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Sorption Isotherms of Water Repellent Treated Concrete

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Abstract

The hygroscopic moisture fixation in water repellent treated concrete was investigated by means of a DVS 1000 Sorption Balance. Treated and untreated concrete samples were studied separately and the results are presented as sorption isotherms. These serve to study in detail the sorption processes. With the use of the Kelvin equation, the sorption isotherms can be recalculated to an equivalent pore radius. The paper presents the dependency of sorption isotherms of water repellent treated concrete on the humidity inside the concrete at the moment of treatment application. This methodology can also provide information regarding which part of the pore system is actually treated.

Some important conclusions can be drawn from the experiments. These are that moisture fixation is affected by a water repellent treatment; and, that this effect is most apparent at high moisture levels. There is, however, still a certain amount of moisture present in a concrete treated with a water repellent agent. From calculations based on the obtained data it can be concluded that the silane molecule can enter pores with almost the same diameter as the molecule itself if the pore is not filled with water.

Keywords: sorption isotherms, moisture fixation, water repellent treatment, silanes

1 Introduction

Moisture plays a role in almost all damage mechanisms in concrete. Water repellent agents currently used on concrete to prolong the service life of structures primarily consist of alkylalkoxysilanes. This objective is accomplished by reducing the moisture content inside the concrete thus protecting the reinforcement bars from chloride attack. When concrete is treated with a water repellent agent the basic conditions for transport and moisture fixation in the surface layer of pores change. As a consequence, the rate of carbonation and chloride ingress are changed as well.

Several investigations in a laboratory environment, e.g., [1], as well as in the field, e.g., [2], indicate that chloride ingress in concrete is decreased by a water repellent treatment. This is sometimes explained by suppressed capillary action, e.g., [3], and the absence of a continuous water film in the treated layer [4]. Studies on the moisture transport in the treated surface layer also support this theory, based on measurements of the moisture transport with the so called cup-method [5], from drying data [6] or from capillary water uptake measurements (see, e.g., [7]).

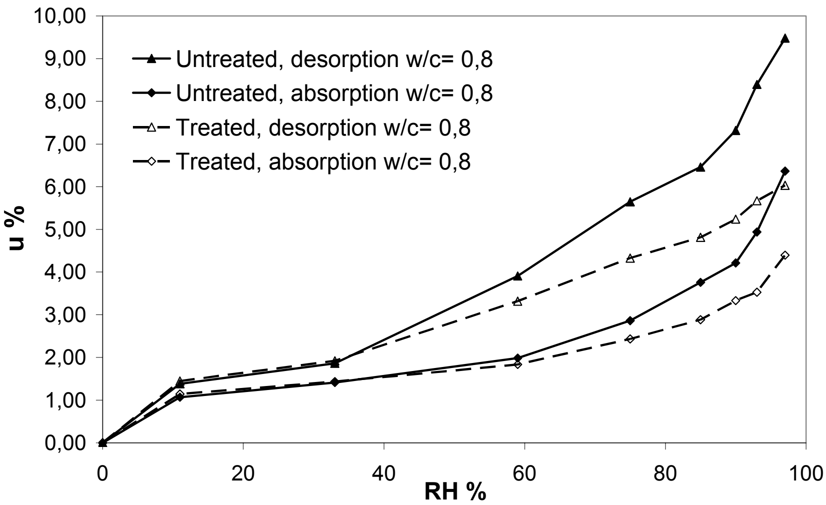

Figure 1: Sorption isotherms of the concrete with w/c = 0.8, untreated and treated with a water repellent [8]. (u = moisture mass divided by dry concrete mass). Samples were conditioned for one month in 70 % RH prior to the water repellent treatment.

In an experiment presented in [8] the sorption isotherms of water repellent treated concrete was studied by means of climate boxes in which both RH (relative humidity) and temperature were kept constant. These samples were conditioned in an environment of 70 % RH a month before they were treated with the water repellent agent. The treatment affects the sorption isotherms, as shown in Figure 1, but the effect is more pronounced at high RH. However, it is not clear why the sorption isotherms are hardly affected at low humidity levels and whether it is a coincidence that the sorption isotherms of the treated samples show a deviation at approximately the same RH as the conditioning environment prior to the treatment (e.g., at 70 % RH in Figure 1).

2 Theory

Concrete is a porous and hydrophilic material and contains a certain amount of physically bound water depending on the surrounding environment. In the hygroscopic range, water can be bound in the pores through adsorption of water molecules on the pore surface or through surface tension effects causing capillary condensation. Adsorption dominates at low moisture levels (approximately up to 50 % RH) and capillary condensation at high (approximately above 50 % RH). The relation between the moisture content in the ambient air and the moisture content in the material represents the moisture storage capacity and is given by sorption isotherms. This relationship is different depending on whether equilibrium is reached by sorption (involving both adsorption and capillary condensation) or desorption.

Capillary-condensed water molecules condense on curved water menisci that are formed in small pores and other narrow spaces. The relationship between the relative humidity ϕ at which condensation takes place and the smallest and the largest curvature radii of the meniscus, r_1 and r_2 [m], is given by Kelvin's equation (Equation 1). The equation can be derived from the capillary rise in a vertical tube and the equivalent pressure difference over the same height, e.g., [8].

$$\ln(\phi) = -\frac{\sigma_w \cdot M_w}{R \cdot T \cdot \rho_w}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad (1)$$

where σ_w = surface tension of water [N/m]. With the assumption of a cylindrical pore model ($r_1 = r_2 = r$), where r is the radius of the pore, and the relation between the radius of the pore and the curvature radii of the meniscus r_m ($r = r_m \cos\theta$) we obtain the following expression for the case of a meniscus formed in a specific pore radius as a function of the RH in the surrounding air:

$$r = -\frac{2 \cdot \sigma_w \cdot \cos\theta \cdot M_w}{\ln\phi \cdot R \cdot T \cdot \rho_w} \quad (2)$$

where: r = radius of the pore [m]
σ_w = surface tension of water [N/m]
θ = contact angle between water and concrete
M_w= molecular weight of water [kg/mol]
ϕ = relative humidity
R = molar gas constant [J/mol K]
T = temperature [K]
ρ_w= density of water [kg/m^3]

The radius of the meniscus is in this case the same as that of the pore. This is only true if the contact angle between concrete and water is $\theta = 0$, which is the usual simplification.

3 Method

3.1 Preparation of samples

Two types of concrete with w/c = 0.80 and 0.45, respectively, were used in this experiment with compositions according to Table 1. The maximum size of the aggregate was set to 8 mm. Both concretes were cast from a CEM I 42.5 BV, LA, SR (Swedish cement for civil engineering structures) according to SS-EN 197-1 [9] and conditioned for three months in 100 % RH and 20°C. At this time, 75 mm cores were drilled and cut into 30 mm thick slices. The first and last slices from each core were not used in the experiment in order to avoid boundary effects. The perimeter of the slice was sealed before they were placed inside climate boxes, leaving only the up- and downside open to ensure a uni-dimensional flow when the samples were treated with the water repellent agent.

Table 1: The concrete mixtures used in the experiments.

w/c	Cement (kg/m^3)	Aggregate 0-8 mm (kg/m^3)	Water (kg/m^3)	Plasticizer (kg/m^3)
0.45	500	1575	225	2.0 (Glenium)
0.80	350	1609	280	-

The samples were conditioned for six months at a different RH. The different humidity levels in the climate boxes were obtained using saturated salt solutions (Table 2) and small rotators.

Table 2: Saturated aqueous salt solutions used to obtain a defined RH at 20ºC. (RH values according to [10].

NaBr	NaCl	K_2SO_4
59 %	75 %	97 %

The conditioned samples were then treated with liquid isooctyltriethoxysilane by capillary absorption on one side for 10 hours.

Four months later, the samples were broken apart and pieces of approximately 40 mg were taken from the region where the water repellent effect was clearly visible. One piece from each plate was used in the experiment. The amount of adsorbed water was related to the amount of cement gel in the piece and expressed as the ratio of the mass of moisture to that of cement. The mass of cement in each piece was calculated based on analysis of the Ca-content with ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy).

Pieces with a large proportion of aggregate were avoided, as well as those with parts of the treated edge. The former, in order to ensure a large amount of cement; and, the latter, in order to avoid boundary effects.

3.2 Equipment

The equipment used in the experiment was a sorption microbalance. It uses two streams of nitrogen gas, one passes through a vapour humidifier to be saturated while the second is kept dry. A mixture of these two streams can then be used to create, in principle, any desired humidity between 0 and 100 % RH. Figure 2 shows a schematic picture of the sorption balance.

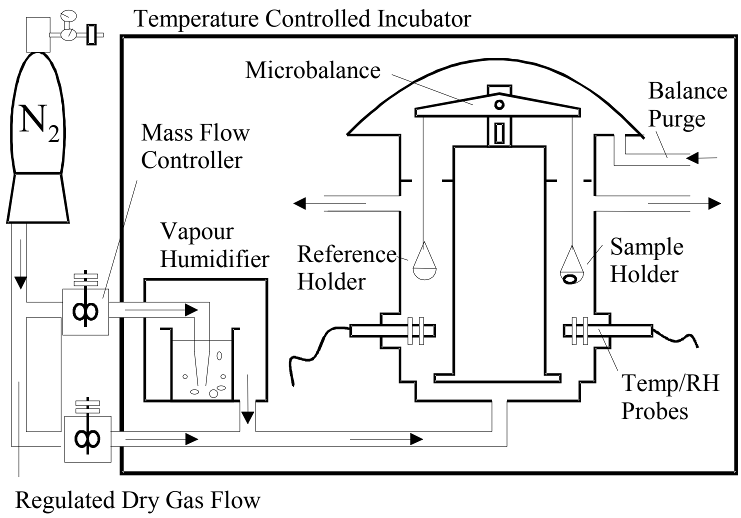

Figure 2: Schematic picture of the DVS 1000 (Dynamic Vapour Sorption instrument) used in the experiments [11]. A mixture of dry nitrogen and nitrogen saturated with moisture makes it possible to regulate the humidity passing through the sample.

The sorption balance registers the change of weight continuously and when the sample has reached an equilibrium weight, defined as a criterion on the gradient of the curve or as a time limit, then it changes to the next humidity level. In the present experiment the steps were interrupted when dm/dt < 0.0002 (percent change in mass per minute) or by a time limit if not reached within 24 hours. The steps as well as the results from one sample can be seen in Figure 3. The endpoint of each step is then used for the presentation of the results.

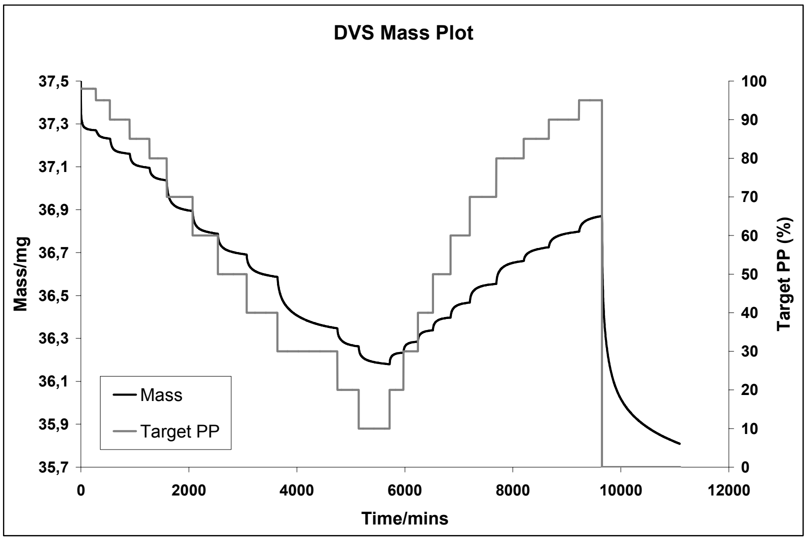

Figure 3: Example of a resulting plot from the sorption balance. Target PP is the RH of the nitrogen gas that streams through the sample.

4 Results

The samples conditioned at 97 % RH prior to the treatment resulted in penetration depths reaching only up to 2 mm. Therefore no specimens were taken from the concrete with w/c = 0.45 conditioned at 97 % RH. The results obtained for w/c =0.80 concrete should be regarded sceptically due to boundary effects. Table 3 shows the penetration depth on the plates used in the experiment.

Table 3: Impregnation depth of water repellent treatments applied on concrete plates conditioned at a different RH. (*Excluded from the analysis)

w/c	97 % RH	75 % RH	59 % RH
0.45	1 [mm] *	3 [mm]	5 [mm]
0.80	2 [mm]	12 [mm]	18 [mm]

Figure 4 shows the sorption isotherms for the w/c = 0.80 concrete. It can be seen that the sorption isotherm of the untreated sample has the familiar exponential shape while this shape is less pronounced for the water repellent treated sample. The isotherms of the treated samples deviate at around 50-60 % RH resulting in a nearly linear sorption, similar to the one previously obtained (see Fig. 1). However, comparison between the treated samples themselves is difficult with this representation.

The desorption isotherms are not presented because several desorption steps were interrupted due to the 24 hour time limit for each step and it is not certain that all samples reached their weight equilibrium. The problem with the last desorption step (from 95 to 0 % RH) can clearly be seen in Figure 3. This is also reflected in the different starting points of the sorption isotherms in Figure 4. For this reason the first sorption step reported corresponds to that at 20 % RH.

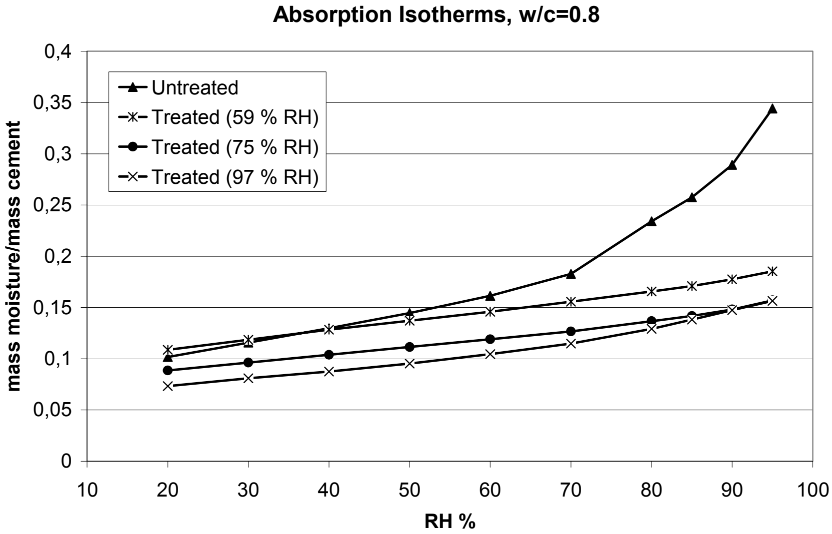

Figure 4: Sorption isotherms of the concrete with w/c = 0.80, untreated and treated with a water repellent. The latter was applied on samples conditioned at a different RH.

In Figures 5 and Figure 6 the same results from the experiments are shown with an adjustment. This is based on the fact that concrete has a huge variation in material properties making it difficult to compare small samples as used in this experiment (approximately 40 mg). In previous studies [8] this problem was avoided by crushing and mixing the concrete before it was divided into almost 200 small crucibles ensuring a similar average composition for each one. In the present analysis the sorption isotherms were adjusted to the untreated reference so that the gradient is the same between 20-30 % RH. This adjustment results in a shape similar to that shown in Figure 1.

The size of a silane molecule is in the region of 10 Å (1 nm) according to [4]. The authors of [12] refer to a more specific diameter of 2.4 nm and an even bigger interaction radius. Therefore the silane molecule cannot enter a pore with a smaller diameter than its size or interaction radius.

From Equation 2, at 50 % RH a water meniscus will form in a pore with 3 nm radius. Consequently, sorption isotherms should not be affected by the water repellent treatment below this RH, a conclusion also reached by previous studies [8]. This is clearly seen in Figures 5 and 6, justifying the adjustment carried out.

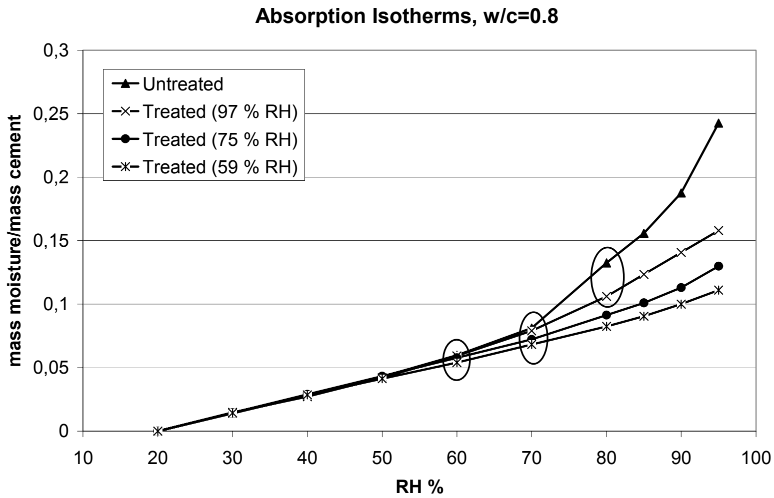

Figure 5: Sorption isotherms of the concrete with w/c = 0.80, untreated and treated with a water repellent, after the adjustments. The rings show where the isotherms separate.

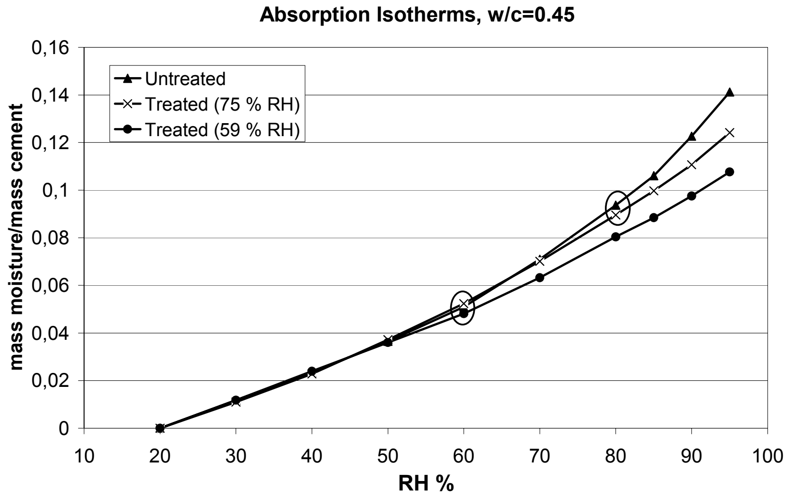

Figure 6: Sorption isotherms of the concrete with w/c = 0.45, untreated and treated with a water repellent, after the adjustments. The rings show where the isotherms separate.

Figures 5 and 6 show that when a water repellent agent is applied to concrete conditioned at different relative humidity, the resulting sorption isotherms deviate negatively (they absorb less moisture) from those of the untreated sample. Furthermore, the deviation starts to occur at about the same RH range at which the concrete had been conditioned when the treatment was applied (marked with rings in Fig. 5 and 6). The one exception corresponds to the w/c=0.80 concrete conditioned at 97 % RH, where the deviation starts at around 80 % RH and that can be attributed to boundary effects as already mentioned. Finally, the higher the moisture content at the time of the treatment the smaller the deviation. This indicates that the silane cannot enter pores that are filled with water.

5 Conclusions

This experiment was performed on a sorption balance on concrete treated with isooctyltriethoxysilane in order to determine the influence of RH at the time the water repellent was applied on the final sorption properties of the treated concrete. It is to be considered a pilot study. Future experiments will try to avoid the problems encountered in this study. Nonetheless, the following conclusions could be drawn:

- The sorption balance is a time efficient equipment as compared to climate boxes with saturated salt solutions inside, when just a few samples are analysed. A problem with the method, however, is the maximum possible size of the samples (approximately 40 mg) which is significantly smaller than the aggregate of the concrete. This causes unavoidable differences between individual samples as can be seen when comparing Figure 4 with Figure 5.

- The moisture content inside the concrete at the time of the water repellent treatment affects the outcome of the treatment. It is well known that penetration depth is affected (see, e.g., [13]) but the sorption isotherms show that it can also affect which pores will be treated.
- The silane molecule cannot enter pores that are filled with water.
- The amount of sorbed moisture is reduced by a water repellent treatment and the effect is clearest at high moisture levels. This corresponds well with how the moisture transport is affected at different humidity levels [5, 6]. However, a certain amount of moisture will also be present in a concrete treated with a water repellent agent. The concrete will not be dry in the treated layer.

Acknowledgments

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