This kinetic approach allows the prediction of the advance of the carbonation front at any condition from the experimental data obtained at any condition. The only parameters that have to be remain constant are the HR and T^a, that have not been taken in this approach. As said, more research is being carried out to include these points.

5. Conclusions

This paper presents a model for the carbonation of cementitious matrixes (UR-CORE). The model is based on the principles of the "unreacted-core" systems, typical of chemical engineering processes, in which the reacted product remains in the solid as a layer inert ash, but adapted for the specific case of carbonation. The development of the model has been undertaken in three steps:

a) Establishment of the controlling step in the global carbonation rate, by using data of fractional conversion of different phases of the cementitious matrixes, obtained by the authors through neutron diffraction data experiments, and reported in [55]. This has been done by adjusting the experimental fractional conversion curves to the theoretical equations. As a result, it has been demonstrated that the controlling step is the penetration and diffusion of the gas through the "reacted shell" to the surface of the core not yet reacted (diffusion of CO_2 through the external carbonated part of the sample).
b) Then, the model has been adapted and applied to the cementitious materials using different concentrations of CO_2. For doing that, some assumptions and factors have been defined and introduced in the model: the Reduction Factors, RF (due to the fact that more amount of alkaline material is carbonated as higher is the concentrations of CO_2) and the CFP (factor correcting the amount of paste in the sample if mortar or concrete is used), for calculating the diffusion coefficient of the gas through the "reacted shell" to the surface. Additionally, an exponential relationship between the diffusion coefficient of CO_2 through the carbonated layer and the percentage of bound water in the uncarbonated sample has been found, that has to be validated for more different matrixes.
c) The equations of the model, for a cylindrical sample, are the following ones:

$$X_S = 1 - \left(\frac{r}{R}\right)^2 \quad (1.1)$$

$$\frac{t}{\tau} = X_S + (1 - X_S) \cdot \ln(1 - X_S) \quad (1.2)$$

$$\tau = \frac{2.905\mathrm{E}^{-5} \cdot (\%\,\mathrm{CaO_{binder}}) \cdot \mathrm{RF} \cdot \mathrm{CPF} \cdot R^2}{D \cdot C_{\mathrm{CO2}}} \quad (1.3^*)$$

Where:

X_s	Fractional conversion of the matrix at time t.
t	Time of carbonation (seg)
τ	Time for complete carbonation of the sample (seg)
D	Effective diffusion coefficient of CO_2 through the carbonated layer (cm^2/seg)
C_{CO2}	Concentration of CO_2 in the gas phase (mol/cm^3)
r	Radius of unreacted-core (cm)
R	Radius of the cylinder (cm)

d) The model has been validated with laboratory data at different concentrations (taken from literature) and for long term natural exposure of concretes, and it seems that the model is reliable enough to be applied to cementitious materials being able to extrapolate the results from accelerated tests in any conditions to predict the rate of carbonation in natural exposure.
e) The model does not incorporate the factor of the Relative Humidity (%HR). More research is being carried out to include this point.

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