IDENTIFICATION OF TRANSPORT PARAMETERS IN COUPLED WATER AND NITRATE TRANSPORT IN CEMENT MORTAR

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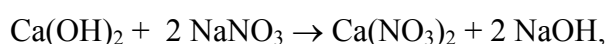Email: pavlikz@fsv.cvut.cz, cernyr@fsv.cvut.cz, rovnanikova.p@fce.vutbr.cz

Abstract

Coupled water and nitrate transport in dry cement mortar specimens is analyzed in the paper. In the experimental part, the $NaNO_3$ solution penetration into cement mortar is investigated and the moisture content and nitrate concentration profiles are measured in three chosen time intervals. Then an inverse analysis of the profiles is performed to identify the transport parameters. It is found that advection is the main mechanism of nitrate transport in the studied case. The diffusion in the solution is much slower so that it is not capable to replace the ions bound on the pore walls.
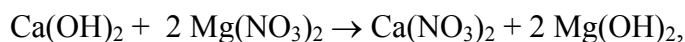
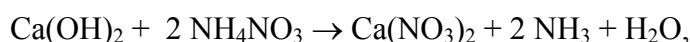**Key words:** water transport, nitrate transport, cement mortar

1 Introduction

The salts of nitric acid, nitrates, are well soluble in water. They convert calcium hydroxide that is formed during Portland cement hydration into well soluble calcium nitrate whereas soluble compound,

$$Ca(OH)_2 + 2\ NaNO_3 \rightarrow Ca(NO_3)_2 + 2\ NaOH,$$

or non-bonding,

$$Ca(OH)_2 + 2\ Mg(NO_3)_2 \rightarrow Ca(NO_3)_2 + 2\ Mg(OH)_2,$$

or gaseous products,

$$Ca(OH)_2 + 2\ NH_4NO_3 \rightarrow Ca(NO_3)_2 + 2\ NH_3 + H_2O,$$

are formed.

The presence of nitrates in concrete can affect negatively its mechanical properties. For instance, Bajza and Rouseková [1] reported formation of $Ca(NO_3)_2$ in cement paste after NH_4NO_3 solution action. They identified the phase of $C_3A \cdot Ca(NO_3)_2 \cdot 10H_2O$. With increasing concentration of NH_4NO_3 solution the content of portlandit has dramatically dropped, which causes the steel reinforced corrosion. At the same time the compressive and bending strength

significantly decreased. Therefore, the transport of nitrate ions in concrete can be considered as an important topic in concrete research.

In this paper, coupled water and nitrate transport into dry samples of cement mortar is analyzed and the water and salt transport parameters identified using an inverse analysis of water and nitrate concentration profiles.

2 Material and samples

In the experimental work, the samples of cement mortar were used. The composition of the mixture of cement mortar for one charge was the following: Portland cement – 450 g (three types of cement were applied for different sample groups, namely CEM I 42.5 R Lafarge, CEM I 52.5 R Lafarge and CEM I 42.5 R Prachovice), natural quartz sand with continuous granulometry I, II, III (the total screen residue on 1.6 mm 2%, on 1.0 mm 35%, on 0.50 mm 66%, on 0.16 mm 85%, on 0.08 mm 99.3% - according to the Czech standard ČSN 72 1208) - 1350 g, water – 225 g. The mixture was put into 40 x 40 x 160 mm moulds and compacted by ten impacts of the compactor. After one day the samples were unmoulded and stored in 100% relative humidity environment for 27 days. Then, the samples were dried, left for several weeks freely in the laboratory (relative humidity 45%, temperature between 20 and 22^{0}C) so that they achieved equilibrium moisture content, and finally all their lateral sides were water and vapor-proof insulated by an Epoxy varnish.

3 Experimental methods

The organization of the experiments was the same as in common water sorption experiments. The samples were exposed by their 40 x 40 mm face to the $NaNO_3$ solution with the concentration of 9.9944 g NO_3 in one liter of the solution. Duration of the experiment was 1 hour, 24 hours and 7 days for three different groups of samples. After this time, the samples were cut into 8 pieces and in each piece water content and nitrate concentration were measured.

Moisture content was determined by the gravimetric method using weighing the moist and dried specimens. In the determination of nitrate concentration, the particular samples were after drying first ground by a vibration mill so that grains smaller than 0.063 mm were obtained. Then 10 g of the ground sample was leached 30 minutes in 180 ml of 80^{0}C warm distilled water, a magnetic stirrer was used to speed up the leaching process. The content of nitrates in the leach was determined by the photometric method with sodium salycilate. Ten milliliters of a leach of the sample was put into a porcelain dish. The sodium hydroxide and sodium salycilate solutions were added to the leach. The leach was very carefully evaporated, and afterwards the solution of sulphuric acid was added. The sample was cooled down before sodium hydroxide solution was put to solution, and content of the dish was overflowed into the volumetric flask. Absorption of light by the yellow color solution was measured by photometer. The nitrate content was determined from the calibration curve.

4 Method of inverse analysis

In the computational inverse analysis of the coupled water and nitrate transport in cement mortar we assumed for simplicity just the diffusion mode of both water and nitrate transport without the cross effects. Therefore, the result of our analysis was the identification of

apparent water and nitrate transport parameters instead of the basic parameters of the coupled water and salt transport defined exactly in the sense of irreversible thermodynamics.

The main difference between the apparent parameters and the thermodynamically "pure" parameters of the coupled water and salt transport is that the apparent parameters do not express "pure" effects but combined effects. So, the apparent salt diffusion coefficients include not only the free salt diffusion in the porous space but also the effect of ion bonding on the pore walls and the effect of salt transport due to the water movement. The notion of apparent moisture diffusivity then means that it is related not to the water itself but to the salt-in-water solution, i.e. the whole liquid phase.

Under these simplifying assumptions, we have formally the same parabolic differential equations and the same boundary and initial conditions for both water transport and salt transport, namely

$$\frac{\partial C}{\partial t} = div\,(D(C)\,grad\,C) \tag{1}$$

$$C(0,t) = C_1 \tag{2}$$

$$C(\infty,t) = C_2 \tag{3}$$

$$C(x,0) = C_2. \tag{4}$$

where C is either water concentration in kg of water per kg of the dry porous body or salt concentration in kg of Cl⁻ per kg of the dry porous body, D is either the apparent moisture diffusivity or the apparent salt diffusion coefficient.

Therefore, the calculation of concentration-dependent diffusion coefficients from the measured salt concentration profiles can be done using basically the same inverse methods as those for the determination of moisture-dependent moisture diffusivity or temperature-dependent thermal conductivity.

In the solution of the inverse problem to the system of equations (1)-(4), we assume that the water or concentration field $C(x,t)$ is known from the experimental measurements as well as the initial and boundary conditions of the experiment. Solving an inverse problem means in this particular case the determination of the $D(C)$ function using the above data.

On the basis of the previous experience with the solution of inverse problems of moisture diffusion and heat conduction (for a detailed analysis see [2]) we employed the double integration method (for moisture diffusion [3], for heat conduction [4]), which was in the previous work shown as the most reliable (see the error analysis in [5]).

5 Results and discussion

Figs. 1, 2 show the measured nitrate concentration profiles and moisture profiles for cement mortar with CEM I 52.5 Lafarge. The results obtained for the other two cements were very similar. There was one feature clearly remarkable on both Figures: the water transport appeared to be much faster than nitrate transport. As the measured concentration of nitrates included both free and bound ions, the slower apparent nitrate transport can be explained by immobilizing of the substantial part of the nitrate ions on the walls of the porous space. In other words, the amount of nitrates bound on the cement matrix was much higher than that remaining for the transport in the solution.
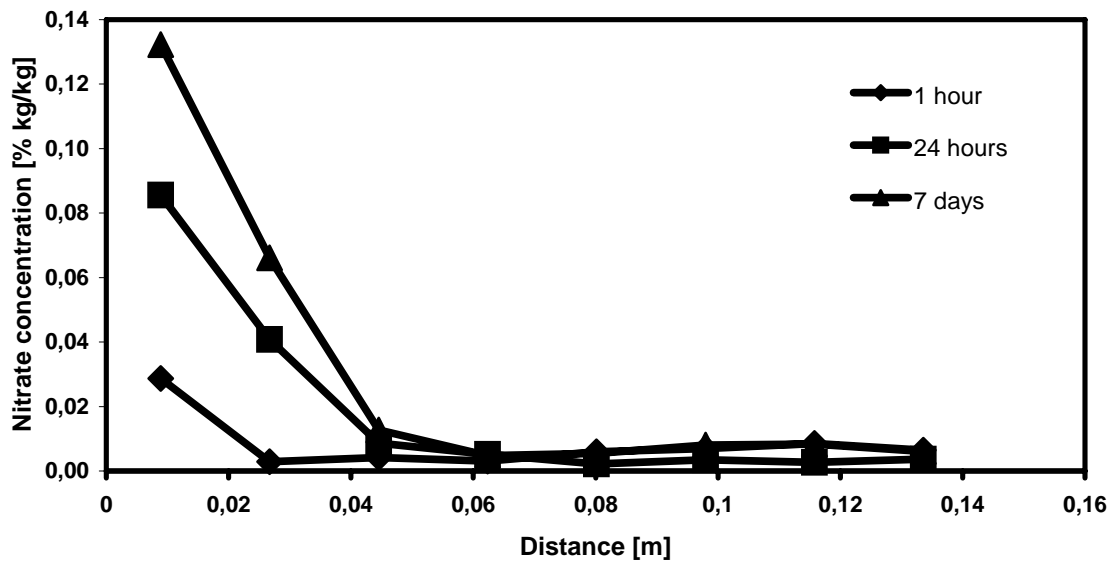
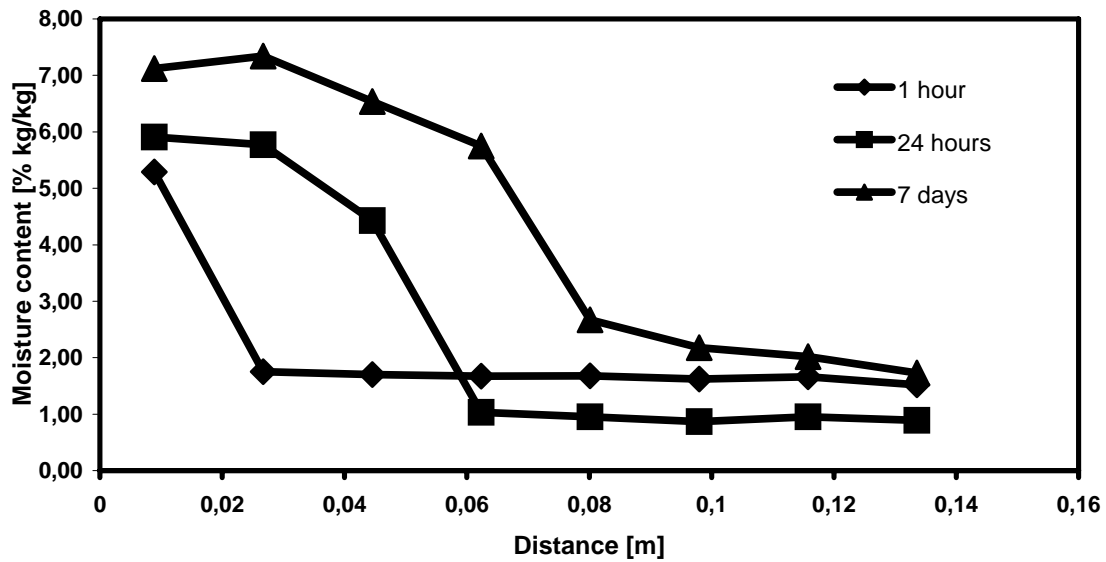Fig. 1 Nitrate concentration profiles - CEM I 52.5 R Lafarge

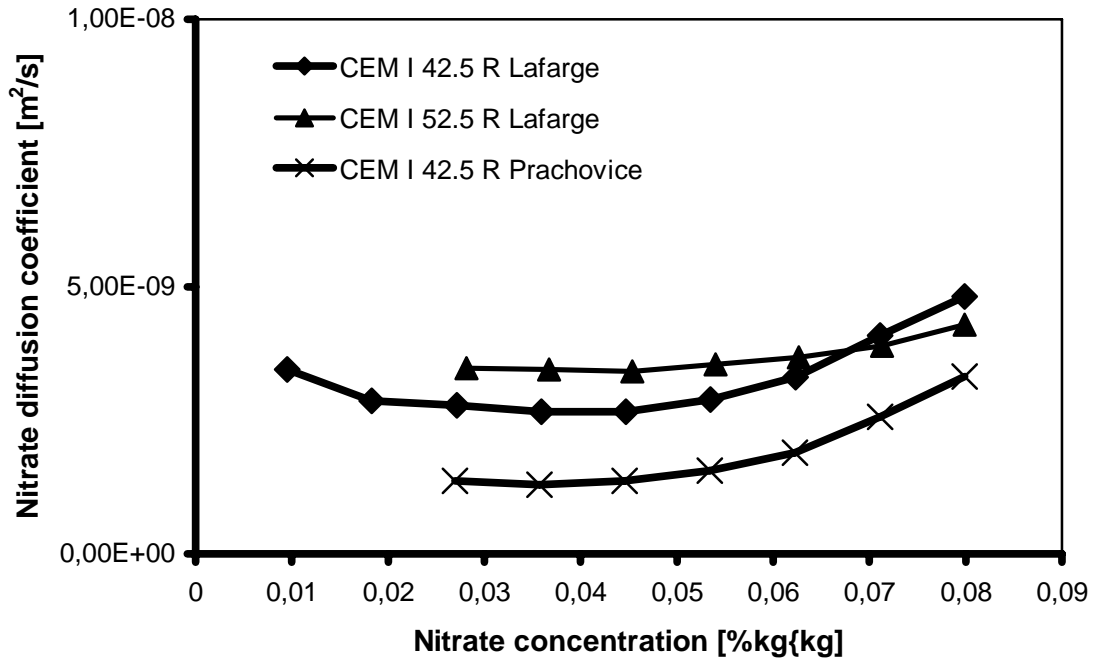Fig. 2 Moisture profiles - CEM I 52.5 R Lafarge
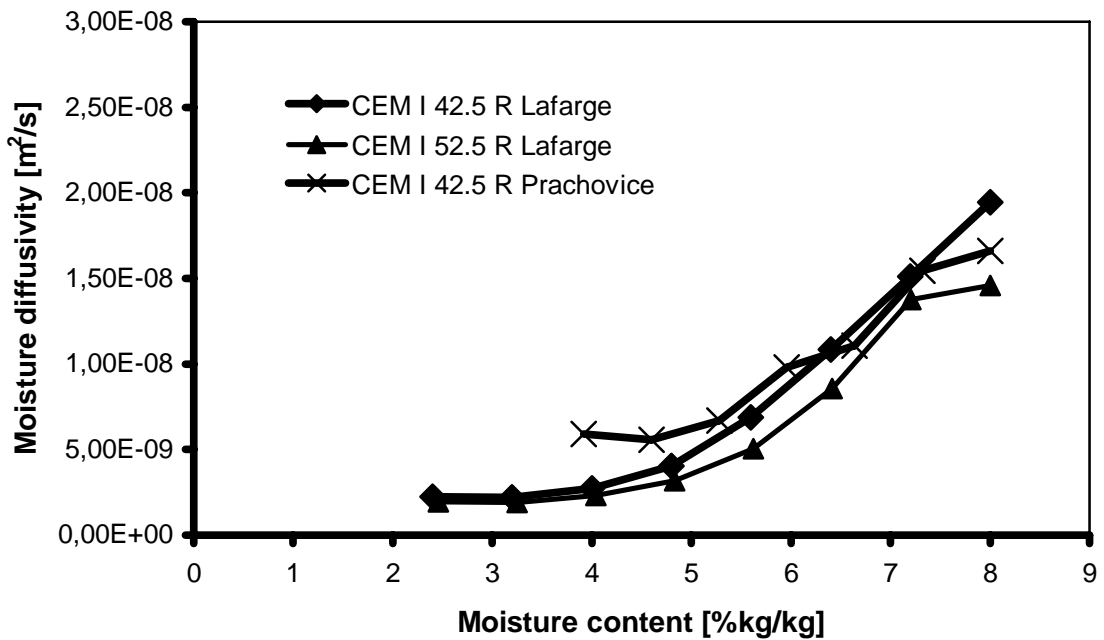
Fig. 3 Apparent nitrate diffusion coefficient

Fig. 4 Apparent moisture diffusivity

Figs. 3, 4 represent the apparent nitrate diffusion coefficients and the apparent moisture diffusivities calculated by the double integration method for all used cements. We can see that the differences in the investigated transport parameters were for the analyzed cement mortars not very high. The results also illustrate the differences in the velocity of the water transport

and nitrate transport in more detail than it could be done from the moisture and concentration profiles. We can see that while the dependence of moisture diffusivity on the moisture content was very remarkable and the differences between the highest and lowest values were about one order of magnitude, the nitrate diffusion coefficient exhibited only slight dependence on the concentration. This further documents the fast bonding of nitrate ions on the pore walls that could most easily occur at the places where the absolute amount of nitrate ions was highest, i.e. in the places with highest water content. The diffusion of the nitrates in the solution was apparently not capable to replace the bound ions fast enough although there was a large reservoir of the ions in the external solution. Therefore, we have a good reason to believe that the water transport was in this case clearly faster than the ion diffusion in the solution and the advection was the dominant mechanism of ion transport in the solution.

6 Conclusions

The investigation of coupled water and nitrate transport in cement mortar performed in this paper documented the significance of two main factors. The first was the fast bonding of nitrates on the pore walls. The second factor was that the amount of bonded ions could not be replaced in time by the diffusion in the solution, which gives evidence about the advection domination of the ion transport process. The inverse analysis of moisture and concentration profiles was performed in this paper in the apparent sense only. Therefore, the calculated coefficients included not only the effect of the main driving force but also some other effects. For a more precise and a more detailed analysis it would be necessary to measure the nitrate-bonding isotherm in order to separate the free ions and the bound ions. Also, the advection mechanism should be separated from the diffusion mechanism. These are two basic tasks that will be solved in the next step of the inverse analysis of moisture and concentration profiles.

Acknowledgement

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