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Moisture Diffusion in and Capillary Suction of Integral Water Repellent Cement based Materials

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Abstract

All properties of concrete depend on moisture content. Pre-dried concrete absorbs comparatively big amounts of water quickly by capillary action if the surface gets temporarily wet or is permanently in contact with liquid water. Capillary suction of water is an efficient mechanism for transport of dissolved salts such as sulphates, chlorides, and ammonium compounds into the porous structure of concrete. This ion migration is known to be at the origin of the most frequently observed deterioration of reinforced concrete structures in aggressive environment. It has been shown recently that capillary action can be practically suppressed by surface impregnation of concrete with liquid silanes. In practice and for some cases at least, it would be beneficial, if the entire volume of a structural element could be water repellent and not only the areas close to the surface. This goal can be reached, in principle at least, by adding silane emulsion to the fresh mix of cement based materials. Materials produced in this way may be called integral water repellent concrete or mortar.

The contribution presents results obtained for the moisture diffusion coefficients of the first drying process as determined by inverse analysis on the basis of drying data. Capillary suction of control and integral water repellent concrete has been determined. As expected, capillary suction of integral water repellent concrete is significantly reduced as compared to similar control concrete, prepared without the water repellent agent. The protective effect of surface impregnation of concrete, however, is superior. Nevertheless, service life of concrete structures in aggressive environment can be extended substantially by using integral water repellent concrete instead of normal concrete.

Keywords: integral water repellent concrete, mortar, moisture diffusion, capillary suction.

1 Introduction

It is well-known that moisture plays a key role in nearly all deteriorating processes in concrete and reinforced concrete structures. The sorption isotherm clearly indicates that at low relative humidity (RH < 50 %) most of the water is adsorbed on the huge internal surface (S_i > 100 m^2/g) of the hydration products. Changes in moisture content in this humidity range leads to shrinkage or swelling due to a characteristic change of the surface energy [1, 2]. Hygral length changes are most frequently at the origin of crack formation. At higher relative humidity concrete absorbs water by capillary condensation. Capillary condensed water is chemically reactive and is part of the pore solution. The interaction of the pore solution with the solid skeleton of the hydration products leads to disjoining pressures in the nano pores and hence to additional hygral length changes [1, 2]. A series of deteriorating processes can take place while the pore solution interacts with the solid skeleton formed by the hydration products such as hydrolyzis, alkali-silica reaction, and carbonation. Furthermore in case of high moisture content frost sensitivity becomes a serious risk. High moisture content leads also to high electric conductivity and as a consequence high rate of corrosion of steel reinforcement in carbonated or chloride contaminated concrete. The high thermal conductivity of humid concrete can cause serious damage in dwelling-houses in particular.

After removal of the formwork, the concrete surface is in many cases exposed to an environment with an average relative humidity below 90 % in general. If the water-cement ratio of concrete is higher than 0.5, a long lasting drying process of the porous material will begin. Pre-dried concrete will absorb aqueous salt solutions by capillary suction as soon as the surface gets in contact with them. This mass flow is the most frequent and most efficient mechanism of transportation of dissolved ions such as sulphates and chlorides into the pore space of cement based materials. Surface impregnation with liquid silanes has proved to be an efficient protective measure to suppress, or to at least reduce significantly, capillary suction of concrete [3-6].

In the meantime recommendations on design and application of water repellent agents on surfaces of concrete structures have been published in several countries (see for example [7, 8]). Experience and experimental results have shown that surface impregnation can be considered to be a reliable and durable chloride barrier only if a penetration depth of at least six to ten mm has been reached. Only in this case, the impregnation may be called deep impregnation.

For some applications it may be advantageous to add a silane emulsion to the fresh concrete mix instead of impregnating the surface. The aim of this technology is to produce a cement based material that is water repellent throughout its volume and not only in areas close to the surface which is the case of surface impregnation of concrete. This type of building material can be called integral water repellent cement based material. The use of a silane-based admixture can be of particular interest for the production of structural elements with a high surface to volume ratio. As the penetration depth of silanes in case of a surface impregnation is limited, integral water repellent concrete should be less sensitive to damage by crack formation or abrasion for instance. Another potential application of an integral water repellent cement based material is the production of protective rendering.

The paper reports on the results obtained from drying of integral water repellent mortar in three environments with different relative humidity. From the drying data, moisture diffusion coefficients can be determined by inverse analysis. The objective was to find out if capillary suction of integral water repellent concrete is low enough to protect concrete structures from ingress of aggressive compounds.

2 Theoretical background

It has been shown by many authors that the drying process of concrete can be adequately described by means of Fick's second law [9]. If we consider one-dimensional transport only, the differential equation can be written as follows:

$$dW/dt = d/dx[D(w)\ dW/dx] \qquad (1)$$

where: W stands for the water content, t is drying time, x represents the distance from the drying surface and D(w) is the moisture dependent hygral diffusion coefficient. For convenience W is sometimes replaced by the moisture potential h (h = RH/100). In the case of a drying experiment W can be related to h by the desorption branch of the sorption isotherm. To simulate the drying process realistically it is necessary to take the film coefficient H_F into consideration [9]. The film coefficient is defined as follows:

$$H_F = q_s/(h_s-h_a) \qquad (2)$$

where: q_s is the moisture flux normal to the exposed surface, H_F is the coefficient of surface hygral transfer, usually called film coefficient, and h_s and h_a are the moisture potentials at the surface and in the surrounding atmosphere respectively. The film coefficient depends essentially on the roughness of the surface and the wind speed close to the surface.

Diffusion coefficient D(w) is strongly dependent on the water content. At high water content, mass transport is governed by liquid water movement. This is a most efficient transport mechanism and as a consequence D can be expected to be high when h, the moisture potential, is close to one. Under these conditions the water mass in the porous material forms a continuous body. Liquid water is transported by capillary action to the drying surface. As the moisture content decreases the remaining water is trapped in ever finer capillaries. Then the mass transport becomes more complex and less efficient. Liquid water in the capillaries evaporates and mass transfer to the surface is essentially due to vapour diffusion. In addition surface diffusion contributes to mass transfer at low humidity content. It may be expected that the diffusion coefficient decreases with decreasing moisture potential. It is difficult, however, to describe the different and overlapping mechanisms in detail [10]. Therefore usually an empirical expression is used to describe the influence of moisture potential (or water content W) on the diffusion coefficient. The following equation will be used:

$$D(h) = a_1 + a_2[\exp(a_3 h) - 1] \tag{3}$$

where: a_1, a_2, and a_3 are parameters, which have to be determined by inverse analysis [11, 12]. For the numerical solution of this problem the Forward Time Centre Space (FTCS) method is utilized [13].

3 Materials and experimental procedure

3.1 Preparation and curing of mortar specimens

Two different types of mortar were prepared, one plain cement based mortar and an identical mix but with a silane emulsion added. For both mixes ordinary Portland cement 42.5R and local river sand from the Qingdao area with a maximum diameter of 5 mm were used. To improve workability a super-plasticizer of the naphthalene type was added at a concentration of 3.5 M% related to the mass of cement. This plain mortar will be referred to as M0.

In order to obtain a water repellent mortar, 2 M% of a silane emulsion, (Protectosil®, MH 50, an alkylalkoxsilane diluted to 50 %) related to the mass of cement, was added to the second mix, and is henceforward referred to M2. The exact composition of the two mortars is given in Table 1.

With each mortar mix standard prisms of 40 x 40 x 160 mm^3 were cast in steel moulds. All specimens were demoulded after one day curing under a wet cloth in a laboratory environment. Then they were stored in a curing room with controlled climate (T = 20 ± 3 °C and RH > 95 %) for seven days. At this time, the finished and the bottom surfaces of all prisms as well as their small square surfaces (40 x 40 mm^2) were sealed with wax. In this way unidirectional drying was imposed when the specimens were placed in a drying environment.

Table 1: Mix composition of the two types of mortar M0 and M2

Group	Cement	Water	Sand	Fly ash	SP	Silane emulsion	W/B	W/C
M0	637	494	510	773	3.5 %	-	0.35	0.77
M2	637	494	510	773	3.5 %	2.0 %	0.35	0.77

3.2 Test procedures

3.2.1 First drying

All specimens were subdivided into three groups. Each group was placed in a climate box where the relative humidity was kept constant by means of saturated salt solutions. The following three salt solutions were selected: sodium chloride for 76 % RH, sodium bromide for 60 % RH, and potassium carbonate for 47 % RH. The temperature was kept constant at 20 ± 2 °C. The weight change of all drying specimens was followed by means of a balance with an accuracy of ± 0.01 g until the weight had reached approximately hygral equilibrium.

When the specimens at 76 % RH had reached equilibrium with this relative humidity, they will be placed in the box at 60 % RH, while those, which had reached equilibrium with 60 % RH, will be placed in the box at 47 % RH. And those stored at 47 % RH, once they had reached equilibrium, will finally be dried at 105 °C to determine the total evaporable water content.

Specimens placed originally at 76 % RH are identified as M0-76 or M2-76, and those placed initially at a different RH are similarly labelled.

3.2.2 Capillary suction

After the specimens had reached hygral equilibrium with a relative humidity of 76 %, 60 % and 47 % respectively, capillary suction was determined by means of the Karsten's tube (see RILEM recommendation). Capillary suction is considered to be a reliable measure for characterizing durability of cement based materials in marine environment [14]. The experimental set-up is shown in Fig. 1. Water is filled in a calibrated glass pipette. The surface of contact with water is 700 mm^2. The hydraulic pressure is neglected in this case as it is small compared to the capillary action. The absorbed water has been determined as function of time up to 240 minutes of suction time.

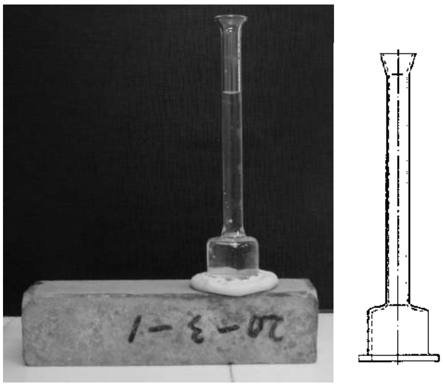

Figure 1: Karsten's tube test for the determination of water absorption.

3.2.3 Re-saturation and second drying

After hygral equilibrium had been reached with the first drying process and the capillary suction had been measured, some of the specimens were totally immersed in water for ten days for re-saturation. The amount of water absorbed during re-saturation was measured. After re-saturation a second drying process was started. Specimens were placed back into the climate boxes subdivided into three groups as described above (a RH of 76 %, 60 %, and 47 %). Detailed evaluation of the second dying process will be presented in a subsequent publication.

4 Results and discussion

4.1 Drying and hygral diffusion coefficient

The water loss during drying in different climatic environments was measured and the results are shown in Fig. 2. Obviously the specimens placed initially in the box with 76 % RH, i.e., M0-76 or M2-76, lose less water than the specimens placed initially in drier environments.

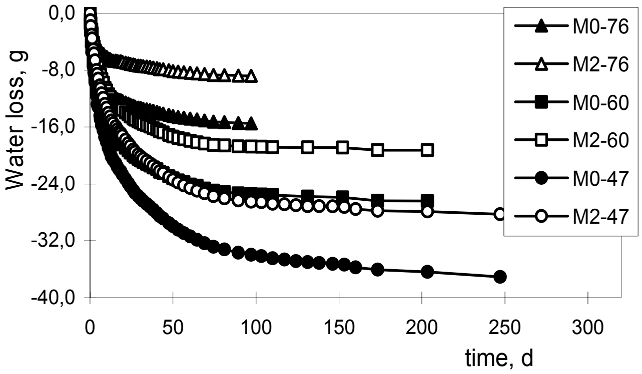

Figure 2: Time-dependent water loss of mortar specimens during the first drying period at 76 %, 60 % and 47 % RH. Full symbols represent data from the control mortars, while outlined ones correspond to the integral water repellent mortar.

On the basis of the drying data measured at 47 % RH shown in Fig. 2 the diffusion coefficient has been determined by means of inverse analysis according to the method developed by B. Villmann et al. [12]. Results are shown in Fig. 3. It can be seen that the diffusion coefficients of the first drying process of the control (M0) and integral water repellent (M2) mortars are the same within the range of accuracy of the experiment. From this result it may be concluded that the first drying process is not really influenced by the addition of silane emulsion. As expected the diffusion coefficient is high and decreases quickly with decreasing moisture potential. At values of $h < 0.5$ the diffusion becomes really very slow.

In order to check the validity of the diffusion coefficients shown in Fig. 3 the water loss in different environments was calculated and compared with the experimental results from Fig. 2. Results are presented in Figures 4 and 5. In Fig. 4 the water loss as function of drying time as obtained on control mortar samples placed in at 76 %, 60 %, and 47 % RH is shown. The experimental data are plotted with symbols, while the calculated water loss is shown by a continuous line. For obvious reasons, the agreement between the calculated and the experimentally determined drying functions is best for drying at 47 % RH. But the prediction of water loss in an environment of 60 % and 76 % RH with the obtained diffusion coefficient is still reasonable when compared with experimental values. In Figure 5 the corresponding results obtained with integral water repellent mortar samples are shown. In this case the agreement between calculated and measured functions is even better. We can conclude that with the diffusion coefficient determined by inverse analysis we can predict water loss in different environment reasonably well.

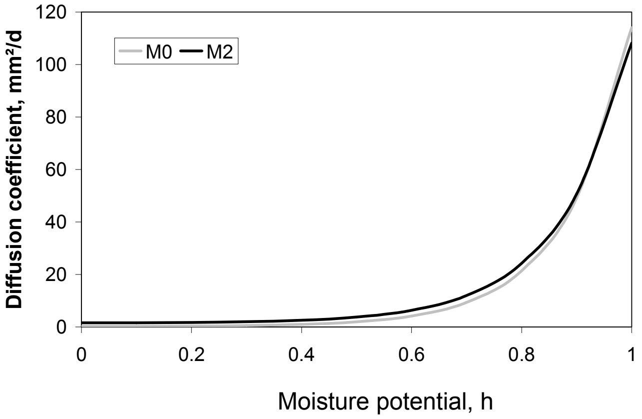

Figure 3: Diffusion coefficient of plain (M0) and integral water repellent (M2) mortar as function of moisture potential.

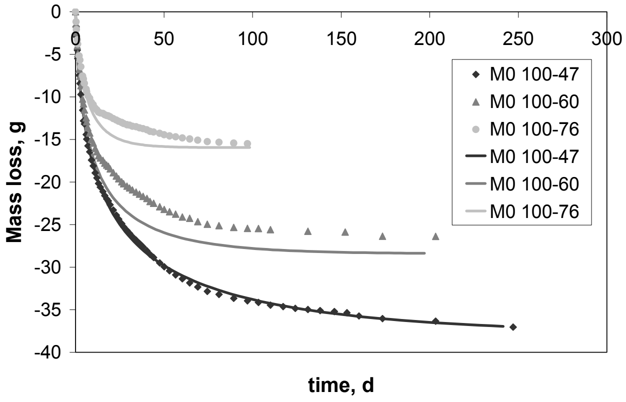

Figure 4: Calculated and measured mass loss during the first drying process of plain mortar in environments with 76 %, 60 % and 47 % RH, respectively.

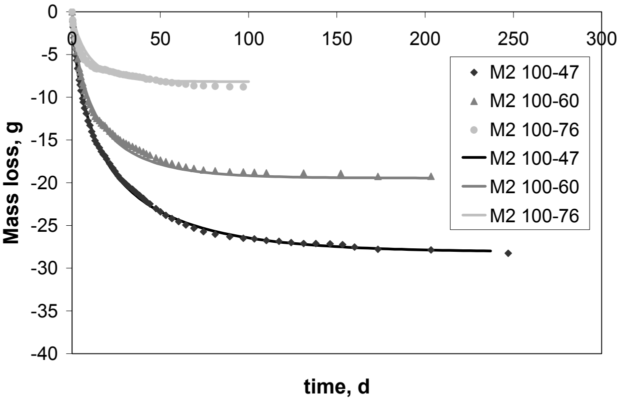

Figure 5: Calculated and measured mass loss during the first drying process of integral water repellent mortar in environments with 76 %, 60 % and 47 % RH, respectively.

After hygral equilibrium had been reached by the first drying, some of the specimens were re-saturated by immersion in water for ten days as mentioned above. The amount of water absorbed by the differently pre-conditioned samples is shown in Fig. 6. The influence of addition of silane emulsion on water absorption is comparatively small for specimens, which have been pre-dried in an environment of 76 % RH. The difference becomes more important, however, if the specimens have been pre-dried down to lower RH. This is a clear indication that addition of silane emulsion needs pre-drying to become really effective. It seems that drying has to be continued until a RH of at least 70 % before the outer layers of the materials become water repellent.

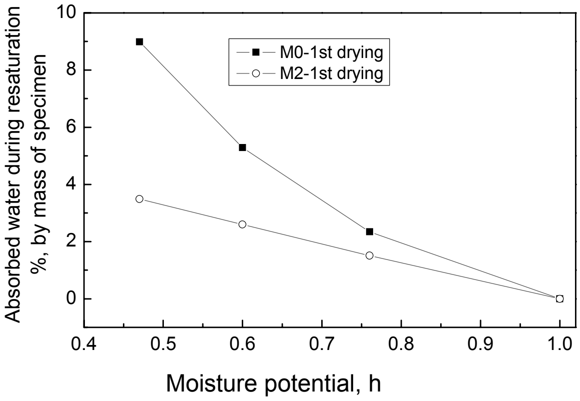

Figure 6: Amount of absorbed water during re-saturation after first drying as function of the moisture potential h.

Recently it has been shown that during the drying process most of the silane is transported with the water flow to the surface [15]. That means that in fact polymerized silanes are concentrated in the surface near zone, a situation that is similar to that resulting from surface impregnation. Therefore, there is a potential for optimizing silane emulsions to avoid internal migration.

4.2 Coefficient of capillary suction

Capillary suction of the samples after drying at 76 %, 60 %,and 47 % RH were determined experimentally. The samples were in hygral equilibrium with the corresponding RH and had an equilibrium water content of 12.1%, 10.5 % and 8.2 % respectively. Results are shown in Fig. 7. From this figure it is obvious that the data, discarding initial values, can be represented reasonably by means of the well-known equation:

$$\Delta W(t) = A\, t^{1/2} \qquad (4)$$

$\Delta W(t)$ is the amount of water absorbed per unit of the surface (g/m^2) by capillary action as function of time t (h) and A is the coefficient of capillary suction (g/m^2 h$^{1/2}$). The coefficient of capillary suction A in eq. (4) has the following physical meaning:

$$A = \Psi\rho[r_{eff}\,\sigma\,\cos\Theta/\,2\eta]^{1/2} \qquad (5)$$

where: Ψ stands for the water capacity (m^3/m^3), ρ is the density of the liquid (kg/m3), r_{eff} is an effective radius (m) characterizing the wide pore size distribution, σ the surface tension of the liquid (N/m2), Θ is the wetting angle and η the viscosity of the liquid (N s/m^2).

Based on the experimental results shown in Fig. 7 the coefficient of capillary suction A can be determined by data fitting with eq. (4). Results are compiled in Table 2. As expected the coefficient of capillary suction of the control mortar (M0) increases when the moisture content of the specimens decreases. In specimens with lower moisture content more pores participate in the process of capillary suction. The effective radius decreases slightly, as more fine pores are freed from absorbed water but at the same time the water capacity Ψ increases with the increase of empty volume in the pore space. The influence of temperature on A is essentially governed by the viscosity η of the liquid.

Table 2: Coefficients of capillary suction (A) for specimens in hygral equilibrium at different relative humidity and the % reduction of A resulting from the addition of the silane emulsion.

	M0-76	M2-76	M0-60	M2-60	M0-47	M2-47
Mass of water absorbed after 4 hours (g/m^2)	789	316	1944	395	4500	789
Coefficient of capillary suction A ($g/m^2h^{0.5}$)	390.7	178.8	915.8	204.3	2150.6	439.7
Reduction of A by addition of silane emulsion, %	**45.8**		**22.3**		**20.4**	

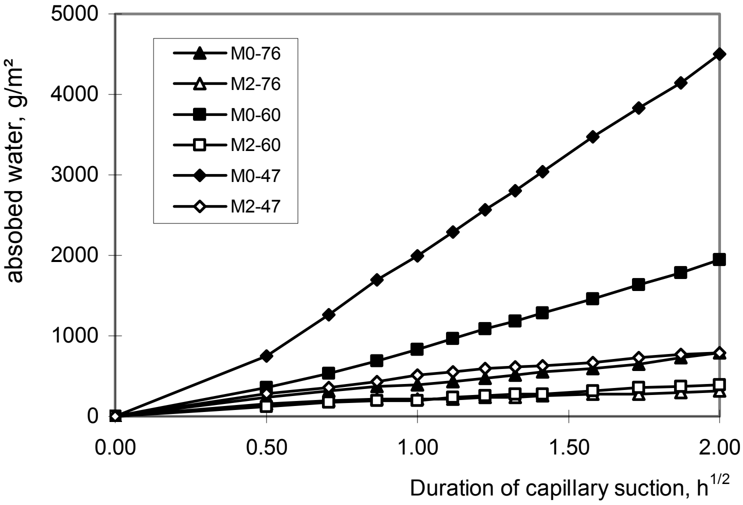

Figure 7: Capillary absorbed water, as determined by means of the Karsten's tube as a function of the square root of time of control and integral water repellent mortar in hygral equilibrium at 76 % RH, 60 % RH, and 47 % RH. Results for the control and integral water repellent mortar are shown with full symbols and with outlined symbols, respectively.

The capillary suction of the mortar with silane emulsion added is noticeably reduced. The corresponding coefficients of capillary suction are also included in Table 3. In the fourth row of Table 3 the reduction of the coefficient of capillary suction by the addition of silane emulsion is shown. If the samples were initially equilibrated at 76 % RH, the coefficient of capillary suction is reduced to 45.8 %, while after equilibration at 47 % RH the coefficient is reduced to 20.4 %. This means that one fifth of water or a salt solution will be absorbed during equivalent time period. This is a clear indication that mortar or concrete mixed with silane emulsion have to be dried first before the material becomes water repellent. Mortars pre-mixed with silane emulsions should be allowed to dry at a RH lower than 70 % before exposed to aggressive environment. It should be stated at this point, however, that the coefficient of capillary suction can be lowered even more by surface impregnation with liquid silane [4-6].

Furthermore, from Fig. 7 it can be seen that capillary suction is somewhat delayed. When the dry surface is brought in contact with water it takes a few minutes before the surface is wetted and the necessary capillary under-pressure in the liquid in contact with the porous material is built up.

5 Conclusions

From the results of this ongoing project, some preliminary conclusions can be drawn:

- The hygral diffusion coefficients of the first drying of control mortar and mortar with silane emulsion added is the same within the accuracy of the measurements.
- Mortar or concrete with silane emulsion added to the fresh mix become water repellent only after drying. The RH of the drying environment must be lower than 70 %.
- The first dying is necessary for the emulsion to break and for the development of a siloxane network on the internal surface of hardened cement paste.
- Surface impregnation with liquid silanes is more efficient than addition of silane emulsion to reduce capillary suction and ingress of dissolved aggressive chemical compounds.

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