Impregnation of Concrete Structures – Transportation and Fixation of Moisture in Water Repellent Treated Concrete

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TRITA-BKN. Bulletin 84, 2006
ISSN 1103-4270
ISRN KTH/BKN/B--84--SE

Licentitate Thesis

PREFACE

The research presented in this thesis was carried out at the Swedish Cement and Concrete Research Institute (CBI) and at the School of Architecture and the Built Environment at the Royal Institute of Technology (KTH), at the Division of Structural Design and Bridges.

The financial support for this research came from the Swedish Research Council for Environment, Agriculture Sciences and Spatial Planning (FORMAS) and the Members´ Association of CBI and they are gratefully acknowledged.

I thank my supervisors Professor *Johan Silfwerbrand*, Dr *Mårten Janz* and Phil. Lic. *Jan Trägårdh* for all the support during this work. Extra thanks to *Johan* for always taking his time to comment my papers.

A special thank to Professor *Andreas Gerdes* at the Forschungszentrum Karlsruhe for the valuable discussions during my visit there in the autumn 2005.

I would also like to thank Lund Institute of Technology for the allowance to use their equipment in the experimental setup used in Paper II.

Finally, thanks to all who have contributed to this work, especially my colleagues at CBI.

Stockholm in September 2006

Anders Johansson

ABSTRACT

Water repellent agents, today mainly consisting of alkylalkoxysilanes, are often used on concrete to prolong the service life of the structure. This is accomplished by protecting the reinforcement bars from chlorides or by changing the moisture content inside. When the concrete is treated with a water repellent agent the properties of the surface layer turn from hydrophilic to hydrophobic and thereby water droplets are stopped from entering, still allowing water vapour to pass through. This property change can reduce chloride ingression and stop heavy rain from penetrating through the surface layer.

This thesis presents results concerning how the moisture transport and fixation in the surface layer of the concrete is affected by a water repellent treatment. It also presents an investigation in which the effective penetration depth and the factors that influence it are studied. The methods used covers uni-dimensional transport of moisture using the so called cup method, measurements on moisture fixation using climate boxes with saturated salt solutions, penetration depth by cracking samples and spraying water on them, and field tests in a harsh tunnel environment.

The moisture diffusion coefficient for a water repellent treated concrete is close to constant and not nearly as dependent on the relative humidity (RH) as for untreated concrete. Unlike untreated concrete, where capillary suction plays an important role for the moisture transport at high RH, the vapour transport is the dominant transport mechanism even at high RH for water repellent treated concrete.

The moisture fixation is affected by a water repellent treatment and the effect is clearest at high moisture levels. There is, however, a certain amount of moisture present in a concrete treated with a water repellent agent. It can also be seen that the main reason for this is that the capillary porosity is affected by the treatment to a relatively high degree while the gel porosity to a large extent remains unaffected.

The three most important factors for the penetration of any water repellent agent into concrete is time, porosity and degree of saturation. An empirical equation is derived that gives an idea on how much these factors affect the efficient penetration depth of the water repellent agent.

Measures prolonging the service life of a concrete structure will lead to savings of natural resources and thus both economical and environmental savings for the community. The aim with the PhD-project is to develop explanation models to the promising results that have been obtained from the empirical research during the last decade and by doing this also create a better knowledge about when and how to apply a water repellent agent in order to benefit as much as possible from the product. The results presented in this Lisenciate thesis will be used as input in these models in the planned second phase of this project.

SAMMANFATTNING

Impregneringsmedlen, som i dagsläget till största del består av alkylalkoxysilaner, används ofta på betong för att förlänga livslängden på konstruktionen. Detta syfte uppnås genom att armeringen skyddas mot klorider eller att fukthalten inuti betongen sänks. När betongen impregneras ändras ytskiktets fuktmekaniska egenskaper från hydrofila till hydrofoba vilket gör att vattendroppar kan stoppas medan vattenånga tillåts passera. Dessa förändrade egenskaper kan medföra att kloridinträngningen minskar och att kraftiga regn inte tränger genom det impregnerade skiktet.

Denna licentiatavhandling presenterar resultat på hur fukttransport och fuktfixering i betongens ytskikt påverkas av en impregnering. Den presenterar också en undersökning på impregneringens inträngningsdjup och vilka faktorer som påverkar resultatet. För att studera fukttransport användes den så kallade koppmetoden med endimensionellt flöde. För att undersöka fuktfixering användes klimatboxar med mättade saltösningar och för att mäta inträngningsdjup fuktades spräckta provkroppar. Dessutom har kloridprofiler tagits fram på provkroppar exponerade i tösaltad miljö.

Till skillnad från obehandlad betong är transportkoefficienten för en impregnerad betong nästan oberoende av den relativa fuktigheten (RF) i omgivningen. Vid höga RF, där största delen av fukttransporten i obehandlad betong sker genom kapillärsugning, är ångtransporten fortfarande den dominerande transportmekanismen i impregnerad.

Fuktfixeringen i betong påverkas av en impregnering och effekten är störst vid höga RF. Det är dock tydligt att en viss mängd fukt finns inuti den impregnerade betongen. Detta kan förklaras med att största delen av kapillärporerna påverkas av impregneringen medan gelporerna förblir obehandlade.

De tre viktigaste faktorerna för alla impregneringsmedels inträngning i betong är tid, porositet och fuktnivå. En empirisk ekvation har tagits fram där det framgår hur dessa tre faktorer påverkar det slutliga inträngningsdjupet för impregneringen.

Åtgärder som förlänger en betongkonstruktions livslängd leder till ett bättre hushållande med naturresurser och därmed både ekonomiska och miljömässiga besparingar för samhället. Projektet syftar till att finna förklaringsmodeller till de lovande mätresultat som erhållits under det senaste decenniets forskning och användning och genom detta även skapa ny kunskap om när och hur ett impregneringsmedel bör användas för att nå bästa resultat. Resultaten som presenteras i denna licentiatavhandling kommer att användas som indata till dessa modeller i den planerade andra fasen av detta projekt.

LIST OF PAPERS

This thesis includes the following appended papers, which will be referred to with their Roman numbers in the text.

I. **Impregnation of Concrete Structures – Introduction to a PhD-project**
A. Johansson, M. Janz, J. Silfwerbrand, & J. Trägårdh, (2005), Proccedings, Hydrophobe IV – 4th International Conference on Water Repellent Treatment of Building Materials, Stockholm, Sweden, April 12-13, pp 59-68.

II. **Moisture Transport in Impregnated Concrete – Moisture Diffusion Coefficient, Modelling, Measurements and Verification**
A. Johansson, M. Janz, J. Silfwerbrand, and J. Trägårdh, (2006) International Journal on Restoration of Buildings and Monuments, Vol. 12, No. 1, pp. 13-24.

III. **Moisture Fixation in Concrete Treated with a Water Repellent Agent**
A. Johansson, M. Janz, J. Silfwerbrand and J. Trägårdh
(Submitted to Materials and Structures)

IV. **Penetration Depth for Water Repellent Agents on Concrete as a Function of Humidity, Porosity and Time**
A. Johansson, M. Janz, J. Silfwerbrand and J. Trägårdh
(Submitted to Restoration of Buildings and Monuments)

CONTENTS

INTRODUCTION

It is nothing new about trying to protect building materials from moisture with surface treatments. As a matter of fact we have been doing it for thousands of years [1]. In the beginning oil and fat were used and today we are using different types of coatings or impregnation with silanes or siloxanes. Water repellent agents, today mainly consisting of alkylalkoxysilanes, are often used on concrete to prolong the service life of the structure. This is accomplished by protecting the reinforcement bars from chlorides or by changing the moisture content inside. When the concrete is treated with a water repellent agent the properties of the surface layer turn from hydrophilic to hydrophobic and thereby water droplets are stopped from entering, still allowing water vapour to pass through. This property change can reduce chloride ingression and stop heavy rain from penetrating through the surface layer. Unlike conventional sealants, such as epoxy or acrylic paints, this surface treatment is open to diffusion and the risk for frost damages caused by entrapment of water is, therefore, decreased.

Measures prolonging the service life of a concrete structure will lead to savings of natural resources and thus both economical and environmental savings for the community. This PhD-project "Impregnation of concrete structures" was started in February 2004 at the Royal Institute of Technology and the Swedish Cement and Concrete Research Institute. The purpose is to develop explanation models to the promising results that have been obtained from the empirical research during the last decade and by doing this also create a better knowledge about when and how to apply a water repellent agent in order to benefit as much as possible from the product.

THE CONCRETE PORE SYSTEM

Fresh concrete basically consist of three parts; cement, aggregate and water. When the cement grains and water are mixed together a reaction starts called cement hydration [2]. Water is consumed during the hydration which means that a fine pore system forms during the process. The size and quantity of the pore system depend on several factors such as the original mixture, access of water, temperature, additives just to mention some of the parameters. The pore system plays a central role in most processes taking place inside the concrete including transport and fixation of moisture. An example of how the pore size distribution can vary for different concrete types is illustrated in Figure 1.

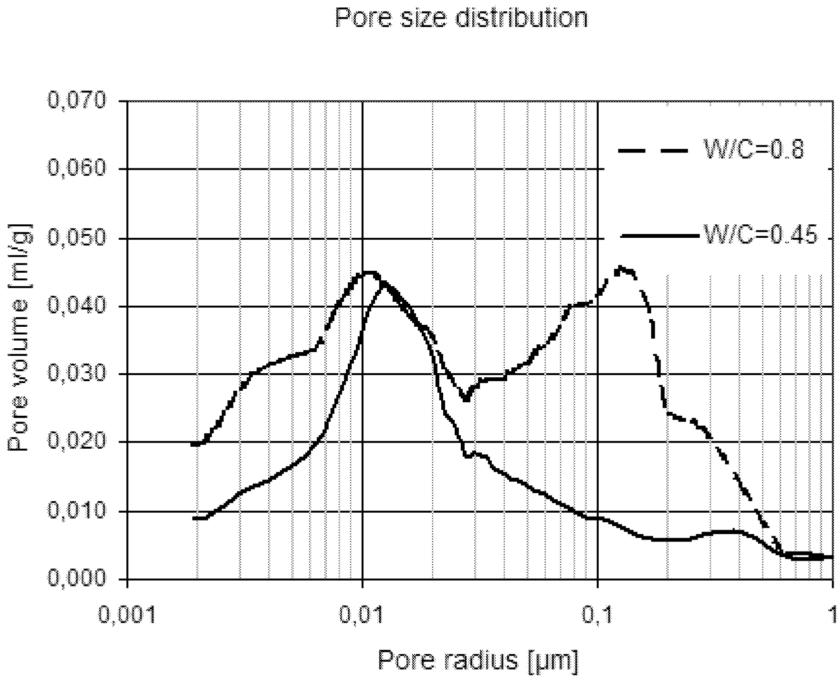

Figure 1: *Example of pore size distribution measured with mercury intrusion porosimetry (MIP) for two different water-cement-ratios.*

THE IMPORTANCE OF MOISTURE CONTENT

Porous materials will always contain a certain amount of water. For concrete, which is a porous material, several durability problems are related to the moisture content inside the pores. The expansion of water, when it turns to ice, can cause severe freeze damages in concrete if the pores are saturated. The alkali silica reaction (ASR) depends on the access of water and the corrosion of reinforcement bars is affected. These are all problems that are linked to the degree of saturation in the pores. Moisture is not always the main reason for the problem but it is one of the most important parameters for rate of the process.

The importance of keeping the moisture below a certain critical level is well illustrated in Figure 2 when considering the reinforcement corrosion as the limit of service life. The corrosion rate is highly dependent on the moisture content inside the pore system, in this figure represented with the relative humidity (RH) inside a reinforced concrete structure. As one can see, the corrosion rate reaches its maximum at around 97% RH. A higher humidity increases the rate below this value while the access of oxygen sets the limit above.

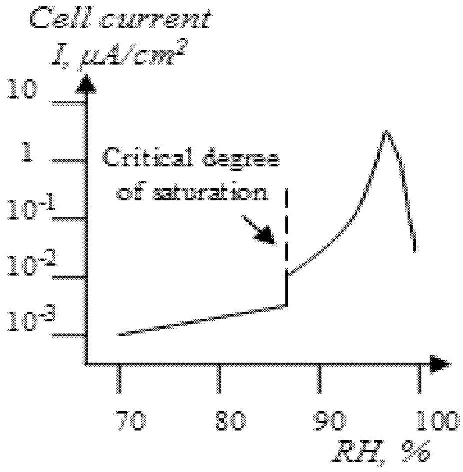

Figure 2: *The corrosion rate as a function of RH for a concrete specimen with w/c-ratio 0.9 (after [3]). The experiments were conducted on carbonated concrete.*

In new-cast concrete, the reinforcement is protected from corrosion by the alkali environment. This may, however, slowly be altered by carbonation or chloride ingress. The initiation time in Figure 3 is affected by carbonation and/or chloride transport. The diffusion rate of carbon dioxide and thus the carbonation rate is low when the moisture content is high. A summary of investigations conducted on carbonation rate as a function of RH is presented in [4]. The conclusion is that a maximum in carbonation rate is reached around 70% RH. This varies with the porosity of the concrete and for a dense concrete the maximum is reached at 10 to 20% lower RH. Transport of chloride ions into the concrete requires on the other hand a continuous water phase in the pore system. The maximum rate for chloride diffusion is reached at saturation and below 50% RH it is close to zero according to [5]. The authors of [6] suggest that the diffusion coefficient (as a function of RH) for chloride ingression can be described with an S-shaped curve which reaches its maximum at full saturation. After the initiation of the corrosion the moisture, the temperature and the access of oxygen are the decisive factors for the corrosion rate.

The point of using the water repellent is to change the concrete properties in the surface layer and change the circumstances for the transport and fixation of moisture. The effect can be, if applied in the right situation, that the concrete is dried out. The effect is than that the RH decreases which in turn means that the chloride diffusion is slowed down but also that the CO_2-diffusion might go faster. Several other factors are decisive for which one of these two factors that sets the limit of the service life of the concrete structure.

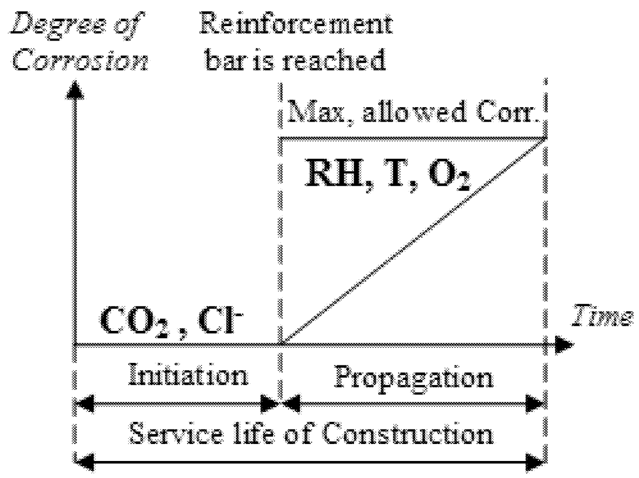

Figure 3: *Corrosion model after [3] that describes the factors which affect the time to initiation and the time of propagation.*

CHEMISTRY OF ALKYLALKOXYSILANES

Silanes or more correctly named alkylalkoxysilanes today used in water repellent agents on concrete were developed in the 1940s as a way to create a covalent bond between organic and inorganic substances. However, it was not until the military in USA started to show interest in glass fibers as reinforcement in organic resins as the need for strong and sustainable bonding arose [7]. A thorough description of the polymerization from silane, via siloxane to silicon resin or polymersiloxane and the bonding to the inorganic surface is presented in [8]. Figure 4 shows a schematic representation of the reaction.

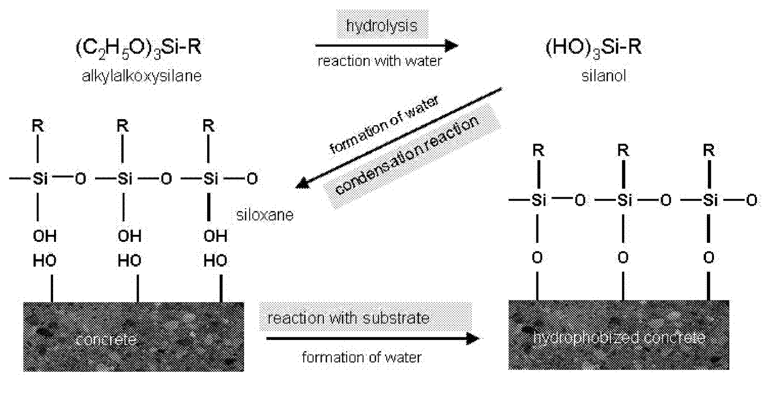

Figure 4: *Reaction of an organofunctional trialkoxysilane with the concrete matrix [9]. Ethanol is liberated during the hydrolysis.*

When the water repellent agent is applied on concrete it is transported into the concrete by capillary suction. The polymerisation starts inside the concrete. The alkoxygroups of the silanes react with the concrete and other alkoxygroups which forms a fine network of polymersiloxane or silicon resin on the walls of the pores.

When hydrophobic surface treatments were first used on concrete structures several different silanes and siloxanes existed on the market but after experiences of practical use and laboratory experiments the amount has decreased. In for example [10,11], where the influence of the size of the alkyl group and the alkoxy group on the reaction kinetics is studied, one can see that silanes with methoxy groups react significantly faster than those with ethoxy groups and that a big alkyl group slows down the reaction as well. Old concrete is often carbonated in the surface layer, meaning that the pH-value is lowered. A summary is presented in [12] of the influence of the pH-value on the polymerization rate. Even though there are variations between different silanes, the curve has a similar V-shape on a log-scale with a minimum around pH-value 6-7. For carbonated concrete, with a lowering of the pH-value from 13 to 9 this would, according to [12], mean a decrease in polymerization rate with a factor around 50. Which silane or siloxane is most suitable varies with the conditions (type of concrete, humidity, pH-value etc.) but today almost all water repellents on the market consist of alkyltriethoxysilanes with three to eight carbon atoms in the alkyl group.

THE MECHANISMS OF WATER REPELLENT AGENTS

The most frequently used way of illustrating the function of water repellent agents is illustrated in Figure 5 sometimes referred to as the lotus effect. For a hydrophilic material such as concrete the contact angle is often considered to be zero. This means that when water is applied on the surface fine system of pores will generate a force which causes a capillary rise. This of course means that particles and ions in the water also are transported into the concrete. Transport of chloride ions is an example of this.

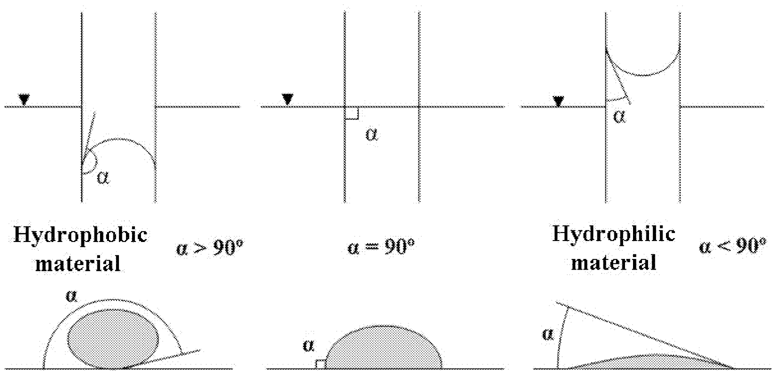

Figure 5: *Illustration of the difference between a hydrophobic and a hydrophilic material by the means of a contact angle: on top capillary pores and underneath a water droplet [13].*

When the concrete is treated with a water repellent agent the surface properties of the concrete turns from hydrophilic to hydrophobic. This means that a thin surface layer of the concrete only is open for gaseous diffusion. The absence of a continuous water phase is an effective way of stopping chloride ions from entering. The effect of a water repellent treatment depends on the source of the moisture inside the concrete structure. The treated surface is open to gaseous diffusion but the breathability is not as high as for untreated concrete Paper II.

EXPERIENCES OF WATER REPELLENT AGENTS

Studies of surface protection systems have been conducted in USA since the 1970s. In [14] the authors write about deep impregnation with polymers to protect the concrete bridge deck against reinforcement corrosion. They describe two experiments executed in 1975 in Bethlehem and in 1985 in Boalsburg in Pennsylvania, respectively. Limited areas on both bridges were treated with a monomer called methyl methacrylat. Based on measurements of chloride content, corrosion potential and corrosion speed the conclusion is drawn that the chloride penetration is slowed down in the treated concrete. However, the result varies with time and depth.

The use of surface protection on a conventionally reinforced Australian bridge outside Melbourne is reported in [15]. Three different types of systems (containing silane, polymer modified cement and epoxy) were investigated. All surface protection systems were functioning well after two years.

Great Britain has a long experience and skill within the area of repairs and maintenance of concrete structures. According to [16] silanes and siloxanes have been used with success, as breathable surface protection systems (water repellent agents), on concrete and masonry structures for at least 10 to 15 years. The work of British TRL is one important reason to the development of new standards for testing and approval of surface protection systems (EN 13579 – 13581, 2002) [17-19].

The experiences in Stockholm of impregnation as a protection against salt and water are good. Salt and water is either the cause or an accelerating factor for most of the damages in concrete according to [20]. If the concrete is protected from external water and salt, the risk for damages can be significantly reduced. A perfect concrete doesn't require any additional protection but is very difficult to manufacture. Specially exposed parts of the structure should therefore be treated with a water repellent on the surface. Silanes and siloxanes are not stable in UV-light. Siloxanes consist of bigger molecules than silanes and it is thereby more difficult to get a sufficient penetration depth with them. Siloxanes should therefore not be used on dense concrete. To get a good result from the impregnation it is important with a clean surface before the treatment. The water repellent can be applied as a fluid or with some sort of emulsion. The penetration depth is increased with the capillary suction time, low humidity and high porosity. Different emulsions can increase the capillary suction time and [20] is therefore recommending this method for dense and moist concrete.

Questions about the combination of graffiti protection and impregnation were studied by Stockholm Konsult and the results were presented in an article by *Nyman* [21]. He concluded that there was no problem with the combination if the water repellent was applied first. However, if the graffiti was removed with chemicals before the impregnation, the penetration depth was decreased. The effects of graffiti removal on concrete was recently studied in [22] and the results show that if the graffiti is removed with mechanical force micro cracks appear which could penetrate through the impregnated layer. With the use of a graffiti protection system and removal with water these cracks are not likely to appear.

The quality of the impregnation is decisive for the performance of the surface protection system and the quality is often related to the penetration depth. In [23] and [24] the topic of effective penetration depth, the influence of relative humidity RH, water-cement-ratio and the capillary suction time, is studied. Among the results in [23] the ratio 30 should be mentioned as the relation between the highest penetration depth (w_0/c = 0.70, RH = 65%) and the lowest (w_0/c = 0.40, RH = 90 %).

The effective penetration depth of the water repellent agent is defined as the distance from the surface to the sharp line between dry and wet concrete after it has been sprayed with water [25]. According to the Swedish Road Administration [26] and [27] a distance of 2 mm is required for a successful impregnation and according to [28] approximately a distance of 5 mm is required. There is not a unified opinion in this area and there are of course different requirements that depend on what the surface is exposed to and the concrete quality. In [29] the authors conclude that 2-3 mm of penetration depth is not sufficient when narrow cracks of up to 0.2 mm are considered. During the past decade several papers have been published where factors having a major influence on the penetration depth have been investigated, see for example [24,30,31]. The conclusions that can be drawn from these papers are that the three most important factors are time, porosity and degree of saturation. The time referred to is the duration of contact between the water repellent agent and the concrete surface. The porosity and degree of saturation refer to the concrete pore system and the amount of moisture inside the concrete is defined at the time of the impregnation.

The influence of impregnation on the sustainability of self compacting concrete was studied in [32]. Laboratory experiments were conducted on concrete for housing and civil engineering structures, respectively, for a few months. One important conclusion in the project was that the impregnation showed no significant effect on the concrete for civil engineering structures on the contrary to the concrete for housing. The question arose if maybe it is unnecessary to impregnate constructions with concrete for civil engineering structures. Short times for exposure, however, give an uncertainty about the long term effects. The best way to find answers to this question is more studies in micro scale of the interaction between the water repellent and the concrete and the transport processes inside the impregnated concrete.

The long term properties have been studied by [27] and they show that impregnation with silane/siloxane can have a major impact on the water absorption still nine years after the treatment. Today most of the water repellents consist of silane based emulsions in order to prolong the capillary suction time and thereby increase the penetration depth. Nothing indicates that the water repellents used today should be less efficient or not have equally good long term properties.

METHOD AND THEORY

Three different methods were used during the experiments presented in Paper II-IV. Paper I contains an introduction to the PhD-project and description of a prediction model in which a number of materiel properties are discussed, how they affect and how they are affected by a water repellent treatment. Paper II focuses on the moisture transport through a layer of water repellent treated concrete, while Paper III focuses on the moisture fixation inside the layer of water repellent treated concrete. The approach, which is also described in Paper I, is to measure these properties for water repellent treated and untreated concrete separately. Paper IV deals with the different factors influencing the effective penetration depth of the water repellent agent.

The experiments with moisture transport and moisture fixation conducted so far was monitored with a balance with 0.001 g accuracy. For measurements of chloride content per cement weight an ion-selective-technique is used in combination with Ca-titration with EDTA.

UNI-DIMENSIONAL TRANSPORT OF MOISTURE IN CONCRETE

This method was used in the experiment described in Paper II.

Moisture transport plays a central role in most of the processes taking place in concrete that is affected by a water repellent treatment. In order to be able to predict the outcome of a water repellent treatment the knowledge of how the moisture transport is affected is essential. In this project, the moisture transport was measured with the cup method [33,34]. The decision to use this method and not the drying and inverse method[1] [35] is that no assumptions are needed regarding the shape of the relationship between the transfer coefficient and the RH. Figure 6 shows a drawing of the cup used in the experiments. A saturated salt solution inside the cup and a controlled environment, regarding RH and temperature, outside the cup result in a steady state uni-dimensional flow of moisture. The diffusion coefficient can then be calculated from the moisture flow.

[1] The loss of weight of saturated and water repellent treated concrete samples is measured. The drying data are then compared with untreated concrete samples and used to back-calculate the moisture diffusion coefficient. The thickness of the treated layer can be measured after the experiment which is essential, but the principle shape of the diffusion coefficient needs to be assumed for treated as well as for untreated concrete.

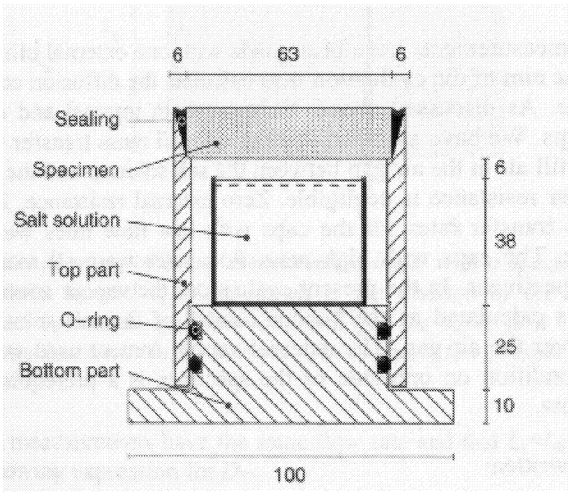

Figure 6: *A drawing of the cup used in the experiments, measures given in mm. [36]*

The mass flow rate was measured by weighing the cup regularly, thus registering the weight change of the cup. The diffusion coefficient is then calculated from Fick´s first law in one dimension and steady state diffusion [37]

$$q = -D_v \frac{dv}{dx} \qquad (1)$$

where q (kg/m^{2}s) is the moisture flow, D_v (m^2/s) the diffusion coefficient and dv (kg/m^3) the difference in vapour content over the distance dx (m). Rewritten with a known thickness of the plate and known vapour content in the air Equation 1 becomes

$$q = -D_v \frac{\Delta v}{\Delta x} \qquad (1b)$$

This is the ordinary way to establish the moisture diffusion coefficient but then it is only possible to determine the diffusion coefficient for certain intervals and not as a continuous function of RH. There is of course the possibility of increasing the number of cups and saturated salt solutions and thereby achieving smaller intervals and a higher accuracy but it would take unreasonable time and effort. Another more efficient way to approach this problem is to use Kirchhoff's flow potential [33,34]

$$\psi = q \cdot dx \qquad (2)$$

and in this setup

$$\psi = q \cdot \Delta x \qquad (2b)$$

where Ψ (kg/ms) is the Kirchhoff's flow potential. The potential is then plotted against RH and a mean value curve is drawn. The derivative to this curve with respect to the vapour content for saturated air at the given temperature (see for example [38]), according to Equation 3, represents the moisture diffusion coefficient (see Figure 7), i.e.,

$$\frac{d\psi}{dv} = -D_v \quad \text{where} \quad v = v_s(T) \cdot \phi \tag{3}$$

where v_s (kg/m^3) is the vapour content of saturated air at a given temperature and Φ is the relative humidity.

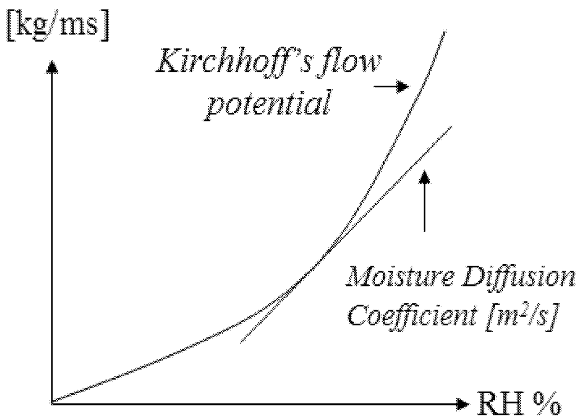

Figure 7: *Principle drawing to illustrate how to calculate the moisture diffusion coefficient. Kirchhoff's flow potential as a function of RH. The moisture diffusion coefficient is given as the gradient multiplied with the vapour content in saturated air at a given temperature. (Paper II).*

With the knowledge of the moisture diffusion coefficient for water repellent treated and untreated concrete it is possible to combine the two layers and simulate the influence of the effective penetration depth. The experimental setup, calculations and verification of the results are described in Paper II and [39].

MOISTURE FIXATION IN CONCRETE

This method was used in the experiment described in Paper III.

Concrete is a porous and hydrophilic material. As such a material it contains a certain amount of moisture depending on the surrounding environment. If the surrounding humidity is kept at a constant level around the concrete specimen, a state of equilibrium will be reached. This is achieved by the processes of diffusion and capillary condensation inside the concrete. However, if this state of equilibrium is reached by desorption it will not be the same as if reached by absorption [38]. The phenomenon is called hysteresis and is often referred to as the "ink bottle effect" and it is explained by the fact that concrete is a hydrophilic material and that the pore radius varies inside the capillaries (see Figure 8). This variation of the radii stops water from entering some areas during the absorption process, when a meniscus forms in a narrow part of the pore system. The same meniscus can also stop water from escaping during the desorption process.

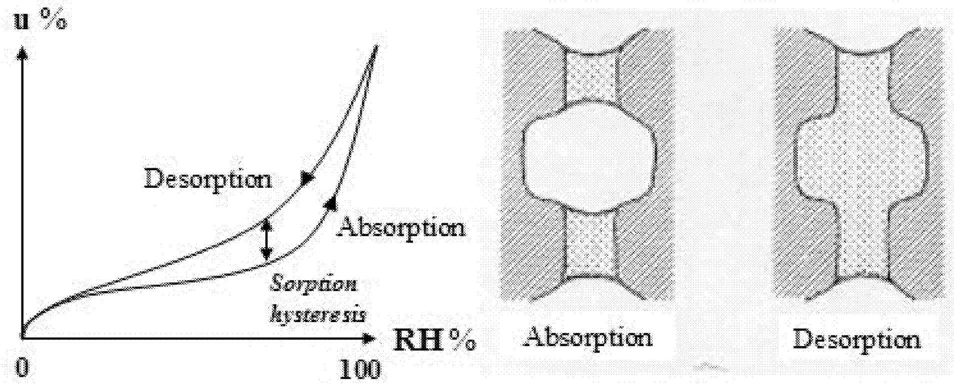

Figure 8: *Principle shape of the sorption isotherms for concrete and a possible explanation to the gap between the absorption isotherm and the desorption isotherm referred to as the sorption hysteresis. u is the moisture content in percent of dry concrete.*

The sorption isotherms were investigated by means of climate boxes with saturated aqueous solutions inside. By using closed boxes and small rotators to circulate the air inside, a fixed relative humidity (RH) was established in each box. A drawing of the equipment used for determining the sorption isotherms is shown in Figure 9.

The principle procedures for each sample is to first dry out the samples used for the absorption isotherm and saturate the samples used for the desorption isotherm. The samples are then placed inside the desired environment and they are kept there until weight equilibrium is reached. The sample weight is denoted m. All the samples are then dried at 105°C until weight equilibrium is reached. The weight is denoted m_{dry}. The moisture content in percent of dry concrete u can then be calculated according to Equation 4.

$$u = \frac{m - m_{\mathrm{dry}}}{m_{\mathrm{dry}}} \cdot 100 \qquad (4)$$

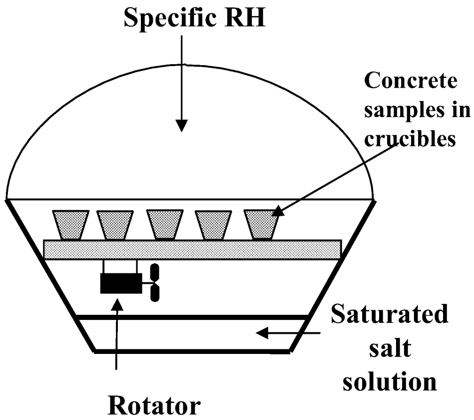

Figure 9: *The figure shows a schematic drawing of the climate boxes used in the experiments. The temperature and RH was checked once a week to ensure that the environment was stable.*

With the assumption of a cylindrical pore model and with the Kelvin equation combined with Laplace´s formula, it is possible to calculate a theoretical pore radius that is filled with water at a certain humidity and temperature [40] (see Equation 13). From a sorption isotherm diagram, it is thereby possible to determine at which humidity level the meniscus forms for a given pore radius and which volume that specific radius represents. It is thereby possible to see in what range, of pore radii, a water repellent treatment is effective.

The Kelvin equation is derived from a vertical tube. The force generated by the surface tension of a fluid and the attraction between the fluid and the capillary wall generate a capillary rise *h* [m] of the fluid inside the tube. This capillary rise can be described with

$$h = \frac{p_{\mathrm{m}}}{\rho_f \cdot g} \tag{5}$$

where p_{m} [N/m^2] is the curvature pressure for the meniscus according to Laplace's formula [37], ρ_f is the density of the fluid [kg/m^3] and g is the acceleration of gravity [m/s^2]. We obtain

$$p_{\mathrm{m}} = \sigma \cdot \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \tag{6}$$

where σ = surface tension of the fluid [N/m] and r_1 and r_2 are the smallest and the largest curvature radii of the meniscus, respectively. The height of the capillary rise can also be derived from the gas pressure difference Δp [N/m^2] over the height Δz [m], i.e.,

$$\Delta p = \rho_{\mathrm{g}} \cdot \Delta z \cdot g \tag{7}$$

where ρ_g is the density of the gas [kg/m^3]. With the use of the ideal gas law ρ_g can be expressed as

$$\rho_{\mathrm{g}} = \frac{p_{\mathrm{g}} \cdot M_{\mathrm{g}}}{R \cdot T} \tag{8}$$

where p_g is the partial pressure of the gas [N/m^2], M_g = molar mass of the gas [mol], R = molar gas constant [J/mol K] and T = temperature [K]. Combining Equation 7 and Equation 8 gives a differential equation which can be solved by separation assuming isothermal condition

$$\frac{dp}{dz} = -\frac{p_g \cdot M_g \cdot g}{R \cdot T} \tag{9}$$

With the partial pressure difference (p_2-p_1) and the height difference (z_2-z_1=h) over the column the solution to Equation 9 becomes

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{M_g \cdot g \cdot h}{R \cdot T} \tag{10}$$

If the fluid is water, p_1 is the partial pressure of vapour for saturated air p_{vs} and p_2 then becomes p_v which is the vapour content at the distance h over the water surface. This means that the pressure difference can be expressed as the relative humidity according to Equation 11

$$\phi = \frac{p_v}{p_{vs}} = \frac{p_2}{p_1} \tag{11}$$

Combining Equations 5 and 6 with 10 and 11 gives us the Kelvin equation

$$\ln(\phi) = -\frac{\sigma \cdot M_w}{R \cdot T \cdot \rho_w}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{12}$$

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 radius of the meniscus r_m (r = $r_m \cos \theta$) we obtain the following expression for when the meniscus forms for a specific pore radius as a function of the RH in the surrounding air:

$$r = -\frac{2 \cdot \sigma_w \cdot \cos\theta \cdot M_w}{\ln\phi \cdot R \cdot T \cdot \rho_w} \tag{13}$$

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 set to θ = 0.

The Kelvin equation combined with sorption isotherms of water repellent treated concrete and untreated concrete gives the possibility to study what range of pore size the water repellent agent can enter. It is also possible to observe how the effectiveness of the water repellent treatment depends on the size of the pores. The experimental setup is presented in Paper III.

CONDITIONING ENVIRONMENTS

The experiments conducted and presented in this thesis all require special conditioning, either before the experiments or during. Three different climate rooms were used which keep a stable RH and temperature, 100%, 70% and 50% RH at 20°C. Table 1 presents the saturated salt solutions needed in the experiments to create additional RH environments.

Table 1: *The saturated salt solutions used in the experiments. The first row presents the salt and the second row the corresponding RH at 20°C according to [41].*

LiCl	$MgCl_2$	NaBr	NaCl	KCl	$BaCl_2$	KNO_3	K_2SO_4
11%	33%	59%	75%	85%	90%	93%	97%

WATER REPELLENT TREATMENT

Three different silanes in liquid form were used during these experiment; triethoxy(propyl)silane, triethoxy(isobutyl)silane and triethoxy(isooctyl)silane. According to the manufacturers the silane concentration is close to 100% in all three products. Figure 10 shows the chemical structure of the used silanes. These three silanes are the most common water repellent agents in commercial products today. The products used in the experiments are listed in Table 2. Only liquid form has been used in the experiments. Since the duration of the treatment is a parameter in most of the experiments the liquid form is easiest to work with. The different dispersions that exist have the primary objective of increasing the duration of contact for the treatment. Time is one of the most important parameters for the success of the treatment (see for example Paper IV).

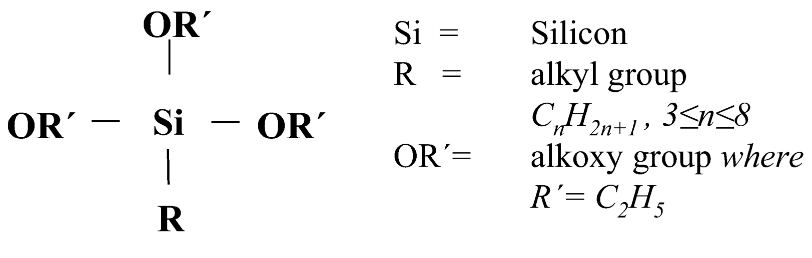

Figure 10: *Chemical structure of a triethoxy(alkyl)silane. The R group in the used silanes consists of 3, 4 and 8 carbon atoms.*

Table 2: *The water repellent agents used in the experiments.*

Water repellent agent	Product name	Company
triethoxy(propyl)silane	Stenimpregnering C1	Nordisk Stenimpregnering
triethoxy(isobutyl)silane	Protectosil BHN	Silanex
triethoxy(isooctyl)silane	StoCryl HP 200	Sto Scandinavia

THE EFFECTIVE PENETRATION DEPTH

This method was used in Paper II-IV.

The effective penetration depth of different silanes was measured by cracking water repellent treated concrete plates, spraying water on the cracked surface and measuring the distance from the surface to the sharp line between dry and wet concrete [25]. This is illustrated in Figure 11. It is important that the polymerization is finished before the sample is cracked. The ethanol liberation is studied in [42] and the authors concludes that only 50% of the theoretical amount of ethanol was liberated after 15 days for triethoxy(isooctyl)silane. The specimen was therefore not cracked until at least four weeks had passed since the treatment.

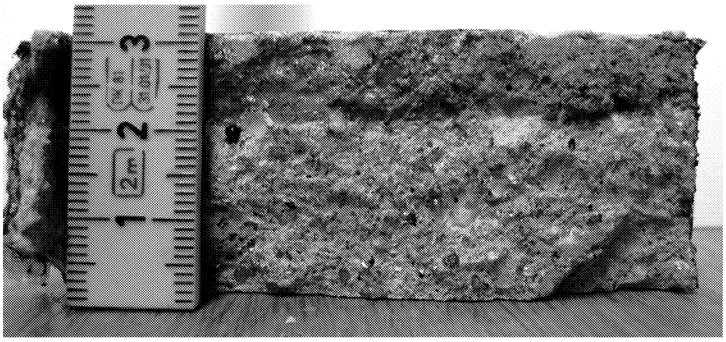

Figure 11: *The effective penetration dept is the distance from the surface (bottom) to the sharp line between wet (dark) and dry (light) concrete. The penetration depth in this picture is 21 mm.*

LONG TERM PROPERTIES OF WATER REPELLENT TREATMENTS

A heavily trafficked tunnel in Stockholm (Eugenia tunnel), which is exposed to de-icing salts for at least four months every year, is used as a field exposure site in this project. The aim is to measure if and if so how the properties of a water repellent treatment changes over time. Chloride profiles will be evaluated continuously during at least four years and measurements on RH and temperature inside as well as outside the concrete specimens will be conducted in a later stage of this project. The site will also be used for verification of accuracy of the results obtained in the laboratory when these measurements are initiated.

Figure 12 shows pictures from the tunnel and the samples placed there. The field exposure site is located 50 m from the entrance of the tunnel. The first samples were placed in the tunnel in November 2004.

Figure 12: *The picture on the left side shows a web camera photo of the traffic going into the Eugenia tunnel. The photo in the right side shows water repellent treated (light) and untreated (dark) samples before they were placed at the field exposure site in the tunnel.*

The concrete samples were treated with triethoxy(isooctyl)silane in liquid form on the exposed surface. The remaining five sides of the cubes were sealed with neoprene film. The effective penetration depth was measured to 2-3 mm on two samples.

RESULTS

MOISTURE TRANSPORT IN WATER REPELLENT TREATED CONCRETE

The moisture diffusion coefficient was derived according to the theory part described in Chapter METHOD AND THEORY. Figure 13 shows the results. The test results indicate that the moisture diffusion coefficient for the treated specimens could be approximated with a constant. The deviation from a straight line somewhere between 90% and 100% RH, however, must be further investigated before it can be established as a fact. Worth to be noted is the magnitude of the difference, regarding the moisture diffusion coefficient, between the water repellent treated and the untreated samples at high RH.

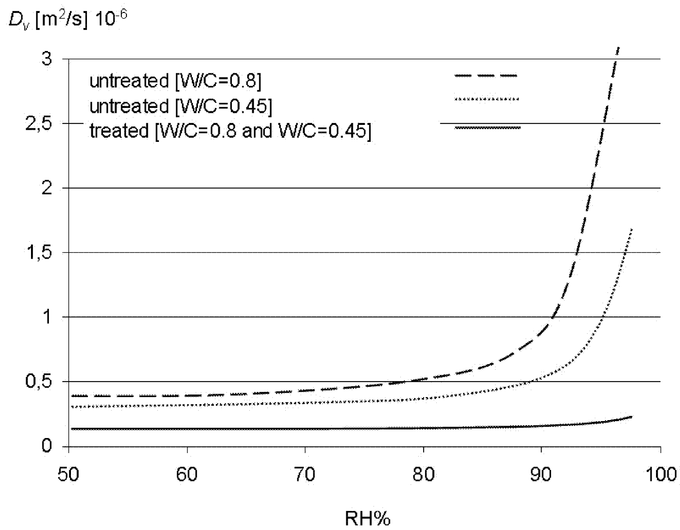

Figure 13: *The moisture diffusion coefficient as a function of RH based on the results in Paper II.*

Verification of the method

The real water repellent treated concrete structure consists of two layers reagarding moisture transport, the superficial treated layer and the interior untreated layer.

The easiest way to confirm the accuracy of the results described in previous paragraph, and thereby also verifying the method of measuring the layers separately as correct, is naturally to combine both layers and try to make a calculation based on the measured moisture diffusion coefficient. To make it as simple as possible the span between 50% RH and 75% RH, where the diffusion coefficient is almost constant, was chosen. Since it is not possible to measure the RH inside the cup and inside the concrete plate, the best approach is to start from the known RH at the surface of the saturated salt solution. Figure 14 shows a drawing of a two layer model used for verifying the results presented in Figure 13.

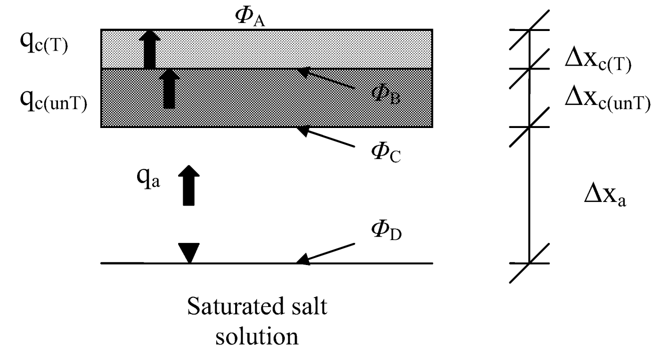

Figure 14: *Picture showing the two-layered concrete specimen, air column and the saturated salt solution.*

The thickness of the two layers was measured by cracking the plate and dipping it in water. The distance to the sharp line between dry and wet concrete was measured and noted as the thickness of the layer. With a known mass flow according to Table 3 and the diffusion coefficient from Figure 13 it is possible to calculate the reduction of RH caused by each layer according to Figure 14. It is thereby possible to see how well the calculated RH corresponds to the actual measured value outside the cup. For these calculations Equation 4 in Paper II was used. The results from the calculation are presented in Table 3. The verification process is fully described in Paper II. The deviations between calculated and measured values are within 8% which indicates that the method works.

Table 3: *The table shows the calculated reduction of the RH (Φ) based on the measured moisture diffusion coefficient. As seen in the last two columns in the table, the calculated RH for all four cups corresponds well to the measured value of 50% RH outside the cups.*

		Air column			**Untreated**			**Treated**				
w_0/c	q 10^{-6} (kg/m^2s)	Φ_D *NaCl*	D_v 10^{-6} (m^2/s)	Δx_a *(mm)*	Φ_C	D_v 10^{-6} (m^2/s)	Δx_c *(mm)*	Φ_B	D_v 10^{-6} (m^2/s)	Δx_c *(mm)*	Φ_A *	Φ_A **
0,8A	0,0944	75	25	10	74,8	0,43	6	67,2	0,11	4	48	50
0,8B	0.0985	75	25	10	74,8	0,43	6	66,9	0,11	4	46	50
0,45A	0,0970	75	25	10	74,8	0,32	8	60,8	0,11	2	51	50
0,45B	0,1042	75	25	10	74,8	0,32	8	59,7	0,11	2	49	50

(calculated, ** measured)*

MOISTURE FIXATION IN WATER REPELLENT TREATED CONCRETE

In Figures 15 and 16 the results from the experiments on moisture fixation are shown. On the y-axis the moisture content is presented as a function of the RH. The sorption isotherms for the untreated concrete show a familiar shape when compared with curves found in the literature (see for example [33] and [43]). Below 50% RH there is no difference between the treated and the untreated samples. The effect of the water repellent treatment is higher on the samples with w_0/c=0.8 than on those with w_0/c=0.45 which seems reasonable since the porosity is higher for w_0/c=0.8. It can also be seen that the hysteresis is reduced by the water repellent treatment, for high RH.

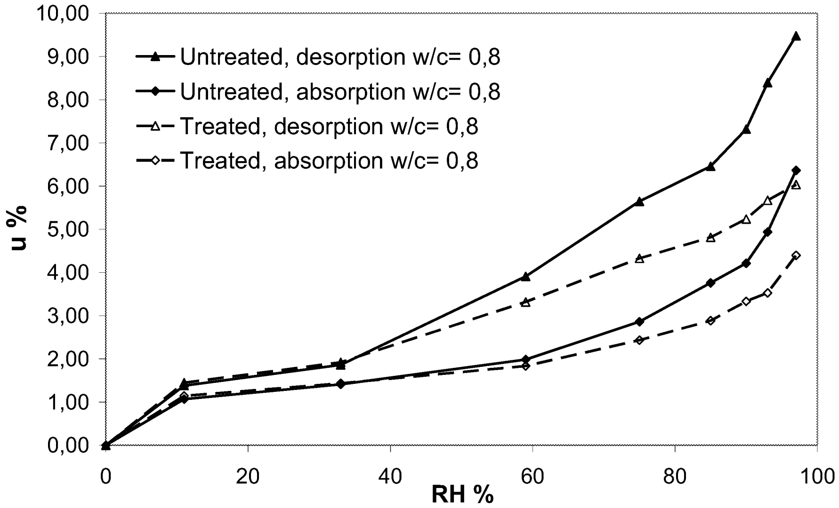

Figure 15: *Sorption isotherms of the concrete with w_0/c = 0.8, with and without a water repellent treatment.*

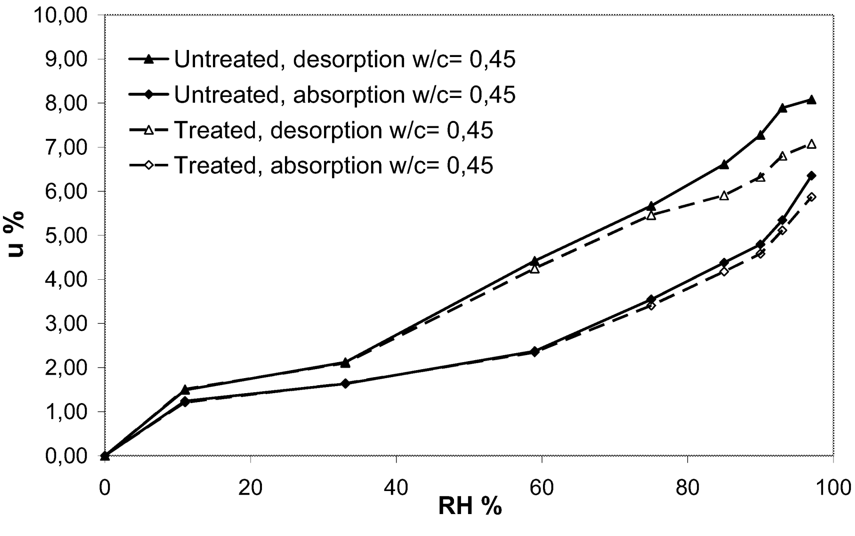

Figure 16: *Sorption isotherms of the concrete with w_0/c = 0.45, with and without a water repellent treatment.*

The size of a silane molecule is in the range of 10 Å (1 nm) [44]. If Equation 13 is used to calculate the RH that a meniscus of such magnitude corresponds to, the result is ~ 35% RH. The silane molecule can therefore not enter smaller pores and this is also confirmed by this experiment when the sorption isotherms are not affected by the water repellent treatment below this RH.

DECISIVE FACTORS FOR THE PENETRATION OF SILANES INTO CONCRETE

The effective penetration depth is the most frequently discussed topic for water repellent agents. During the past decade several papers have been published where factors having a major influence on the penetration depth have been investigated (see for example [23,30,31]). The conclusions that can be drawn from these papers are that the three most important factors are time, porosity and degree of saturation for the penetration of different water repellent agents. The time referred to is the duration of contact between the water repellent agent and the concrete surface. The porosity and degree of saturation refer to the concrete pore system and the amount of moisture inside the concrete at the time of the impregnation. A fourth factor is also considered, the influence of the water repellent agent itself. The chemical reactivity and the molecule size of the water repellent agent affect the penetration as well.

The results presented here are based on the experiments described in Paper IV. The derivation of the empirical Equation 14 is also presented in Paper IV.

Effect of different water repellent agents - Silane

Figure 17 shows the different penetration profiles of three different water repellent agents. In an early stage of the treatment the triethoxy(propyl)silane (with a relatively small molecule size) shows a faster penetration than triethoxy(isooctyl)silane. In an environment of non carbonated concrete the polymerisation of triethoxy(propyl)silane goes fast and the molecule size increases resulting in a capillary rise that is slowed down relatively fast. For triethoxy(isooctyl)silane and triethoxy(isobutyl)silane the polymerisation is a slower process and the capillary rise is not slowed down as quickly. On the other hand, the capillary rise is slower from the beginning.

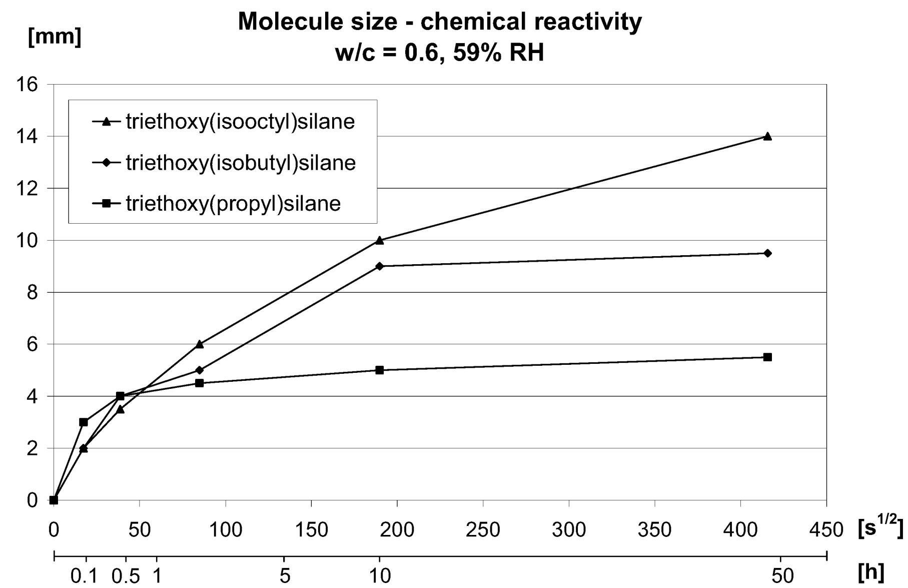

Figure 17: *The penetration profiles of three different water repellent agents. The time on the x-axis is the duration of contact for the treatment. The penetration depth is measured four months later.*

Effect of time - Duration of contact

Time is one of the most important factors when the effective penetration depth of a water repellent agent is considered. The results from this experiment are not an exception. In Figures 17-19 a clear time dependency is shown. The effective penetration depth is almost proportional to the square rout of time in the first few hours, which is also the conclusion of [45], but later on the penetration depth development shows a deviation from a straight line.

Effect of porosity

The porosity of the concrete is an important factor as well. A dense concrete is difficult to impregnate even when it is dry. The w_0/c is used initially as the parameter to represent the porosity of the concrete. Figure 4 shows the difference between the four concrete types used in this experiment. While a water repellent treatment on concrete with w_0/c = 0.8 can show over 20 mm of effective penetration depth the equivalent treatment on w_0/c = 0.35 hardly shows any effect at all.

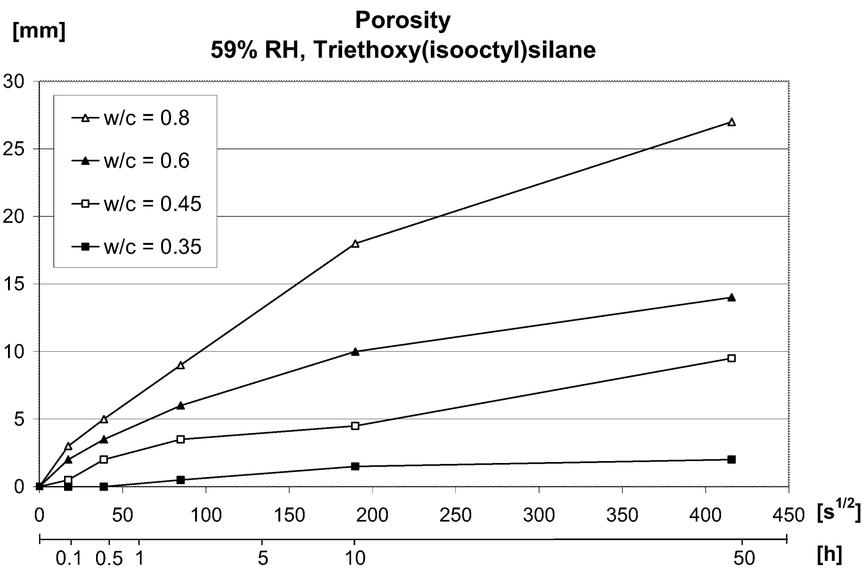

Figure 18: *The influence of porosity on the effective penetration depth. The time on the x-axis is the duration of contact for the treatment. The penetration depth is measured four months later.*

Effect of degree of saturation - Conditioning environment RH and temperature

The fourth important factor is the degree of saturation inside the concrete when it is treated with the water repellent agent. In this experiment it is represented with the RH during the conditioning period. Figure 19 shows the influence of moisture inside the specimen. A high degree of saturation means that a large portion of the pores are filled with water. The water repellent agent enters the pore system mainly by capillary suction. When the pores are filled, this force is neglectable which means that it is difficult to achieve a high effective penetration depth under those conditions. We observe that the penetration depth is more than ten times higher if the RH is changed from 97 to 59%.

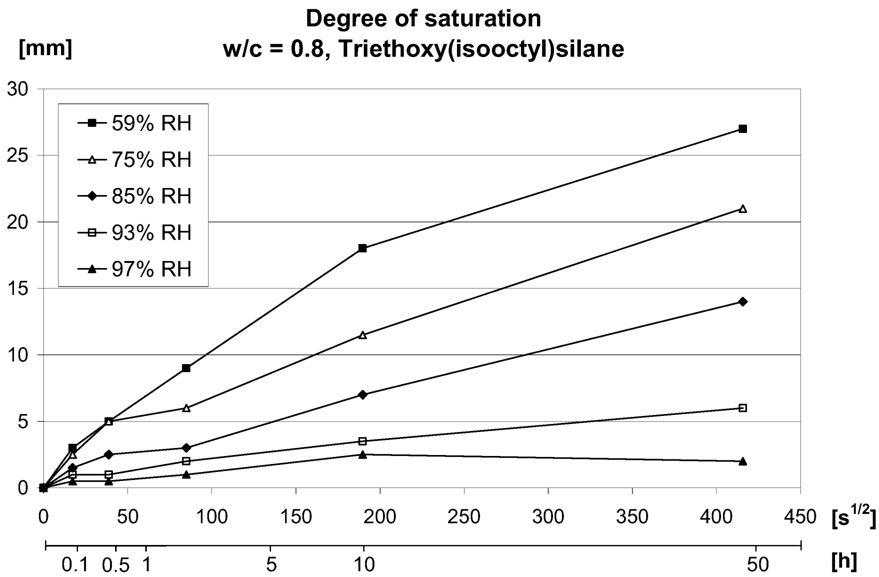

Figure 19: *The influence of the conditioning environment around the specimen. The time on the x-axis is the duration of contact for the treatment. The penetration depth is measured four months later.*

FIELD EXPOSURE SITE

The main purpose of the field exposure site is the evaluation of the long term properties of water repellent treatments. It is thereby difficult to draw any conclusions yet. The first results after one year of exposure are presented in Figure 20. It is clear that the chloride penetration is reduced by the water repellent treatment but longer exposure is needed for this investigation. The high value close to the surface for the water repellent treated concrete can be explained with particles attached to the surface coming from the traffic. If the samples were placed outside the tunnel, the particles would probably be washed off the surface by rain.

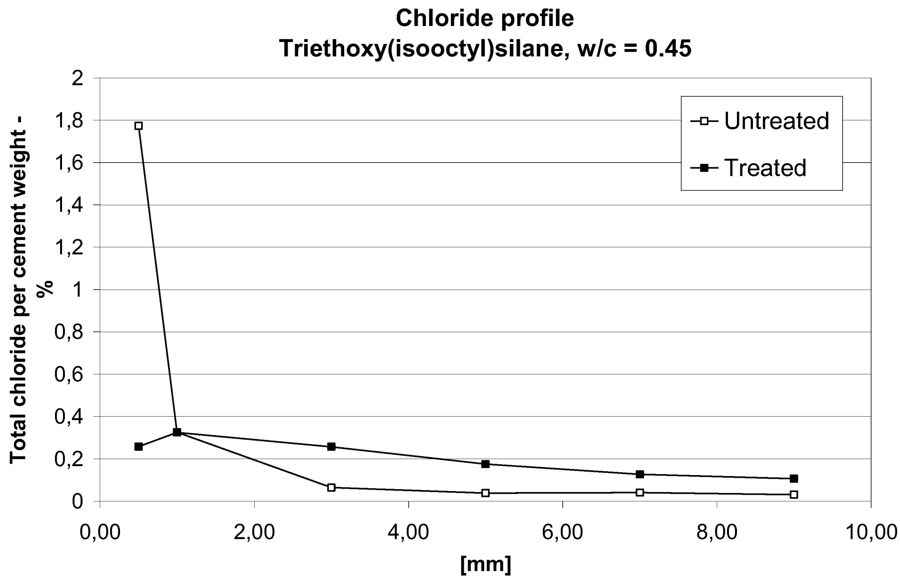

Figure 20: *The results after one year of exposure in the Eugenia tunnel. The x-axis presents the distance from the exposed surface.*

DISCUSSION

The research so far, within the PhD-project, has three major alignments which emphasizes the problems related to moisture. (i) Transport of moisture through an impregnated layer, (ii) Fixation of moisture inside an impregnated layer and (iii) Decisive factors for the penetration, into concrete, of the impregnation. Alignment (i) has resulted in one paper in press (Paper II) and alignment (ii) and (iii) in two papers submitted for publication, Paper III and Paper IV.

Paper I describes a model in which the aim is to predict the outcome of a water repellent treatment regarding the treatment itself as well as the effect of it. The results from Paper IV give an idea of which parameters affect the penetration of the water repellent agent and how much they do it.

The moisture fixation is essential for the ingress of chlorides into concrete. The absence of water as a continuous phase in the surface layer, caused by a water repellent treatment, is an effective way to prevent or decrease the ingress. Paper III presents results on how the moisture fixation in the surface layer is affected by the treatment.

Several problems with concrete are related to the moisture inside the structure. The transport of moisture in and out of the structure depends on material properties, the conditions outside the structure and the interface between the structure and the surrounding environment. A water repellent treatment on a concrete structure surface changes the conditions for the transport processes. The surface turns from hydrophilic to hydrophobic. Paper II presents results on how the moisture diffusion coefficient is affected by a water repellent treatment.

One of the goals with this PhD-project is to create a model where it will be possible to predict the moisture and chloride content over time if the geometry, material properties and environmental conditions of the concrete structure are known. To be able to do this for all scenarios and not just for a specific case there are several parameters that have to be investigated such as for example porosity, humidity, penetration depth of the water repellent agent and diffusion coefficients for moisture and chlorides. Papers II-IV presents results that, after verification, will be used in this model.

THE TWO LAYER MODEL

The approach is to separate the problem of an impregnated concrete piece into a two layer model where we at first establish the material properties of the impregnated concrete and none treated concrete separately and then try to look at what is happening in the interface between. In the discussion part of [45] *Gerdes* defines a minimum of active substrate based on a combination of FTIR-spectroscopy analysis and capillary uptake of water. A possible way to interpret the results from *Gerdes'* investigation is that, if this concentration (minimum of active substrate) is present in the concrete, the material properties of the treated surface layer would be the same. An increase in concentration would not affect the moisture diffusion coefficient for example. If this is the case it should be possible to measure the material properties for each layer separately and then ad them together in order to simulate a real situation. The effect of a change of the thickness in the treated layer could then be investigated. The results presented in Paper II support this theory.

DESCRIBING THE EFFECTIVE PENETRATION DEPTH MATHEMATICALLY

Paper IV describes an experiment where 300 concrete samples were used to determine how much time, porosity and degree of saturation influence the effective penetration depth for three different water repellent agents. An empirical equation was derived based on this experiment and it is presented as Equation 14. It is important to say that the experiments were conducted on non carbonated concrete and at a temperature of 20°C. The coefficients presented in Table 4 probably need to be revised if those conditions change. Equation 14 yields

$$z = C_1 \cdot A \cdot [1-\phi] \cdot \ln\left(C_2 \cdot \sqrt{t} + 1\right) \qquad (14)$$

where z is the effective penetration depth in [m] and t the duration of contact in [s]. The sorption coefficient A [$kg/m^2s^{1/2}$] is a material parameter that can be used to characterise the porosity of the concrete. C_1 and C_2 are experimentally determined material coefficients for the water repellent agents used in this experiment. The coefficients are related to the absorption and reaction of the molecule. A description of how A can be determined is presented in Paper IV and the values are presented in Table 5. An example of the results from this equation is shown in Figure 21.

Table 4: *C_1 and C_2 for three different water repellent agents.*

	Triethoxy(propyl)silane	Triethoxy(isobutyl)silane	Triethoxy(isooctyl)silane
C_1 [$m^3s^{1/2}/kg$]	$86.4 \cdot 10^{-3}$	$270 \cdot 10^{-3}$	$930 \cdot 10^{-3}$
C_2 [$s^{-1/2}$]	4.17	0.167	0.0133

Table 5: *The sorption coefficient A for the four concrete types used in this experiment. In addition to these, three test results are added from [38] to illustrate the spread of these values.*

w_0/c	0.3 [38]	0.35	0.45	0.5 [38]	0.6	0.7 [38]	0.8
A [$kg/m^2s^{1/2}$]	0.010	0.006	0.013	0.020	0.021	0.028	0.039

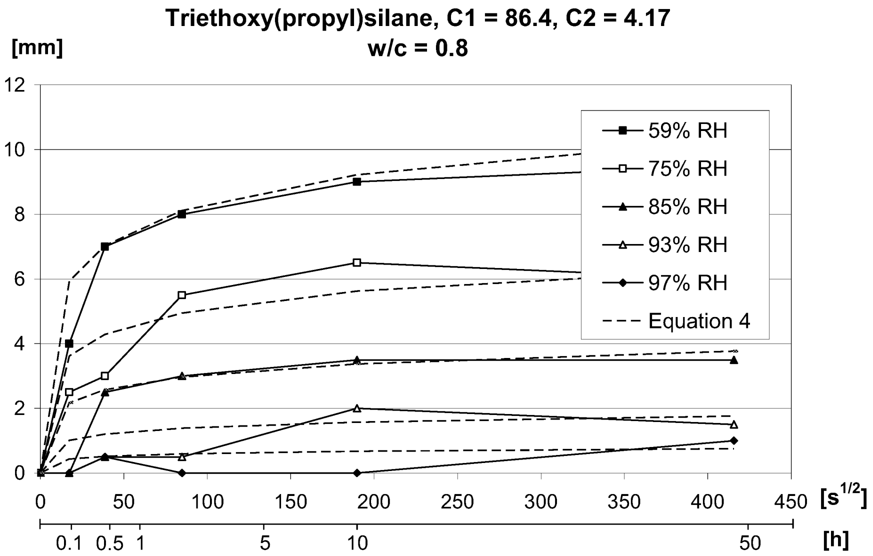

Figure 21: *Example of how Equation 14 (in this figure denoted Equation 4 according to Paper IV) can be used with values from Table 4. The time on the x-axis is the duration of contact for the treatment. The penetration depth is measured four months later.*

This mathematical description of the effective penetration depth need to be verified on field samples before it can be used as some sort of guideline but it gives an idea of how much these parameters influence the penetration.

CONCLUSIONS

The main results from this thesis can be summarized as follows:

- **Moisture transport in water repellent treated concrete**
  The moisture diffusion coefficient for water repellent treated concrete is close to constant and not nearly as dependent on the RH as for untreated concrete. Unlike untreated concrete, where capillary suction plays an important role for the moisture transport at high RH, the vapour transport is the dominant transport mechanism even at high RH for water repellent treated concrete (see Paper II). It can also be concluded that the vapour transport in water repellent treated concrete is highly reduced if compared with untreated concrete.

- **Two layer model – Water repellent treated and untreated concrete**
  The first step of verification, presented in Paper II, indicates that it is possible to measure the material properties for water repellent treated and untreated concrete separately. This gives the possibility of simulating situations where different thicknesses of the layers can be compared.

- **Moisture fixation in water repellent treated concrete**
  The moisture fixation is reduced by a water repellent treatment and the effect is clearest at high moisture levels. This can be seen in Paper III. There is, however, a certain amount of moisture present also in a concrete treated with a water repellent agent. The concrete does not become dry in the treated layer.

  The capillary porosity is affected by the treatment to a relatively high degree while the gel porosity to a large portion remains unaffected and as an effect of this a water repellent treatment is far more efficient on a concrete with high porosity.

  The silane molecule can enter pores with almost the same diameter as the molecule itself. This can be seen with the use of the Kelvin equation and the sorption isotherms. However, to what degree this is likely to happen before the polymerisation starts is identified as a task of future research.

- **Decisive factors for the penetration of silanes into concrete**
  Duration of contact, degree of saturation and porosity have all a major influence on the outcome of a water repellent treatment and the empirical equation derived in Paper IV gives an idea on how much these factors affect the effective penetration depth of the water repellent agent.

  The chemical reactivity and the molecule size of the water repellent agent affect the effective penetration depth. A small silane enters the concrete faster than a big silane which thereby results in a higher effective penetration depth. A high chemical reactivity of the silane has the opposite effect. When the polymerisation starts the molecule size increases and the uptake is slowed down.

FUTURE RESEARCH

The work in this project so far has focused on the experimental work. The measurements on how different parameters influence the result of a water repellent treatment and how a water repellent treatment changes the properties of concrete were in focus. The continuation of the project is oriented towards the use of the results obtained. Simulations of moisture flow and moisture fixations in water repellent treated concrete will be conducted based on the results presented in this thesis. Verifications against field exposed samples are necessary and will be done.

Paper IV presents an empirical equation for the penetration of water repellent agents in concrete. It is based on one experiment regarding 300 specimens under a number of given conditions. It is a helpful tool to see how important some factors are for the penetration of the water repellent agent. This Equation will be tested on field samples to see how well it can predict the effective penetration depth. The results from Paper IV also indicate that the chemical reactivity has a major influence on the effective penetration depth. This will be further investigated and also considered in future simulations of the penetration phase of the water repellent treatment.

Prediction models are often used to estimate the service life for concrete structures. These models are based on carbonation rate or chloride ingression in untreated concrete. If a surface treatment, such as a water repellent agent, is applied these models need to be revised. The results presented in Paper II and Paper III regard the properties of water repellent concrete a few months after the treatment. Is there an aging factor that has to be considered? The field exposure site in the Eugenia tunnel will hopefully give answers to this question.

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