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DIFFUSION OF ORGANIC SUBSTANCES INHIBITING REINFORCEMENT CORROSION IN CONCRETE

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Abstract. This paper will present the results of tests on the diffusion properties of the migrating inhibitor DME and KCR. The tests were done by determining the distribution of concentrations of inhibitors in concrete, and then the values of a reliable diffusion coefficient were calculated on the basis of the solution to the reverse-task diffusion equation. Inhibitors have shown very good diffusion properties, which were about 5 rows better than the properties of the inhibitors on the market. Inhibitors DME and KCR were able to quickly penetrate deep into the concrete through the entire thickness of reinforcement concrete cover.

Keywords: concrete, inhibitor, corrosion, diffusion, protection, reinforcement, reinforced concrete.

1. Introduction

To protect the reinforcement of existing reinforced concrete structures against corrosion migrating inhibitors have been trialled (Czarnecki, Emmons 2002). One of the basic conditions for proper functioning of these inhibitors is good diffusion properties in concrete. Applied to the surface of the object, inhibitors must reach the reinforcement as soon as possible, and have reached this point at the concentration for the inhibition of iron dissolution reaction (Czarnecki *et al.* 2008). Changes in the concentration of inhibitor in the concrete can be predicted on the basis of diffusion equations, knowing in advance the value of a reliable diffusion coefficient designated experimentally.

An inhibitor diffusion coefficient is usually determined using diffusion chambers (Czarnecki *et al.* 2008). The study is carried out in stationary conditions with significant differences in the concentrations on both sides of the sample. The mass flow of inhibitor flowing through the sample is designated and on the basis of I Fick's law the constant value of diffusion coefficient is calculated. However, the test conditions differ significantly from those affecting inhibitor application to a structure. In studies inhibitor flow is forced by a very high concentration difference between the chambers, and throughout period of measurement a constant concentration of inhibitor is kept in a chamber containing a flowing substance, moreover the sample is saturated with water.

The research presented in the paper was done in different ways, trying to simulate real conditions. A reliable value of the diffusion coefficient was determined on the basis of the distribution of the concentration of inhibitor in the concrete, determined at several time intervals after application on the surface of concrete samples, located under air–dry conditions. Calculations were made according to the reverse-task solution of the diffusion equation (Zybura 2007).

2. The scope and course of study

Two types of inhibitors that have been proposed for protection of reinforcement in reinforced structures (Klakočar-Ciepacz, Falewicz 2003) were submitted to diffusion tests. One substance was an organic compound marked DME, with the chemical formula $(CH_3)_2NCH_2CH_2OH$, so far used to protect steel process equipment in contact with alkaline solutions. The second inhibitor, specified with the symbol KCR, was obtained by mixing the compound DME with a solution facilitating penetration of narrow slits.

Experiments were carried out on 13 concrete specimens with cubic dimensions of 100 mm. Quick performing cement CEM I supplied by "Górażdże Cement SA" cement mill and a mineral aggregate were used.

Three cubes for the diffusion test on the inhibitor DME were made of medium strength f_{cm} = 43.2 MPa concrete (series 1), while the remaining number of cubes were used to study, the diffusion of the inhibitor KCR – of concrete strength f_{cm} = 32.0 MPa (series 2).

After 28 days of maturing of the concrete, the inhibitors DME and KCR were applied to the samples at a quantity 3 g/dm^2, as recommended by the manufacturers of other migrating inhibitors. The substances were applied twice on the concrete surface perpendicular to the direction of concreting.

The entire surface of a series of two cubes was covered with DME compound, while the third cube was left as a control reference. The distribution of inhibitor concentration in one cube was set 14 days after application, while in the second one, after 28 days. KCR inhibitor was applied to the surface of nine cubes of the second series. The tenth cube served as a control reference. Distribution of the KCR inhibitor concentration was determined in three cubes after 14 days from the application of the inhibitor, while in the next three cubes, after 28 days, and in the last three cubes, after 56 days. As before, the tenth cube was treated as control reference. After a planned period of inhibitor operation, from each sample there were collected layers of crumbled material for a chemical test. From the two samples of series 1 treated with the compound DME material was taken to a depth of 38 mm, while from the nine samples of series 2 treated with inhibitor KCR, to a depth of 20 mm. The thickness of each layer was 2 mm. From control reference from series 1 and 2 were taken after two layers of crumbled material. The concrete was crumbled with the Profile Grinding Kit device from Germann Instruments AS.

3. Results of tests

The concentration values of DME tests were established by specifying nitrogen content in the samples of crumbled concrete. Since nitrogen does not occur in the natural composition of the concrete, it therefore clearly identifies the presence of the inhibitor. Chemical analysis was performed by the Kjeldahl method in accordance with the standard PN-90-C-87030/16 [PN-90-C-87030/16], on the assumption that in one molecule of DME there is one nitrogen atom (chemical analysis was performed at the Institute of Inorganic Technology and Mineral Fertilizers, Wroclaw University of Technology).

After determining the mass m_N of nitrogen, in proportion to the atomic weight of other elements in the molecule, the concentration of the compound DME was determined.

$$C_{DME} = \frac{m_{DME}}{V}, \quad V = 0{,}00837\,\mathrm{dm}^3, \quad m_{DME} = \frac{m_N}{0.1571}, \tag{1}$$

where: V is the volume of the zone from which the layer of material was collected; m_{DME} – inhibitor mass calculated, taking into account that the atomic mass of nitrogen is 15.71% of the DME molecular weight.

The KCR inhibitor concentration in the concrete was determined in a similar way, by adjusting the mass of the inhibitor

$$m_{KCR} = \frac{m_N}{0.0743}, \tag{2}$$

in accordance with the results of chemical analysis, which showed that nitrogen was 7.43% by weight of inhibitor KCR.

In setting the concentration of inhibitors in the concrete, it was assumed that all components diffused at the same speed. Studies of crumbled material taken from the control cubes did not show in the concrete of series 1 and 2 the existence of nitrogen.

Distributions of concentrations of tested inhibitors in the concrete of test items are shown in Fig. 1.

4. Reverse task solution of the diffusion equations

The results of experimental tests were generalized by formulating an inverse task diffusion equation, similarly to that in paper (Zybura 2007). It was assumed that experimental conditions would allow the assumption of a one-way inhibitor flow described by the equation of diffusion

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right), \tag{3}$$

where: $C = C(x,t)$ is the concentration of inhibitor at any point with coordinates x and time t, while D – diffusion coefficient as a function of concentration.

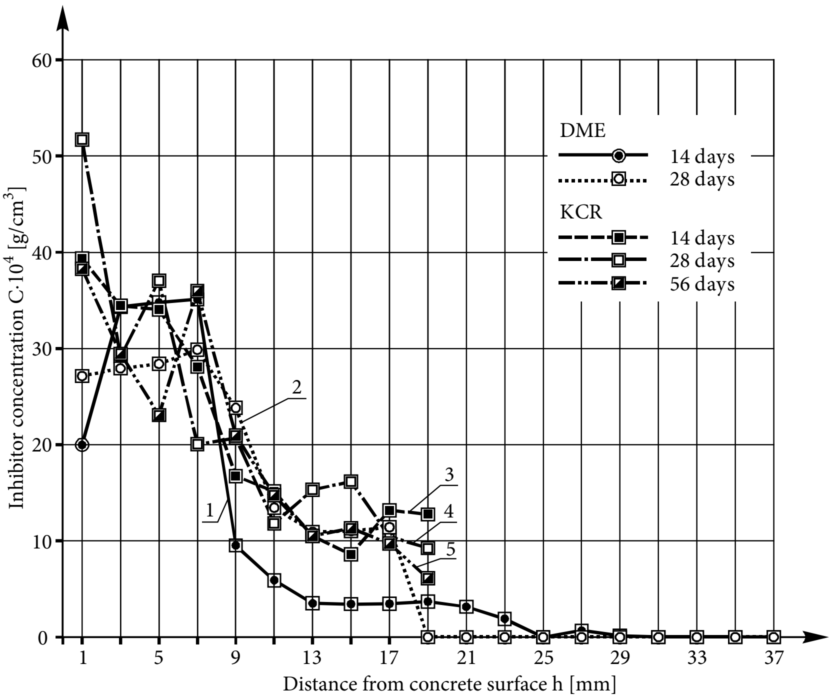

Fig. 1. Distribution of concentrations of inhibitors in concrete – DME after the application: 1 – 14 days, 2 – 28 days; KCR after the application: 3 – 14 days, 4 – 28 days, 5 – 56 days

The cubes used in the experimental studies are parameterized with a coordinate system in which the concrete surface to which the inhibitor was applied corresponds to the surface of the coordinate $x = 0$, while gauge lying inside the concrete of the analyzed layer is defined by the surface $x = a$ (Fig. 2a).

Diffusion resistance Q_x of separate concrete layer thickness x' and the diffusion resistance Q across entire concrete layer thickness a can be written as

$$Q_x = \int_0^{x'} D(x')^{-1}\,dx', \quad Q = \int_0^{a} D(x')^{-1}\,dx'. \tag{4}$$

Then in the flow equation (3) both sides are multiplied by the ratio Q_x/Q and integrated over the thickness of concrete cover x between 0 and a,

$$\int_0^a \frac{Q_x}{Q}\frac{\partial C}{\partial t}dx = \int_0^a \frac{Q_x}{Q}\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}dx\right). \tag{5}$$

The right side of equation (5) is integrated over the part and the definite integral is determined,

$$\int_0^a \frac{Q_x}{Q}\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)dx =$$

$$\frac{Q_x}{Q}D\frac{\partial C}{\partial x}x \Big|_{x=0}^{x=a} - \int_0^a \frac{\partial}{\partial x}\left(\frac{Q_x}{Q}\right)D\frac{\partial C}{\partial x}dx =$$

$$-\mathbf{j}(a)\cdot a + \frac{1}{Q}[C(0)-C(a)]. \tag{6}$$

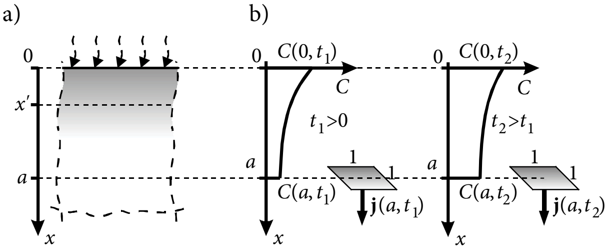

Fig. 2. Flow diagram of the inhibitor in the concrete. Description in text

Then both sides of the equation are integrated over the range $[t, t + \Delta t]$,

$$\int_t^{t+\Delta t}\int_0^a \frac{Q_x}{Q}\frac{\partial C}{\partial t}dx\,d\tau =$$

$$-\int_t^{t+\Delta t}\left\{\mathbf{j}(a)\mathbf{n}a - \frac{1}{Q}[C(0)-C(a)]\right\}d\tau, \tag{7}$$

$$\int_t^{t+\Delta t}\int_0^a \frac{Q_x}{Q}\frac{\partial C}{\partial t}dx\,d\tau =$$

$$\frac{1}{Q}\int_0^a Q_x[C(x,t+\Delta t)-C(x,t)]dx. \tag{8}$$

After replacing the integral on the right side of equation (7) with average values multiplied by the increment of time Δt and execution of the transformation expression for the diffusion coefficient of the inhibitor in concrete the following equation is obtained,

$$D = \frac{1}{Q} =$$

$$\frac{\overline{\mathbf{j}}(a)\,\mathbf{n}a\,\Delta t}{[\overline{C}(0) - \overline{C}(a)]\Delta t - \int_0^a Q_x\,[C(x,\,t+\Delta t) - C(x,\,t)]dx}, \quad (9)$$

where: $\overline{\mathbf{j}}(a)$ is time averaged Δt value of the inhibitor mass flow flowing through the surface of the coordinate $x = a$; $\overline{C}(0)$, $\overline{C}(a)$ – time averaged Δt concentration of the inhibitor on the surface levels of the coordinate $x = 0$ and $x = a$ (Fig. 2b).

In the denominator of expression (9) the first component corresponds to the stationary part of the inhibitor flow, while the second component includes the non-stationary part of the flow. Omitting the second component in the denominator of expression (9), the value of the diffusion coefficient in the case of stationary flow is obtained, and while estimating the value of this component, non-stationary influences can be assessed.

5. Numerical value of inhibitor diffusion coefficient

The experimental results obtained enabled the analysis of several model layers, which consisted of appropriately grouped layers of crumbled concrete samples. The principle of construction of the model layers is shown in Fig. 3.

The first model layer marked with the letter "A" thickness a = 4 mm was a samples of the collected material of layers 1 and 2. The average concentration at time t in the outer zone of the model layer and the difference in average boundary concentrations were defined with the formulas

$$\overline{C}(0) = 0{,}5C_1(t),\ \ \overline{C}(a) = 0{,}5C_2(t),$$
$$\Delta\overline{C} = \overline{C}(0) - \overline{C}(a), \quad (10)$$

where the subscripts 1 and 2 represent the number of the layer of donated material.

The average mass flux of DME inhibitor flowing at time t = 14 days for the boundary surface $x = a = 4$ mm was determined by aggregating the concentration of inhibitor present in all layers of crumbled concrete, outside of the model layer

$$\overline{\mathbf{j}}(a) = \frac{m}{A \cdot t} = \frac{g}{t}(C_3 + C_4 + \ldots + C_{12}), \quad (11)$$

where m is the inhibitor mass flow flowing through the surface of the area A at time t; g = 2 mm – the thickness of the crumbled material; subscripts correspond to the layer number.

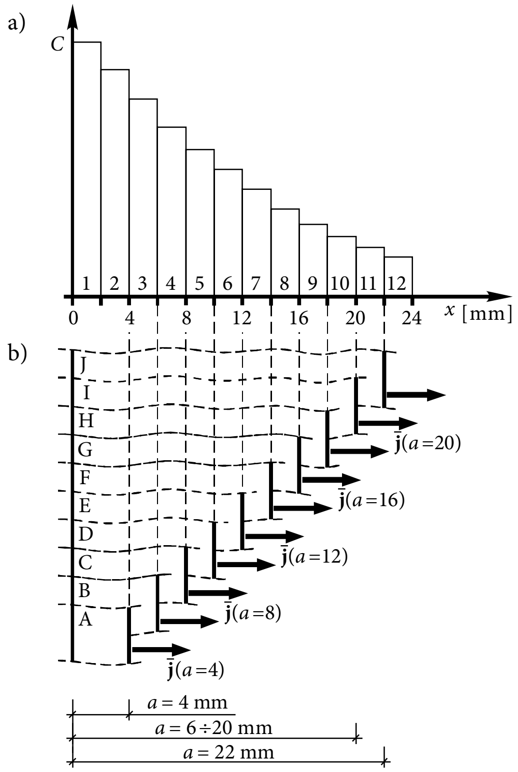

Fig. 3. Pattern of calculation: a) distribution of an inhibitor concentration experimentally determined in layered samples, b) analyzed model layers

Values of DME inhibitor diffusion coefficient determined by the relation (9) omitting the component including non-stationary part of the flow are given by

$$D = \frac{\overline{\mathbf{j}}(a) \cdot \mathbf{n} \cdot a}{\Delta\overline{C}}. \quad (12)$$

The formation of model layer "B" thickness a = 6 mm includes three layers of collected material 1, 2 and 3. Average boundary concentrations in time were calculated from the formula

$$\overline{C}(0) = 0{,}5C_1(t),\ \ \overline{C}(a) = 0{,}5C_3(t), \quad (13)$$

while the average DME inhibitor mass flow flowing at time t = 14 days for boundary surface $x = a = 6$ mm was determined from the relation

$$\overline{\mathbf{j}}(a) = \frac{m}{A \cdot t} = \frac{g}{t}(C_4 + C_5 + \ldots + C_{12}). \quad (14)$$

Similarly, calculations were made for the values of diffusion coefficients of DME and KCR inhibitors based on flows through the other model layers at time t = 14 days, 28 days and 56 days. Distribution of the determined inhibitor diffusion coefficient values depending on the difference in average concentrations $\Delta\overline{C}$ at the edges of the layer are shown graphically in Fig. 4a (DME) and Fig. 4b (KCR).

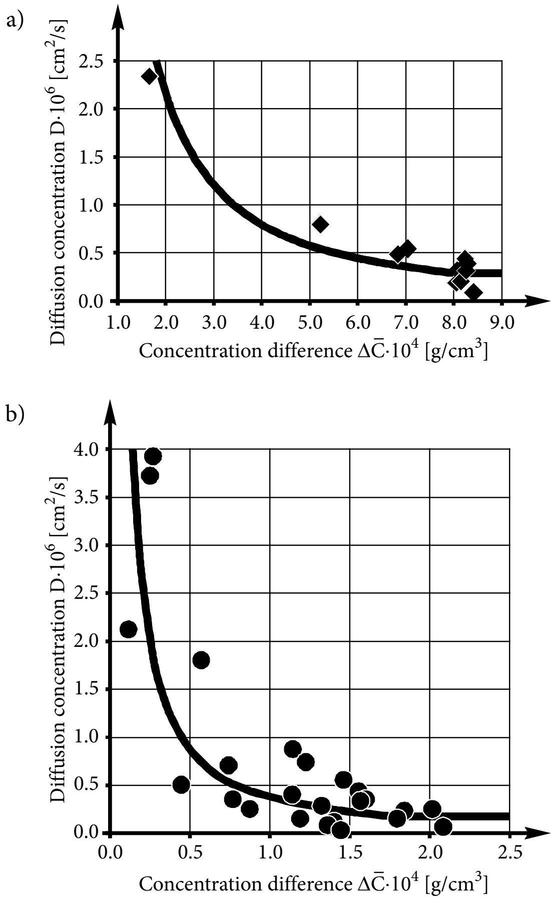

Fig. 4. The distribution of diffusion coefficient values depending on the difference in average concentrations at the edges of layers: a) compound DME, b) inhibitor KCR

The curve of graph indicates that the diffusion coefficient of compound DME reached a stable value $D_{DME} = 2.776\times10^{-7}$ cm^2/s at a difference of average boundary concentration $\Delta\overline{C} > 8.00\times10^{-4}$ g/cm^3. The KCR inhibitor diffusion coefficient reached a stable value $D_{KCR} = 1.740\times10^{-7}$ cm^2/s when the difference of average boundary concentration $\Delta\overline{C}$ was greater than 17.50×10^{-4} g/cm^3.

6. Summary

Compound DME and inhibitor KCR have shown very good diffusion properties. After 14 days of the imposition on the concrete surface their presence was found at a depth greater than 20 mm, corresponding to the average thickness of concrete cover for existing reinforced structures.

The results obtained indicate that an additional component serving to improve the penetration of the KCR inhibitor had no significant effect on the diffusion properties of the inhibitor. The DME inhibitor diffusion coefficient was about 60% greater than the diffusion coefficient of compound KCR.

In the papers (Eydelnant *et al.* 1995; Flis, Zakroczymski 1996) it was found that the diffusion coefficient of the current market inhibitor, tested in two types of concrete covers containing chloride ions, was $D = 1.78\times10^{-12}$ cm^2/s and $D = 1.45\times10^{-12}$ cm^2/s. Very active Cl^- ions in the same conditions were characterized by a diffusion coefficient of $D = 1.27\times10^{-8}$ cm^2/s. The obtained values of KCR and DME inhibitor diffusion coefficients, in comparison with the flow rate of chlorides, show very good diffusion properties, 5 rows better than industrially produced inhibitors currently offered on the market.

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ORGANINIŲ MEDŽIAGŲ DIFUZIJA BETONE, STABDANTI ARMATŪROS KOROZIJĄ

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Santrauka. Straipsnyje pateikti eksperimentiniai difuzijos savybių rezultatai naudojant DME ir KCR inhibitorius. Atliekant bandymus buvo nustatytas inhibitorių koncentracijos pasiskirstymas betone ir patikimos difuzijos koeficiento vertės buvo apskaičiuotos sprendžiant atvirkštinį difuzijos lygties uždavinį. Inhibitoriai parodė labai geras difuzijos savybes, lyginant su kitų rinkoje esančių inhibitorių savybėmis. Inhibitoriai DME ir KCR turi savybę greitai ir giliai įsiskverbti į apsauginį betono sluoksnį.

Reikšminiai žodžiai: betonas, inhibitorius, korozija, difuzija, apsauga, armatūra, gelžbetonis.

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