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Stochastic Modelling of the Diffusion Coefficient for Concrete

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Stochastic Modelling of the DiffusionCoefficient for Concrete

P. Thoft-Christensen

STOCHASTIC MODELLING OF THE DIFFUSION COEFFICIENT FOR CONCRETE

Palle Thoft-Christensen[1]

ABSTRACT: In the paper, a new stochastic modelling of the diffusion coefficient D is presented. The modelling is based on a physical understanding of the diffusion process and on some recent experimental results. The diffusion coefficient D is strongly dependent on the w/c ratio and the temperature. A deterministic relationship between the diffusion coefficient and the w/c ratio and the temperature is used for the stochastic modelling. The w/c ratio and the temperature are modelled by log-normally and normally distributed stochastic variables, respectively. It is then shown by Monte Carlo simulation that the diffusion coefficient D may be modelled by a normally distributed stochastic variable. The sensitivities of D with regard to the mean values and the standard deviations are evaluated.

1. INTRODUCTION:

Corrosion of the reinforcement is the major reason for deterioration of reinforced concrete structures in many countries. Modelling the corrosion process is very complex and it is often based on observations or speculations rather than a clear understanding of the physical and chemical processes behind the corrosion process.

Corrosion initiation period refers to the period of time during which the passivation of steel is destroyed and the reinforcement starts corroding actively. Fick's law of diffusion can represent the rate of chloride penetration into concrete, as a function of depth from the concrete surface and as a function of time

$$\frac{dC(x,t)}{dt} = D\ \frac{d^2C(x,t)}{dx^2} \tag{1}$$

where $C(x,t)$ is the chloride ion concentration, as % by weight of cement, at a distance of x m from the concrete surface after t seconds of exposure to the chloride source. D is the chloride diffusion coefficient expressed in m^2/sec. If C_{cr} is assumed to be the critical chloride corrosion concentration and d is the thickness of concrete cover, then the corrosion initiation period T_{corr} can be calculated by

$$T_{corr} = \frac{d^2}{4D}(\text{erf}^{-1}(\frac{C_{cr} - C_0}{C_i - C_0}))^{-2} \tag{2}$$[1]

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where C_0 is the equilibrium chloride concentration on the concrete surface, as % by weight of cement, erf is the error function.

It follows from (2) that the time to corrosion imitation is inversely proportional in D. It is therefore of great interest to get a good estimate of D. According to extensive experimental investigations [1], [2] it can be concluded that the most important factors are the water/cement ratio w/c, the temperature Φ, and the amount of e.g. silica fume s.f. The experiments show that the diffusion coefficient D increases significantly with w/c as well as with the temperature Φ. The influence of w/c and the temperature Φ may be explained by the chloride binding. Only the free chloride is important for the diffusion coefficient D. With increased w/c ratio less chloride is bound and therefore D is increased. The strong influence of the temperature is mainly caused by thermal activation of the diffusion process, but may also be due to a reduced chloride binding when the temperature is increased. The purpose of the paper is to use the experimental results in [1] and [2] to make an improved stochastic modelling of the diffusion coefficient D, se also [3] and [4].

2. THE CORROSION PROCESS

In principle, reinforced concrete is an excellent type of structure from a corrosion point of view, since the alkaline environment in the concrete maintains a passive film on the surface of the reinforcement, and this film protects the reinforcement against corrosion. However, if the concrete is penetrated by e.g. water or carbon dioxide, then this passive film breaks down and the reinforcement is open to corrosion [5].

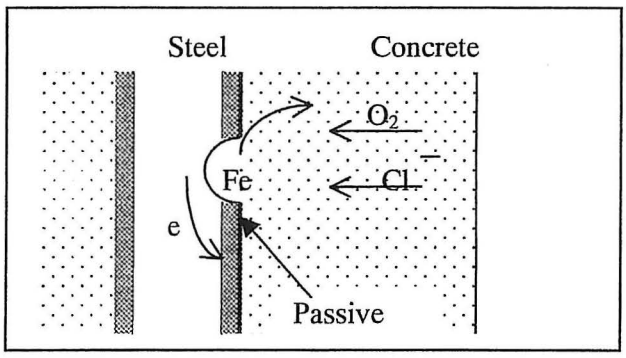

Figure1. Chloride-induced corrosion

The chloride-induced corrosion is schematically illustrated in figure 1. An anodic region is established, where the passive film is broken down and an electrochemical cell is formed. The passive surface is the cathode, and the electrolyte is the pore water in the concrete. At the anode the following reactions take place:

$$Fe \rightarrow Fe^{++} + 2e^-$$

$$Fe^{++}+2(OH)^{-} \rightarrow \mathbf{Fe(OH)_2} \quad (3)$$

$$4Fe(OH)_2+2H_2O+O_2 \rightarrow 4\,\mathbf{Fe(OH)_3}$$

Chloride ions Cl^- activate the unprotected surface and form an anode. The chemical reactions are

$$Fe^{++}+2Cl^{-} \rightarrow FeCl_2$$

$$FeCl_2+2H_2O \rightarrow \mathbf{Fe(OH)_2}+2HCL \quad (4)$$

It follows from (3) and (4) that two rust products $Fe(OH)_2$ and $Fe(OH)_3$ are produced. The different types of rust products are interesting to study because they have great influence on corrosion cracking, since the volume of the rust products corresponding to 1 cm^3 steel varies a lot [6].

Corrosion product	Colour	Volume, cm^3
Fe_3O_4	Black	2.1
$Fe(OH)_2$	White	3.8
$Fe(OH)_3$	Brown	4.2
$Fe(OH)_3$, $3H_2$	Yellow	6.4

Table 1. Volume of corrosion products, from [6].

3. THE DIFFUSION COEFFICIENT

The diffusion coefficient D is not a real physical constant for a given concrete structure since it depends on a number of factors. According to extensive experimental investigations [1], [2] it can , as mentioned earlier, be concluded that the most important factors are the water/cement ratio w/c, the temperature Φ, and the amount of e.g. silica fume s.f. In figure 2 is shown the diffusion coefficient D as a function of the water-cement ratio w/c and the temperature Φ °C for cement pastes with 0% silica fume. It is clear from figure 2 that the diffusion coefficient D increases significantly with w/c as well as the temperature Φ. In the example illustrated in figure 2 the minimum value of D is 0.31×10^{-12} m^2/s corresponding to w/c = 0.2 and the temperature Φ = 4°C. The maximum value of D is 80.00×10^{-12} m^2/s corresponding to w/c = 0.70 and Φ = 35 °C. In figure 3 the contour lines for the same data are shown. The diffusion coefficient D (10^{-12} m^2/s) as a function of the water-cement ratio w/c is shown in figure 4, and the diffusion coefficient D (10^{-12} m^2/s) as a function of the temperature Φ is shown in figure 5. Taking into account the chloride binding also improves the modelling of the chloride ingress profiles.

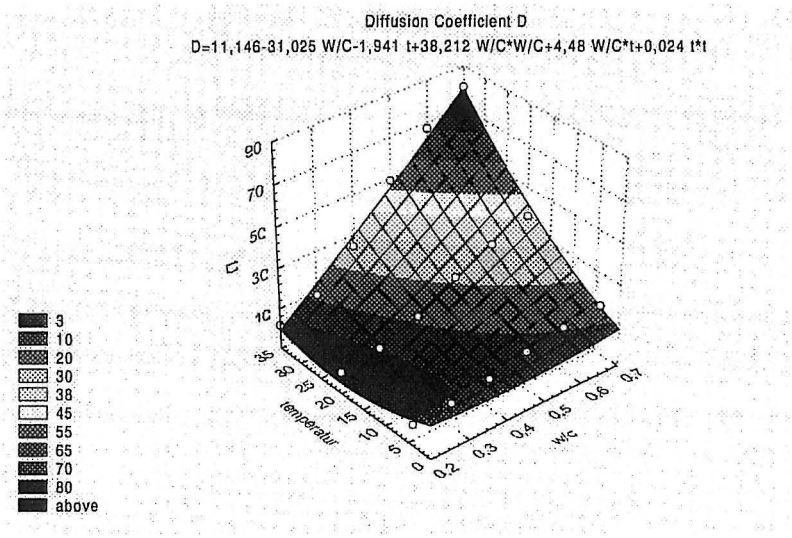

Figure 2. The diffusion coefficient D (10^{-12} m^2/s) as a function of the water-cement ratio w/c and of the temperature t °C (Celsius).

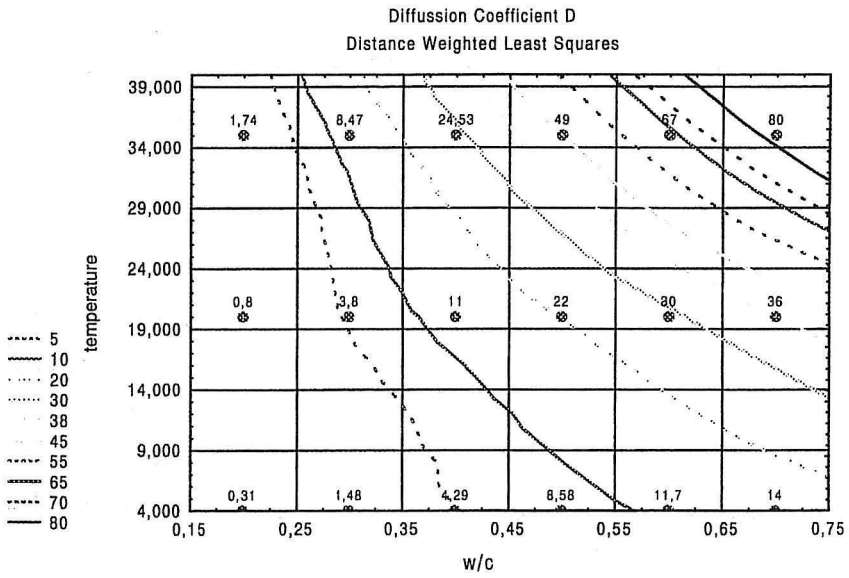

Figure 3. The diffusion coefficient D (10^{-12} m^2/s) as a function of the water-cement ratio w/c and the temperature Φ °C (Celsius).

It follows from figures 2 and 3 that it is of great importance to get good estimates of w/c and Φ. The *w/c* value to be used is the original *w/c* value when the concrete was produced. If the original value of w/c is not available, then it can be estimated by testing thin sections of the concrete. Estimation of the temperature Φ is more complicated, since the temperature usually varies a lot. As a first estimate it is suggested to use an equivalent value based on information of the variation of the temperature during the year at the site of the structure.

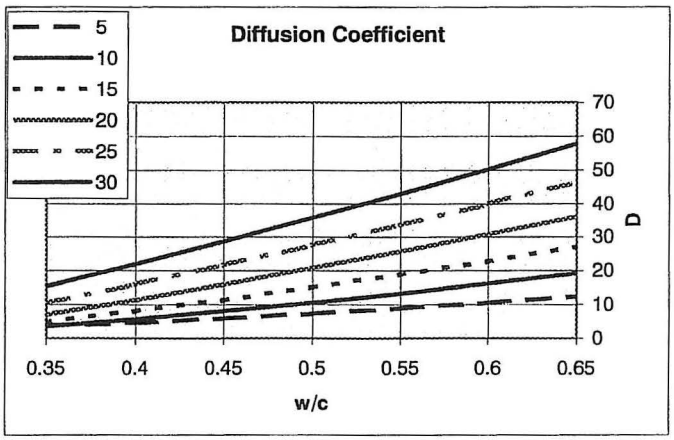

Figure 4. Diffusion coefficient D (10^{-12} m^2/s) as a function of the w/c ratio for different values of the temperature Φ (C).

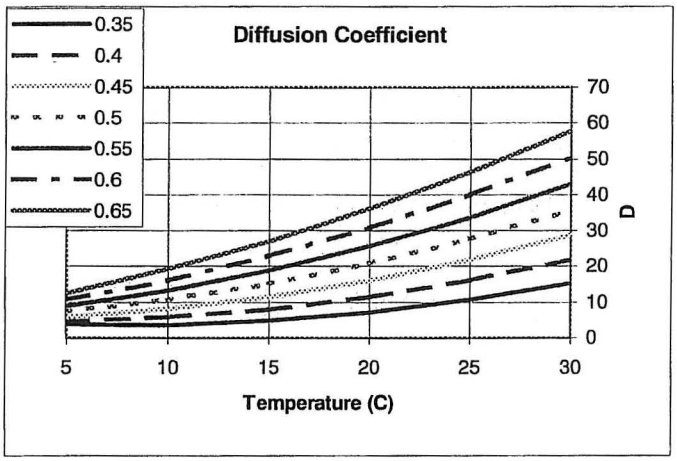

Figure 5. Diffusion coefficient D (10^{-12} m^2/s) as a function of the temperature Φ (C) for different values of the w/c ratio.

The addition of silica fume is of great importance for the chloride ingress. Silica fume additions reduce the chloride ingress because of changes in the pore structure, see table 2, [1].

w/c	0.3					0.5				
% s.f.	0	3	6	10	20	0	3	6	10	20
D (10^{-12} m^2/s)	3.8	2.0	0.42	0.12	0.05	22	13	4.2	1.6	0.30

Table 2. The diffusion coefficient D as a function of % s.f. for two values of w/c and Φ =20 °C.

The data above clearly indicate that site information is needed to make e.g. an estimation of the remaining life cycle or any estimation where the diffusion coefficient is involved. This has clearly been confirmed by several authors e.g. in [11], where important information of the

distribution of the diffusion coefficient D in Japan is shown. Figure 6 shows the mean air temperature Φ and the w/c ratio in Japan. As expected, the temperature is much higher (21-25°C) in the southern part of Japan than in the northern part (4-9°C). The w/c ratio has a smaller variation, but the highest ratios are in the Kanto area where also the temperature Φ is relatively high.

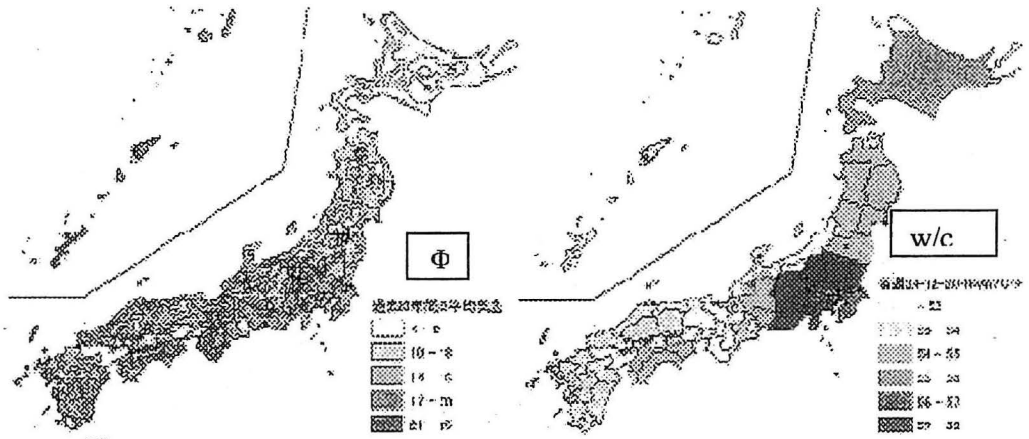

Figure 6. Mean air temperature Φ and w/c ratio in Japan, figures 3 and 5 in [11].

The distribution of the diffusion coefficient D in Japan is shown in figure 7. The D values in the Kanto Area are relatively high in good agreement with the temperature and w/c ratios shown in figure 5.

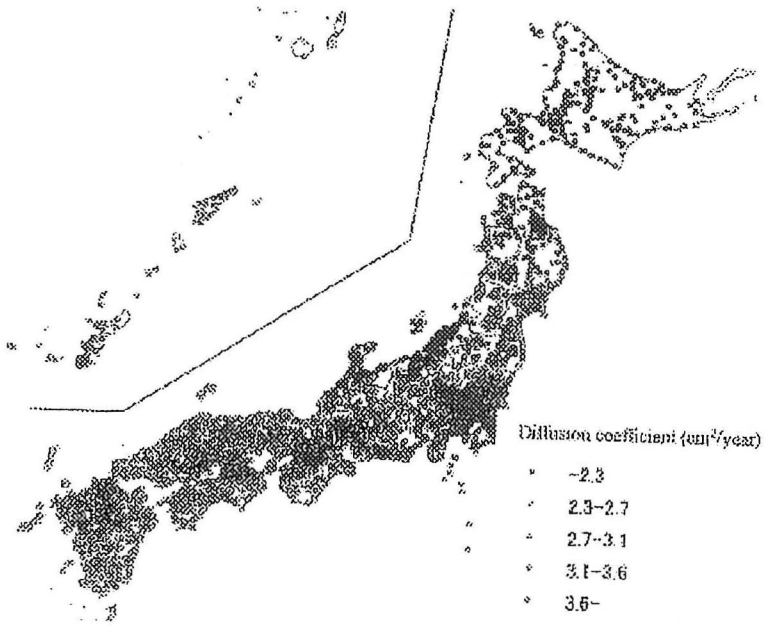

Figure 7. Distribution of diffusion coefficient D (cm^2/year) in Japan, figure 15 in [11].

4. BINDING MODIFIED DIFFUSION LAW

Fick's law for diffusion was used as early as 1970 for calculation of the diffusion coefficients for various concrete compositions [7]. Since then, Fick's law has been the basis for chloride ingress modelling, but a large number of modifications have been introduced [1]. Fick's diffusion law has e.g. been modified taking into account binding of chloride by assuming that the free chloride follows Fick's law [1], [2]. It is also assumed that the chloride binding follows a Freundlich isothermal equation [8]

$$c_b = \alpha \times c_f^{\beta} \tag{5}$$

where c_b [mg/n-gel] is the bound chloride, c_f [mol Cl/l solution] and α and β are empirical constants. The chloride binding significantly modifies the shape of the chloride ingress profiles as well as the calculated chloride diffusion coefficient D. In figure 8 the principal difference between chloride ingress profiles with and without binding is shown. Without bonding the profile is strongly concave and with binding the profile is almost linear. Generally, measured profiles are almost linear so a modelling with binding seems to be a great improvement.

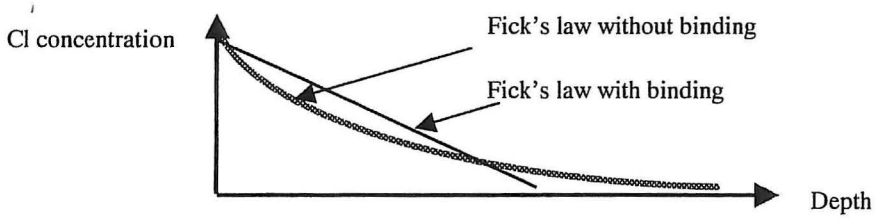

Figure 8. Chloride ingress profiles

In [1] an example strongly supporting this conclusion is presented. A cement paste with w/c = 0.3 and with no additives was exposed to chlorides for 30 days at 35°. Without binding the diffusion coefficient is $1.5 \times 10^{-12} m^2/s$ and with binding included the diffusion coefficient for the free chloride is $3.7 \times 10^{-12} m^2/s$. If binding is included the description is substantially improved.

5. THE W/C RATIO

The w/c ratio for an existing concrete element may be estimated using Optical Fluorescence Microscopy [9], [10]. Thin sections of the concrete are fluorescent impregnated and analysed under an optical microscope using a combination of a blue excitation filter and a yellow blocking filter In fluorescent light the epoxy filled air voids and cracks then appear yellow. Cement paste appears as shades of green and aggregates black. The shade of green of the cement paste depends on the capillary porosity. A sample with a low w/c ratio appears dark green and a sample with high w/c ratio appears light green. These shades of green are use to

estimate the w/c ratio by comparing with the colours of a standard cement pastes where the w/c ratios are known.

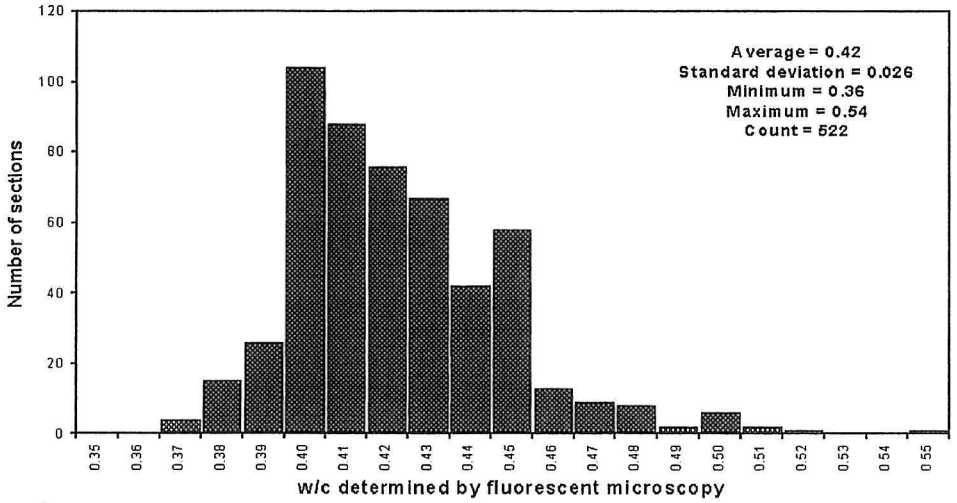

Figure 9. Distribution of w/c measure in 522 thin sections by fluorescence microscopy [10].

In figure 9 is shown the determination of the w/c ratio of precast railroad ties performed on 522 thin sections representing 127 ties. The average value is 0.42 and the standard deviation is 0.026 (the coefficient of variation is 6%).

6. THE TEMPERATURE Φ

It is suggested to model the temperature Φ as a stochastic variable based on the temperature at the site of the structure. The modelling should take into account that the different seasons effect e.g. corrosion differently. The data needed for the stochastic modelling are in most cases available from national meteorological institutions.

7. STOCHASTIC MODELLING OF THE DIFFUSION COEFFICIENT *D*

Based on the experimental results presented in section 3, the following formula may be used to approximately describe the diffusion coefficient D as a function of the w/c ratio and the temperature Φ:

$$D = 11.146 - 31.025 \times w/c - 1.941 \times \Phi + 38.212 \times (w/c)^2 + 4.48 \times w/c \times \Phi + 0.024 \times \Phi^2 \quad (6)$$

As an example assume that w/c is log-normally distributed LN(0.45,0.02) and that the temperature Φ is normally distributed N(10.0°C , 1.0°C). Then by crude Monte Carlo simulation (10.000 samples) it may be shown that the diffusion coefficient may be modelled by a normally distributed stochastic variable N(8.11×10^{-12} m^2/s, 1.11×10^{-12} m^2/s) that is with a coefficient of variation equal to 14%, see figure 10.

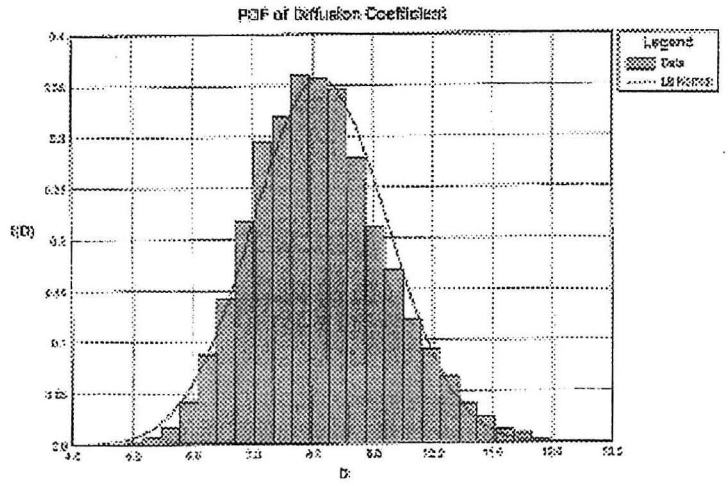

Figure 10. PDF of the diffusion coefficient D (10^{-12} m^2/s).

The diffusion coefficient D is, as expected strongly sensitive to the mean values of w/c and Φ as shown in figure 11. In the diagram to the left, w/c is log-normally distributed LN(E[w/c],0.02) and the temperature Φ is normally distributed N(10.0°C , 1.0°C) and E[D] is the expected value of D. In the diagram to the right, w/c is log-normally distributed LN(0.45,0.02) and the temperature Φ is normally distributed N(E[Temperature] , 1.0°C).

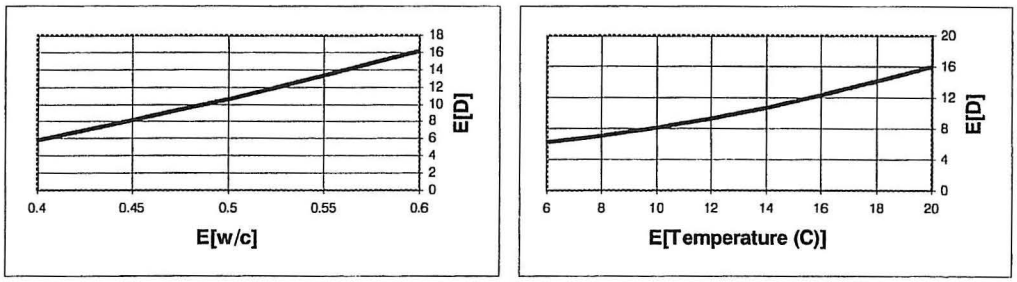

Figure 11. Sensitivity analysis with regard to the mean values of w/c and of the temperature.

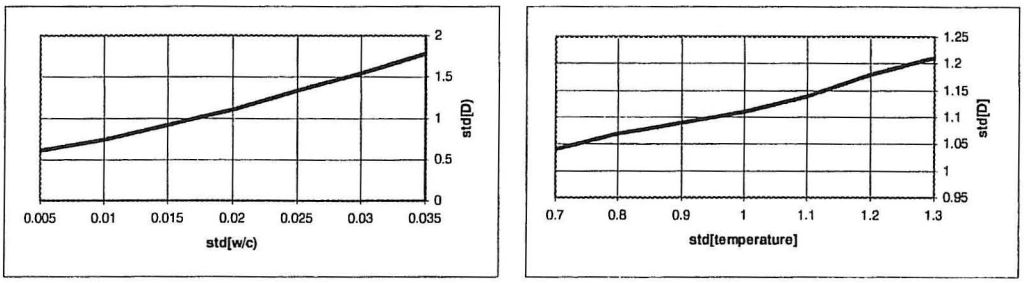

Figure 12. Sensitivity analysis with regard to the standard deviations of w/c and of the temperature.

The standard deviation std[D] of the diffusion coefficient D (but not the expected value E[D]) is sensitive to the standard deviations of w/c and Φ as shown in figure 12. In the diagram to the left, w/c is log-normally distributed LN(0.45,std[w/c]) and the temperature Φ is normally

distributed N(10.0°C , 1.0°C). In the diagram to the right, w/c is log-normally distributed LN(0.45,0.02) and the temperature Φ is normally distributed N(10 °C , std[temperature]).

8. CONCLUSIONS

In the paper the importance of taking into account the site dependency of the diffusion coefficient is emphasized. The diffusion coefficient D depends on several parameters. The two most important parameters seem to be the w/c ratio and the temperature. In the paper a stochastic modeling of D based on recent experimental results is presented using crude Monte Carlo simulation. The dependency of the w/c ratio and the temperature is included.

ACKNOWLEDGEMENT

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