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Testing the variability of the chloride ion diffusion coefficient depending on the concrete curing time

Badanie zmienności wartości współczynnika dyfuzji jonów chlorkowych w początkowym okresie dojrzewania betonu lekkiego

This paper presents tests and results on the penetration of chloride ions, accelerated by an electric field, into concrete specimens made of lightweight concrete with foam glass filling. The tests were carried out in four series, depending on the curing time of the concrete, namely after 7, 14, 28 and 56 days of curing at 100% humidity. Based on the chloride ion concentration values obtained, the diffusion coefficients were determined using a thermodynamic migration model. During the first two weeks, the diffusion coefficient value increased by 18% from the value obtained after 7 days of curing. After a longer curing period (28 days), the value of the coefficient decreased by 22% from the initial value. After a further 28 days, there was a further downward trend in the value of the diffusion coefficient of as much as 78% from the initial value.

Keywords: *lightweight concrete, diffusion coefficient, concrete curing time, durability prediction*

W pracy przedstawiono przebieg i wyniki badań wnikania jonów chlorkowych, przyspieszonego polem elektrycznym, do próbek betonowych wykonanych z betonu lekkiego z wypełnieniem ze szkła piankowego. Badania wykonano w czterech seriach w różnym czasie dojrzewania betonu: po 7, 14, 28 oraz 56 dniach dojrzewania w warunkach 100-procentowej wilgotności. Na podstawie uzyskanych wartości stężenia jonów chlorkowych wyznaczono wartości współczynników dyfuzji z wykorzystaniem metody termodynamicznego modelu migracji. W ciągu pierwszych dwóch tygodni wartość współczynnika dyfuzji wzrosła o 18% w porównaniu z wartością uzyskaną po 7 dniach dojrzewania betonu. Po dłuższym okresie dojrzewania (28 dniach) wartość współczynnika zmalała o 22% w stosunku do wartości początkowej. Po kolejnych 28 dniach nadal obserwowano tendencję spadkową wartości współczynnika dyfuzji, wynoszącą aż 78% w stosunku do wartości początkowej.

Słowa kluczowe: *beton lekki, współczynnik dyfuzji, czas dojrzewania betonu, prognozowanie trwałości*

1. Introduction

The diffusion coefficient of chloride ions in concrete is not a constant value, but is strictly time-dependent [1]. It takes the form of a dual dependence on time. Different values of the diffusion coefficient are obtained depending on the duration of exposure to an NaCl solution. It was found that the longer the test lasted, the lower the diffusion coefficient value was. This phenomenon is related to the binding process of chloride ions, which can have a physical and chemical nature. It is also usual for the value of the diffusion coefficient to decrease as the test concrete matures, as the capillary pore system will change as a result of the hydration processes taking place and the binding of chloride ions in the cement matrix [2, 3]. This variation is described by the following correlation:

$$D(t) = D_{\mathrm{ref}}\left(\frac{t_{\mathrm{ref}}}{t}\right)^{m}, \tag{1}$$

where D_{ref} is the diffusion coefficient at a given reference time of t_{ref}, while m – the ageing coefficient which determines the rate of change of diffusion over time (dependent on the composition of the concrete mix). The values of the m coefficient determined in different concretes have not yet been definitively established, although values determined for some concrete mixtures can be found in the literature [4, 5]. There are also different approaches to the determination of the m coefficient. In the first case, the m_{total} coefficient is determined, which refers in sum to t_1, namely

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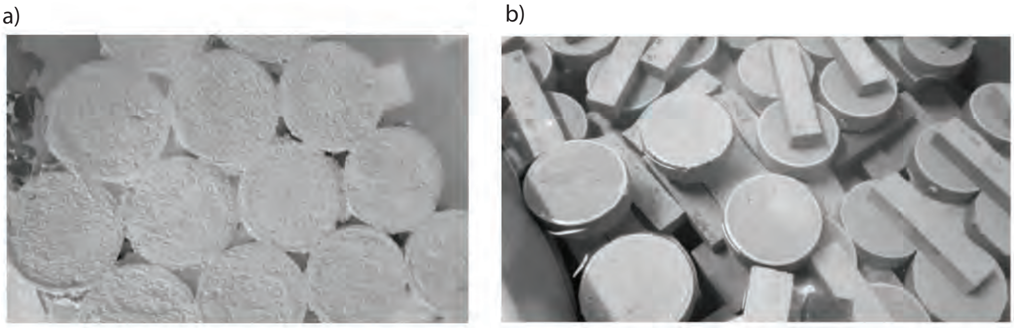

Fig. 1. Samples: a) concreted in moulds, b) cured, fully immersed in water

Rys. 1. Próbki: a) zabetonowane w formach, b) dojrzewające, całkowicie zanurzone w wodzie

the concrete maturity time and t_2, the duration of the test for diffusion of chloride ions into the concrete. In another approach, the m_{avr} coefficient is determined, which refers to the t_{avr} time, which is the average value of two different test durations for the diffusion of chloride ions into the concrete [6]. Depending on how the time is determined, different values for the m coefficient are obtained [7]. Various mathematical methods are also used to determine the ageing coefficient: the logarithmic method and the least squares method [8]. The correct determination of the m coefficient has great significance in the process of predicting the durability of reinforced concrete structures. This coefficient is also used in the method for determining the correct thickness of the concrete cover proposed in the FIB bulletin [9], where the effect of ageing of the designed concrete is taken into account [10].

The main objective of this study was to investigate the influence of the curing time of lightweight concrete on the rate of chloride ion penetration. Lightweight concrete is used in the manufacture of small- and large-format precast elements, but also in monolithic construction and often, as an external cladding layer. Thanks to the foamed glass granules, the weight of the concrete is significantly reduced and it also exhibits good thermal insulation, sound insulation and fire protection properties. Four series of concrete samples cured for 7, 14, 28 and 56 days were investigated.

The rate of penetration was determined by chloride ion diffusion coefficients determined using a thermodynamic migration model. This method has been described in detail in works [11–13] and also compared with other standard methods in different types of concrete [14]. By using this method, diffusion coefficient values could be obtained after fairly short migration tests of 24 and 48 hours in each range. The coefficient values obtained were values averaged over the duration of the test itself. This approach allows us to disregard the variability in diffusion coefficient values due to the duration of the test itself and therefore it can be considered that the method used relates to the averaged m_{avr} coefficient. The focus was on assessing the influence of the concrete curing process itself on the value of chloride ion diffusion coefficients. Afterwards, for the determined values of the diffusion coefficients, a numerical prediction of the durability of reinforced concrete structures made of the concrete studied was prepared. The results of the forecast show that determining the value of the diffusion coefficient too quickly can lead to a considerable overestimation of its value.

2. Research methodology and results

For the tests, 16 cylindrical specimens with a diameter of 11 cm and a height of 5 cm, and 12 cuboidal specimens with dimensions of 4 × 4 × 16 cm were prepared from ready-mix dry concrete – lightweight concrete with foam glass (Fig. 1a). The specimens were cured at 100% moisture content (fully immersed in water at approximately 21°C; Fig. 1b).

Unfortunately, the exact composition of the mix is not known for reasons of commercial confidentiality. A sieve analysis was carried out to determine the approximate cement compactness of the concrete mix. The mixture used also contains perlite and has a strong tendency to become electrostatically charged. Consequently, small amounts of material "stuck" to the sieves. During the test, a loss of material amounting to 5 g was determined by weighing the starting material obtained after passing through the sieves and adding it up. Using a coarse method of determining the cement content, sufficient to demonstrate the reality of the time-dependent diffusion coefficient values, the material that stopped on the 0.125 mm and smaller sieves was considered to be the binder (cement). Using 12 cuboidal concrete samples measuring 4 × 4 × 16 cm, an average density of the concrete of 826.95 kg/m^3 was determined using the hydrostatic method. Based on the calculations, the percentage of cement was determined to be 69.77%, based on which the cement content itself amounted to 577 kg/m^3. The w/c ratio of the tested concrete was 0.62. Table 1 shows the results of the sieve analysis.

Table 1. Results of sieve analysis – corrected mass of the individual fractions
Tabela 1. Wyniki analizy sitowej – skorygowane masy poszczególnych frakcji

Mesh size of the sieve [mm]	Material weight remaining on the sieve		Losses [g]	Corrected mass [g]
	[g]	[%]		
4	4.70	0.47	0.02	4.72
2	31.00	3.08	0.15	31.15
1	95.80	9.51	0.48	96.28
0.5	80.50	7.99	0.40	80.90
0.25	92.70	9.20	0.46	93.16
0.125	385.20	38.22	1.91	387.11
0.063	260.60	25.86	1.29	261.89
<0.063	57.30	5.69	0.28	57.58
Sum	1007.80	100.00	5.00	1012.80

This was followed by an electric field accelerated study of the rate of penetration of chloride ions into the concrete. The test was carried out in four series: after curing for 7 days, after curing for 14 days, after curing for 28 days and after curing for 56 days. Four concrete specimens were prepared for each series: without removing them from the moulds – sealed casings were glued on and filled with a 3% NaCl solution so that the migration of chlorides

a) b) c)

Fig. 2. Workstations: a) for chloride migration testing, b) for concrete abrasion with a diamond crown, c) the powder taken from the selected range

Rys. 2. Stanowiska: a) do badań migracji chlorków, b) do ścierania betonu koronką diamentową, c) pobrany proszek z wybranego przedziału

was only in one direction. They were then fitted with electrodes made of corrosion-resistant steel. The samples were then placed in a vessel with a grid made of platinum-coated titanium (anode) and tap water. The electrodes were connected to an 18 V DC source for 24 h (four samples) and 48 h (two samples) successively, in such a way that there were two samples for each chloride loading scheme (Fig. 2a). At the end of the specified time, the samples were disconnected from the current, removed from the water, the salt solution poured out and the previously glued casings cut off. The laboratory-dried specimens were subjected to abrasion with a diamond core drill on a prepared workstation (Fig. 2b). Ten layers 2 mm thick were taken from the concrete cylinders – up to a total depth of 20 mm. The average of two samples from each sampled section was then used for testing (Fig. 2c).

The material thus prepared from each layer, in the form of concrete powder, was mixed 2 : 1 (water : powder) by weight with distilled water. The mixture was then filtered by gravity through a medium filter pads to obtain a solution for testing the chloride ion content using Elmetron's CX-701 multifunction meter device. Table 2 shows the results of the chemical analyses.

In the next step, the diffusion coefficient values of the tested concrete were determined using the method of the thermodynamic migration model described in [11]. The following formulae were used in the calculations:

$$\rho^1 = \frac{2c^1\gamma_b}{\gamma_w}, \qquad \overline{j}^1(a) = \frac{m^1}{At} = \frac{g}{t}\rho^1, \qquad D_s^1 = \frac{\overline{j}^1(a)a}{\frac{z^1FUg}{RTh}\overline{\rho^1}(t)}, \quad (2)$$

where:

ρ^1 – mass density of chloride ions,
c^1 – chloride ion concentration,
γ_b – volumetric weight of concrete,
γ_w – water weight by volume,
m^1 – mass of chloride ions,
$\overline{j}^1(a)$ – averaged mass flux of chloride ions,
$\overline{\rho^1}$ – averaged mass density of chloride ions,
A – cross-sectional area,
t – ion flow time,
g – the thickness of the layers of the ground material taken for testing,
D_s^1 – chloride ion diffusion coefficient,
a – distance of test layer from edge of concrete,
z^1 – ion valence,
F – Faraday's constant,
U – potential,
g – the thickness of the layers of the ground material taken for testing,
R – gas constant,
T – absolute temperature,
h – sample height.

Next, the least sum of squares of the differences between $\overline{D_t^1} \cdot 10^{-12}$ [m^2/s], i.e. the diffusion coefficient values determined in the tests and the values shown in the curve determined according to the formula (1), were determined. The curve uses a $D_{ref} = 13.10 \cdot 10^{-12}$ [m^2/s]

Table 2. Values of chloride ion concentration c^1 [mg/dm^3] determined in the test solutions extracted from the concrete in series: I – after 7 days, II – after 14 days, III – after 28 days, IV –after 56 days of maturity of concrete

Tabela 2. Wartości stężenia jonów chlorkowych c^1 [mg/dm^3] określone w badanych roztworach ekstrahowanych z betonu w kolejnych seriach: I – po 7 dniach, II – po 14 dniach, III – po 28 dniach, IV – po 56 dniach dojrzewania betonu

Series	Duration of the study [h]	Cl^- concentration in solution (c^1) [mg/dm^3]									
I	$t_1 = 24$	819	648	603	590	610	612	621	659	679	670
	$t_2 = 48$	821	708	686	677	660	666	704	704	775	831
II	$t_1 = 24$	670	666	700	692	762	746	815	790	833	465
	$t_2 = 48$	700	700	730	758	775	826	869	925	888	871
III	$t_1 = 24$	715	871	897	1000	1005	817	404	94	29	21
	$t_2 = 48$	540	580	596	634	627	610	612	569	425	166
IV	$t_1 = 24$	999	1295	1480	575	110	33	37	31	28	28
	$t_2 = 48$	1410	1870	1610	1572	1360	570	95	65	43	33
Coordinate [mm]		1	3	5	7	9	11	13	15	17	19

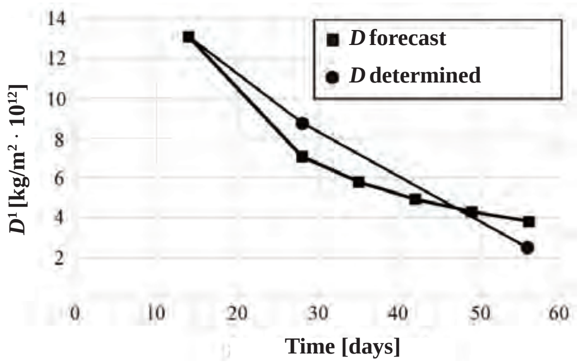

Fig. 3. Values of diffusion coefficients $\overline{D_s^1} \cdot 10^{-12}$ [m²/s] determined in the studies, and of $\overline{D_t^1} \cdot 10^{-12}$ [m²/s] – forecasted by means of the diffusion coefficient as a function of the concrete curing time

Rys. 3. Wartości współczynników dyfuzji $\overline{D_s^1} \cdot 10^{-12}$ [m²/s] wyznaczonych w badaniach oraz $\overline{D_t^1} \cdot 10^{-12}$ [m²/s] – prognozowanych wartościami współczynnika dyfuzji w zależności od czasu dojrzewania betonu

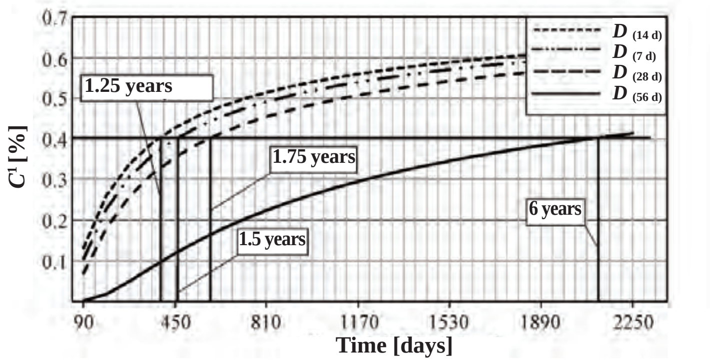

Fig. 4. Forecasting durability of reinforced concrete structures according to equation (3) using different values of the diffusion coefficient depending on the concrete curing time

Rys. 4. Prognozowanie trwałości konstrukcji żelbetowych według wzoru (3) z wykorzystaniem różnych wartości współczynnika dyfuzji w zależności od czasu dojrzewania betonu

value as a reference coefficient determined after the curing time of $t_{ref} = 14$ days, and the ageing coefficient value of $m = 0.89$ was determined as well. The value of the coefficient determined after a curing time of 7 days was omitted from the analyses, as it deviates from the trend obtained for the other values (Fig. 3).

In the next step, in order to illustrate the differences in the estimated durability times of the structure made of the tested concrete, the chloride ion concentration distributions over the concrete cover thickness c_{nom} = 20 mm were predicted taking into account the different values of the diffusion coefficient determined after successive concrete curing times of 7, 14, 28 and 56 days and also using the predicted value of the diffusion coefficient at 56 days and the value of the ageing coefficient $m = 0.89$. The prediction was made according to the formula:

$$C(x,t) = C_0(x,t)\left(1 - erf\,\frac{x}{2\sqrt{Dt}}\right), \quad (3)$$

where:

$C_0(x,t)$ – the chloride ion concentration at the edge of the element (determined in diffusion time t in the first tested concrete layer),

erf – Gaussian error function,

t – time.

A value of C_{cr} = 0.4% of the mass of chlorides to the mass of the cement was the value adopted to define the critical concentration of chloride ions at the surface of the reinforcing steel, as recommended by the standard [15]. To simplify the analysis, the chloride ion concentration at the edge of the element was taken as a constant value of $C_0(x, t)$ = 0.8%. Fig. 3 shows the durability forecast of reinforced concrete structures according to formula (3) for different values of the diffusion coefficient depending on the concrete curing time.

Table 3 shows the values of p^1 [kg/m³] – the mass density of chloride ions and $\overline{j}^1(a) \cdot 10^6$ [kg/m²s] – chloride ion mass fluxes

Table 3. Values of the diffusion coefficient of Cl⁻ ions – concrete after curing times of 7, 14, 28 and 56 days
Tabela 3. Wartości współczynnika dyfuzji jonów Cl⁻ – po dojrzewaniu betonu przez 7, 14, 28 i 56 dni

Calculated values	Curing time [days]	Coordinate [mm]				Determined average value of the diffusion coefficient $\overline{D_s^1} \cdot 10^{12}$ [m²/s]	Forecast value of the diffusion coefficient $\overline{D_t^1} \cdot 10^{12}$ [m²/s]	m – ageing coefficient
		1		19				
		t = 24 h	t = 48 h	t = 24 h	t = 48 h			
p^1 [kg/m³]	7	10.70	11.70	11.07	13.73	×	×	×
	14	11.00	11.56	7.68	14.39			
	28	9.58	14.39	2.74	0.35			
	56	21.39	30.89	0.46	0.55			
$\overline{j}^1$ [kg/m²s]	7	247.38	140.38	17.78	16.65			
	14	217.66	122.58	25.62	15.88			
	28	184.28	98.24	6.35	0.40			
	56	138.32	138.01	1.07	0.63			
$\overline{D_s^1} \cdot 10^{12}$ [m²/s]	7	22.57	12.68	2.23	1.90	11.24		
	14	31.35	17.03	1.36	1.77	13.10	13.10	
	28	28.98	11.67	0.62	0.05	8.76	7.06	0.58
	56	11.76	8.31	0.12	0.06	2.45	3.81	1.21

calculated for selected layers of abraded concrete. The values of $\overline{D_s^1} \cdot 10^{-12}$ [m^2/s] as determined in the study, namely of the diffusion coefficients using formulae (2) as a function of the curing time of the lightweight concrete tested, are also presented. Also shown are the least-squares values of the ageing coefficient m, determined from equation (1), which determines the rate of change of diffusion over time, and $\overline{D_t^1} \cdot 10^{-12}$ [m^2/s] – the forecasted values of diffusion coefficients determined using an average ageing coefficient of $m = 0.89$. The reference time was a curing time of 14 days.

3. Discussion and conclusion

A comparison of the determined values of the diffusion coefficient in relation to the time of concrete curing shows that the value of this coefficient changes rapidly during the initial period of concrete maturation. The average value of the diffusion coefficient determined after migration tests conducted at two times of 24 and 48 hours was determined in each case, so that the effect of the test duration on the value of the diffusion coefficient was taken into account. The value of the diffusion coefficient determined after two weeks of concrete curing was 18% higher than the value obtained after seven days of curing. The increase in the value of this coefficient can probably be attributed to the higher binding capacity of the chloride ions at a very early stage of concrete curing (after 7 days), similar to the way in which they have been added to fresh concrete. After a longer curing period (28 days), the value of the coefficient decreases by 22% in relation to the initial value (determined after 7 days of curing). After a further 28 days, there is a further downward trend in the value of the diffusion coefficient of up to 78% in relation to the initial value (determined after 7 days of curing). If the diffusion coefficient value determined after a concrete curing time of 14 days is used uncritically, a very short durability of the reinforced concrete structure of only 1.5 years is obtained. After the 28 days recommended as reference time in [16], a durability of 1.75 years was achieved. On the other hand, a durability of 6 years was achieved using the diffusion coefficient determined after testing concrete cured for 56 days, while using the value of the diffusion coefficient determined numerically using relationship (1) and the value of the ageing coefficient $m = 0.89$ at 56 days, an average durability of 3.75 years was achieved.

The observed diffusion properties of the tested lightweight concrete confirm that determining the value of the diffusion coefficient during the initial period of concrete maturation can result in large errors in the process of predicting the durability of structures made from the concrete material in question. It is very important to take into account the curing time of the tested concrete, during which the value of the diffusion coefficient is determined, when predicting the durability of the structure. The research was deliberately carried out on a concrete material subjected to rapid changes resulting from hydration processes in order to illustrate how much the curing time of the tested concrete has an impact on its diffusion properties.

CRediT authorship contribution statement

Zofia Szweda: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

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