

Hydrophobic Impregnation of Concrete Structures

– Effects on Concrete Properties

Anders Selander

Division of Structural Design and Bridges
Department of Civil and Architectural Engineering
School of Architecture and the Built Environment
Royal Institute of Technology

TRITA-BKN. Bulletin 104, 2010
ISSN 1103-4270
ISRN KTH/BKN/B--104--SE

Doctoral Thesis

Akademisk avhandling som med tillstånd av Kungliga Tekniska Högskolan i Stockholm framlägges till offentlig granskning för avläggande av teknologie doktorsexamen fredagen den 16 april kl. 10:00 i Sal D2, Lindstedtsvägen 5, Kungliga Tekniska Högskolan, Stockholm

© Anders Selander

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 came from the Swedish Research Council for Environment, Agriculture Sciences and Spatial Planning (FORMAS) and the Members' Association of CBI. Additional help with field objects came from the City of Stockholm and the Swedish Road Administration. They are all gratefully acknowledged.

I would first of all like to thank my supervisors for all the support during this work, *Mårten Janz* especially for your valuable input at the beginning of this project which pointed out the direction, *Jan Trägårdh* for being such an understanding boss and always taking your time to listen and discuss all sorts of problems and finally *Professor Johan Silfwerbrand* for finding time to comment my papers despite a full agenda and last but not least for your never ending optimism and enthusiasm for my research.

A special thank to *Professor Andreas Gerdes* and his colleagues at the Forschungszentrum Karlsruhe for the warm welcoming, valuable discussions and help with FTIR-experiments during my visit in the autumn of 2005.

I would also like to thank the Division of Building Materials at Lund Institute of Technology for the allowance to use their equipment in the experimental setup used in Paper IV as well as the essential help from *Lars Wadsö* with the experiments in Paper VI.

To all my colleagues at CBI, I wish to express my gratitude for all the help given whenever needed and for creating such an inspiring atmosphere to work in. *Annika, Carsten, Micke,* and *Johan*, you all have a special part in this as fellow PhD-students and friends.

Finally I would like to thank my family, especially you *Sara* for always being there for me and our daughters *Emma* and *Klara*, you are an endless source of joy and energy.

Stockholm in March 2010

Anders Selander

ABSTRACT

Hydrophobic impregnations often referred to as 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 becomes hydrophobic and thereby water droplets are stopped from entering, still allowing water vapour to pass through. This change can reduce chloride ingress and stop heavy rain from penetrating through the surface layer.

This thesis presents results concerning how the properties of concrete are affected by a hydrophobic impregnation. Moisture transport and fixation in the surface layer of the concrete are studied as well as the secondary effects of more practical use such as the effect on chloride ingress, water absorption and humidity level. It also presents results on how the penetration depth and concentration of the water repellent agent (i) depend on a number of parameters, and (ii) affect the outcome of the treatment. Water repellent treatments on a number of different concrete structures in Stockholm, ranging from tunnel to high-rise building, are evaluated as well.

The three most important factors for the penetration of any water repellent agent into concrete are time, porosity and degree of saturation. A semi-empirical equation is derived that gives an idea on how much these factors affect the efficient penetration depth of the water repellent agent. The depth and concentration have a major effect on the performance of the treatment.

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. 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. A hypothesis is presented which suggests that the RH inside the concrete at the time of the treatment affects not only the depth and concentration but also in which range of pore radii the water repellent agent is present and active.

The durability of hydrophobic impregnations can be divided into surface effects and in depth effects. The first is sensitive to the environmental and mechanical loadings and normally disappears within a year while the later can be long lasting if a sufficient depth is reached.

Hydrophobic impregnations are not the answer to all problems in concrete related to moisture, but if correctly used it can prolong the service life of the structure which will lead to savings of natural resources and thus both economical and environmental savings for the community.

SAMMANFATTNING

Vattenavvisande impregneringsmedel, 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 avhandling presenterar resultat om hur betongen påverkas av en vattenavvisande impregnering. Fukttransport och fuktfixering i betongens ytskikt har undersökts men även sekundära effekter som kloridinträngning, vattenabsorption och förändring i fuktinnehåll vilka alla är av större praktisk nytta. Avhandlingen presenterar också resultat om vilka faktorer som påverkar impregneringens inträngningsdjup och koncentration samt vilken betydelse dessa har för funktionen. För att utvärdera impregneringars effekt i olika miljöer har ett stort antal objekt i Stockholm undersökts, innefattande olika konstruktioner från en tunnel till höghus.

Impregneringens inträngningsdjup och koncentration har en avgörande betydelse för dess funktion. De tre viktigaste faktorerna för alla impregneringsmedels inträngning i betong är tid, porositet och fuktnivå. En semiempirisk ekvation har tagits fram där det framgår hur dessa tre faktorer påverkar det slutliga inträngningsdjupet för impregneringen.

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 på grund av kapillärkrafter, är ångtransporten fortfarande den dominerande transportmekanismen i impregnerad betong.

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. Resultaten indikerar också att fuktnivån vid impregneringstillfället avgör vilken del av porsystemet som kan behandlas och inte bara koncentrationen och inträngningsdjupet.

Långtidsegenskaperna hos impregneringen kan delas upp i yt- och djupeffekt. Effekten på ytan avtar normalt sett inom ett år på grund av damm och partiklar, UV-ljus, slitage mm. Djupeffekten påverkas däremot inte av dessa faktorer och kan finnas kvar i decennier.

Vattenavvisande impregneringar är inte lösningen på alla fuktrelaterade problem i betong, men om de används på rätt sätt så kan det förlänga livslängden på många konstruktioner. Detta leder till ett bättre hushållande med naturresurser och därmed både ekonomiska och miljömässiga besparingar för samhället.

LIST OF PAPERS

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

- I. Penetration Depth for Water Repellent Agents on Concrete as a Function of Humidity, Porosity and Time**
Johansson, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., International Journal on Restoration of Buildings and Monuments, Vol. 13, No. 1, 2007, pp. 3-16.
- II. Penetration profiles of Water Repellent Agents in Concrete as a function of Time - Determined with FTIR-Spectrometer**
Johansson-Selander, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., (*Submitted to Int. J*)
- III. Water Repellent Treatments–The importance of reaching a sufficient penetration depth**
Johansson-Selander, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., Proceedings, CONSEC'10, Merida, Mexico, (*Accepted*)
- IV. Moisture Transport in Impregnated Concrete – Moisture Diffusion Coefficient, Modelling, Measurements and Verification**
Johansson, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., International Journal on Restoration of Buildings and Monuments, Vol. 12, No. 1, 2006, pp. 13-24.
- V. Moisture Fixation in Concrete Treated with a Water Repellent Agent**
Johansson, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., (*Submitted to Int. J*)
- VI. Sorption Isotherms of Water Repellent Treated Concrete**
Johansson, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., Proceedings, Hydrophobe V, Brussels, Belgium, April 15-16, 2008, pp. 261-271.
- VII. Preventing Chloride Ingress in Concrete with Water Repellent Treatments**
Johansson-Selander, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., Proceedings, CONSEC'10, Merida, Mexico, (*Accepted*)
- VIII. Decreasing Humidity in Concrete Facades after Water Repellent Treatment**
Johansson, A., Nyman, B. & Silfwerbrand, J., Proceedings, Hydrophobe V, Brussels, Belgium, April 15-16, 2008, pp. 379-386.
- IX. Long Term Performance of Water Repellent Treatment - Water Absorption Tests of Field Objects in Stockholm**
Johansson, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., International Journal on Restoration of Buildings and Monuments, Vol. 14, No. 1, 2008, pp. 39-47.

Anders Selanders' contribution to the publications with co-authors:

Paper I-VII and IX Major part of experiment, Major part of writing.
Paper VII Minor part of experiment, Major part of writing.

APPENDICES

The papers included in the thesis are presented in appendices I-IX. Additional data from the experiments presented in Paper I and Paper VI are presented in Appendix X and Appendix XI and will be referred to by their Roman number:

I-IX. Paper I – Paper IX

X. Experimental data, Paper I

Johansson, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., “Penetration Depth for Water Repellent Agents on Concrete as a Function of Humidity, Porosity and Time”, *International Journal on Restoration of Buildings and Monuments*, Vol. 13, No. 1, 2007, pp. 3-16.

XI. Experimental data, Paper VI

Johansson, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., “Sorption Isotherms of Water Repellent Treated Concrete”, *Proceedings, Hydrophobe V*, Brussels, Belgium, April 15-16, 2008, pp. 261-271.

CONTENTS

PREFACE.....	I
ABSTRACT	III
SAMMANFATTNING	V
LIST OF PAPERS	VII
APPENDICES	IX
CHAPTER 1 - Introduction	1
The importance of moisture content.....	1
Chemistry of alkylalkoxysilanes	3
The mechanisms of water repellent agents	5
CHAPTER 2 – Aim and limitation.....	7
CHAPTER 3 - Summary of methods	9
Penetration depth.....	9
Penetration profiles	9
Relative humidity	9
Moisture transport	10
Moisture fixation	10
Chloride ingress.....	10
CHAPTER 4 - The penetration phase.....	11
Decisive factors for the penetration of silanes into concrete	11
Effect of porosity, degree of saturation and time	12
Effect of different water repellent agents - silane	13
Describing the effective penetration depth mathematically	14
The importance of reaching a sufficient depth.....	15
CHAPTER 5 - Material properties.....	17
Moisture transport	17
Moisture fixation	19
CHAPTER 6 - Experiences	25
Water absorption and desorption.....	25
Chloride ingress.....	26
Changing humidity.....	27
Carbonation	29
Durability	29
CHAPTER 7 - Conclusions	31
CHAPTER 8 - Future research.....	33
CHAPTER 9 - References	35
Citations in the extended summary	35
Additional citations in Papers I-IX.....	44

CHAPTER 1 - INTRODUCTION

The need for protection of building materials against moisture has always existed and surface treatments have been used for thousands of years [1]. The option in the beginning was oil and fat and today we are using different types of coatings or hydrophobic impregnations. 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 ingress 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, eliminated or decreased. Hydrophobic impregnations have the highest ratio between breathability and reduction in water absorption in comparison with other surface treatments for concrete [2].

THE IMPORTANCE OF MOISTURE CONTENT

Fresh concrete basically consists of three parts; cement, aggregate and water. When the cement grains and water are mixed together a reaction starts called cement hydration [3]. Water is consumed during the hydration and a fine pore system forms during the process. The size and quantity of the pores 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 [4].

Porous materials will always contain a certain amount of water in their natural environment. 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 frost damages in concrete if the pores are saturated [5]. The alkali silica reaction (ASR) depends on the access of water [6] and the corrosion of reinforcement bars is affected [7]. 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 the rate of the degradation process. The importance of keeping the moisture below a certain critical level is well illustrated in Figure 1, when considering the reinforcement corrosion as the limit of service life for the concrete structure. 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.

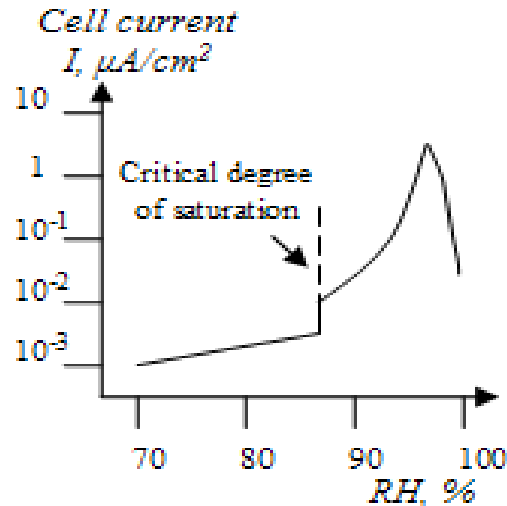


Figure 1: The corrosion rate as a function of RH for a concrete specimen with w/c-ratio 0.9 (after [7]). The experiments were conducted on carbonated concrete.

In new-cast concrete, the reinforcement is protected from corrosion by the alkali environment [8]. This may, however, slowly be altered by carbonation or chloride ingress. The initiation time until corrosion starts is affected by carbonation and/or chloride transport [7]. The diffusion rate of carbon dioxide and thus the carbonation rate are low when the moisture content is high. A summary of investigations conducted on carbonation rate as a function of RH is presented in [9]. The conclusion is that a maximum in carbonation rate is reached around 70 % RH. This value 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 [10]. The authors of [11] suggest that the diffusion coefficient (as a function of RH) for chloride ingress 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. Figure 2 illustrates schematically how the rates of the above mentioned processes depend on the relative humidity.

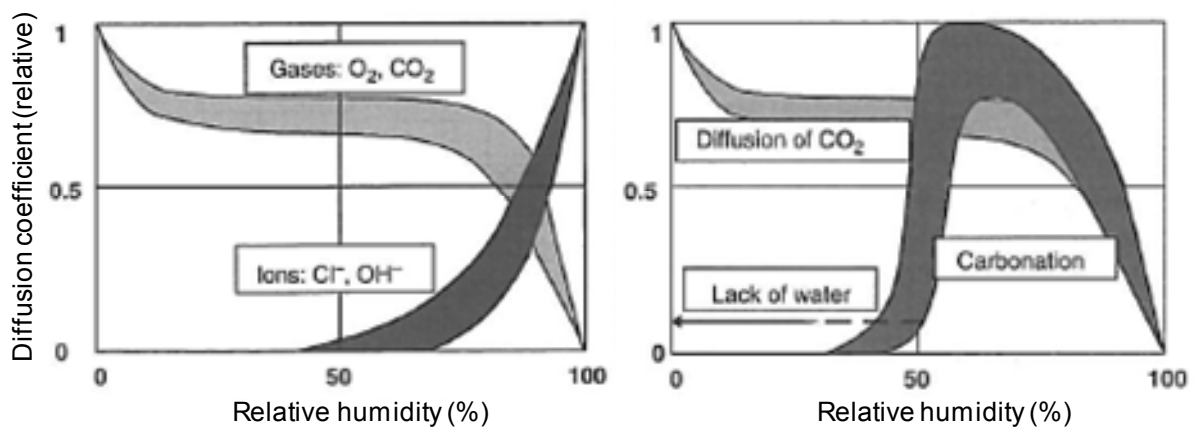


Figure 2: Simplified sketch of how the transport of ions and gases as well as carbonation depend on the relative humidity in the concrete [8].

In the service life model by Tutti [7] an initiation phase is defined as the time until the corrosion starts on the reinforcement bar and after that a propagation phase which last until a repair is necessary or the service life ended, see Figure 3 (left). The point of using a water repellent agent is to change the concrete properties in the surface layer and change the circumstances for the transport and fixation of moisture. The chloride ingress can be reduced if the water repellent agent is successfully applied during the initiation period. The effect during the phase of propagation can be, if applied in the right situation, that the concrete is dried out which results in a lower corrosion rate. This scenario is illustrated in Figure 3 (right) with the extended service life. The initiation as well as the propagation period is prolonged resulting in a longer time before the maximum allowed corrosion is reached. The effect in this scenario is then that the relative humidity decreases which in turn means that the chloride diffusion is slowed down. However, it also means that the CO_2 -diffusion and carbonation might go faster as illustrated in Figure 2. Several factors affect which one of these two factors (chloride ingress and carbonation) that sets the limit of the service life for the concrete structure.

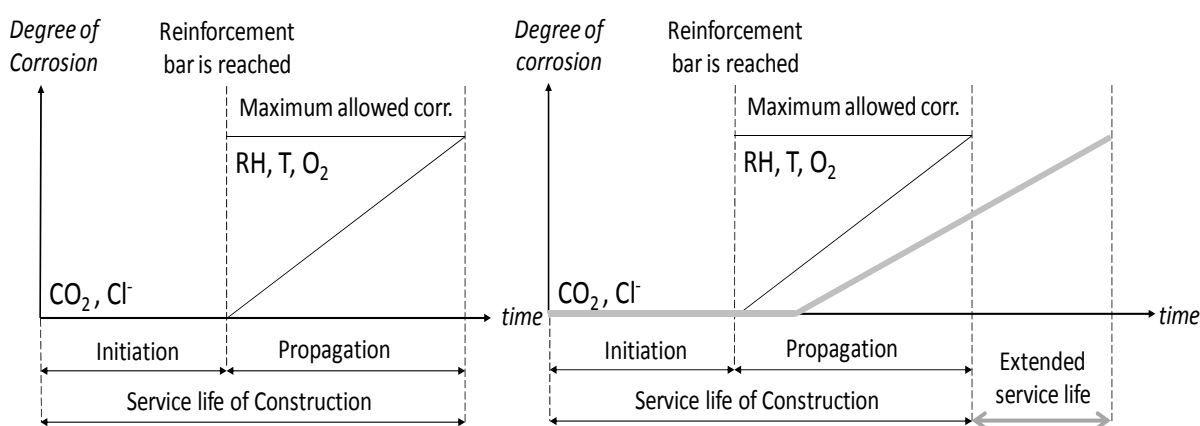


Figure 3: Service life model after [7] that describes the factors which affect the time of initiation and the time of propagation before the maximum allowed degree of corrosion is reached. The gray line on the right hand side represents the scenario of a successful water repellent treatment with the result of an extended service life of the concrete structure.

CHEMISTRY OF ALKYLALKOXYSILANES

Silanes or more correctly named alkylalkoxysilanes used today 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 [12]. 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 [13]. Figure 4 shows a schematic representation of the reaction. 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 form a fine network of polymersiloxane on the walls of the pores or a silicon resin. To what degree the network is chemically linked to the pore walls of the concrete is difficult to determine. In a study on water repellent treated limestone, brick and sandstone the chemically linked mass of polymerized material to the substrate corresponded to 0-48 % depending on the choice of silane and substrate [14]. The two different scenarios are presented in Figure 4 as (A) and (B) respectively. The stages in the reaction will be the same if the product is based on a siloxane.

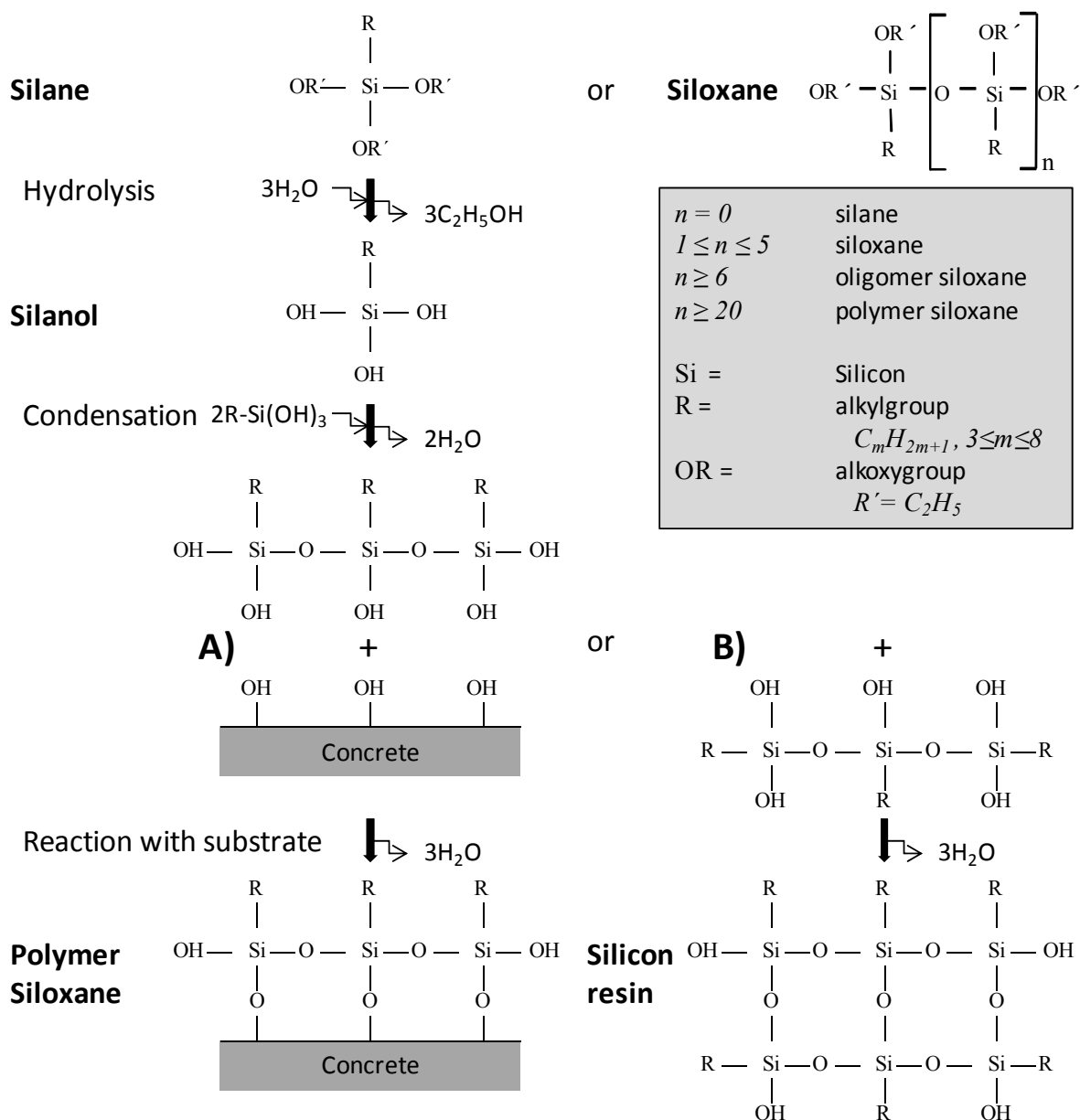


Figure 4: Reaction of an organofunctional triethoxysilane with the concrete matrix, based on [13, 15, 16]. Ethanol is liberated during the hydrolysis. A) and B) represent two different scenarios whereas a fine network of polymer siloxane on the pore walls forms (A) or a silicon resin (B).

When hydrophobic surface treatments were first introduced 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. Summarizing [17-19] where the influence of the size of the alkylgroup and the alkoxygroup on the reaction kinetics is studied, one can see that silanes with methoxygroups react significantly faster than those with ethoxygroups and that a big alkylgroup slows down the reaction as well. This can be explained with the different properties of the molecules such as energy and geometry of the molecular orbital [20]. Old concrete is often carbonated in the surface layer, meaning that the pH-value is lowered. A summary is presented in [21] on 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 [21], mean a

decrease in polymerization rate with a factor around 50. The risk for the reaction becoming too slow in carbonated and/or dry concrete is also pointed out in [22]. The influence of temperature, at the time of the application, on the effectiveness in terms of water absorption of the treatment is studied in [23]. The conclusions are that a high temperature 50-55°C results in a high polymerization rate and 0-5°C in a low rate of evaporation for the volatile silanes. Both scenarios results in a better performance than for the period in between. Which silane or siloxane that 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.

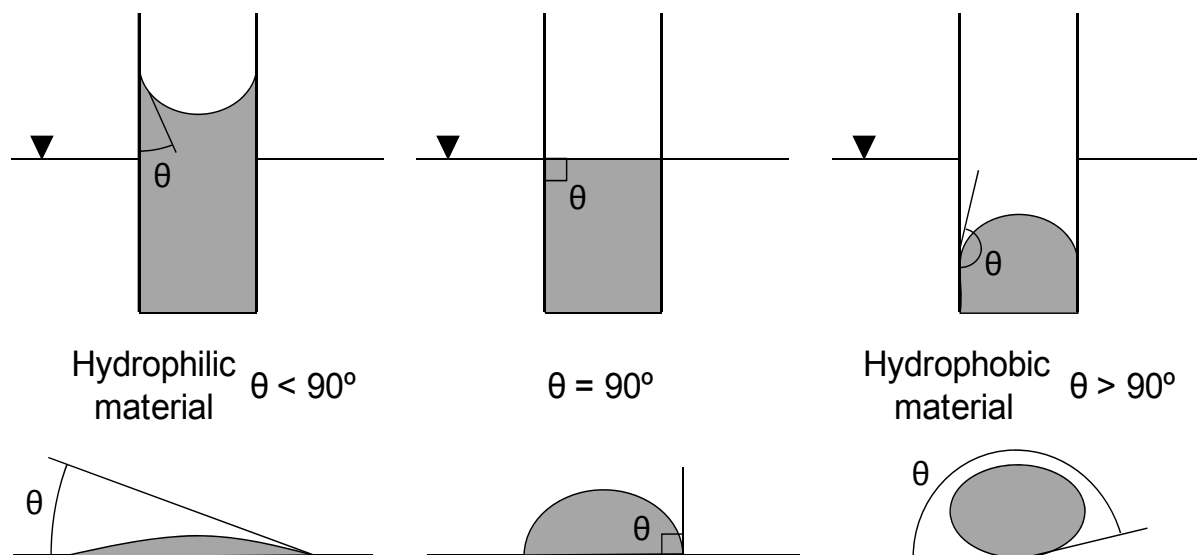


Figure 5: Illustration of the difference between a hydrophilic and a hydrophobic material by the means of a contact angle: on top capillary pores and underneath a water droplet [24].

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 [25].

CHAPTER 2 – AIM AND LIMITATION

The cost for operation, maintenance and reparation of bridges is very high globally. Just to repair the damages on Swedish bridges can be estimated to around 4 billion SEK [26]. Damages do not exclusively exist on bridges but also on other structures in exposed environments, such as harbors and tunnels exposed to deicing salts and several buildings in use for agriculture and industry. If a surface treatment can prolong the service life of a concrete structure it will lead to substantial savings of natural resources and thus both economical and environmental savings for the community. Hydrophobic impregnation of concrete with silanes and siloxanes has been shown to give a good protection and thereby prolonging the service life for the structure.

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 was to develop explanation models to the promising results that have been obtained from the empirical research during the last decades 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 focus in this project was set on existing products on the market, how they change the properties of concrete and how they should be used to optimize the outcome in terms of reduced water absorption and chloride ingress. The optimization of the molecules and the products has not been studied. Neither have the economical aspects of the treatment.

Impregnations and coatings are words which includes several different categories of products. Water repellent agents or hydrophobic impregnations are more specific and is normally used for silane- and siloxane-based products. Siloxane based products are referred to in the literature in this thesis but in the laboratory experiments, solely silanes or more specifically alkyltriethoxysilanes are studied. They represent the major part of the commercially available water repellent agents intended for concrete structures today.

CHAPTER 3 - SUMMARY OF METHODS

This chapter gives a short summary of the different experimental methods of significance used to obtain the results in the thesis. These methods are described in detail in the appended papers and a reference to a description of each method is given in the summary below:

PENETRATION DEPTH

The effective penetration depth of different treatments 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. This method has been used in most of the appended papers but is best described in Paper I. It is important to allow the silane or siloxane to fully polymerize before the specimen is cracked in order to get a reliable result. If it is difficult to see the line between treated and untreated concrete, a short period of drying before the measurement can facilitate.

PENETRATION PROFILES

The FTIR-spectrometer has been used to determine penetration profiles of water repellent agents in concrete. FT-IR stands for Fourier Transform InfraRed, where FT refers to the method used to interpret the results. This is the preferred method of infrared spectroscopy. In infrared spectroscopy, infrared radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission of the sample, creating a molecular fingerprint of the sample. This makes infrared spectroscopy useful for several types of analysis as for example organic materials in concrete. A specific peak in the resulting spectra, caused by the water repellent treatment, is identified and the area of that peak is related to the amount of the fully reacted water repellent agent present in the concrete. A calibration curve with known concentrations is necessary in this method. A thorough description of the method can be found in Paper II.

RELATIVE HUMIDITY

The measurements on relative humidity described in Paper VIII used moisture and temperature sensors of single-use type. During the first period reported in the paper, the measurements were manually performed while in the second period a monitoring campaign was executed with data logger as well as computer software. Additional humidity measurements have been performed with a protimeter in the CBI laboratory mainly to control the climate inside various climate boxes.

MOISTURE TRANSPORT

The moisture transport was measured with the cup-method. With a saturated salt solution inside the cup and a controlled environment, regarding RH and temperature, outside the cup the result is a steady state uni-dimensional flow of moisture. The moisture diffusion coefficient can then be calculated from the moisture flow. In order to obtain a continuous function of RH the Kirchhoff's flow potential was used in the calculations. The experimental setup is presented in Paper IV.

Tests on water absorption and capillary suction in different forms have been used in order to determine material properties or to evaluate the performance of water repellent treatments in several experimental setups. Two different methods are described in Paper I and Paper IX, respectively.

MOISTURE FIXATION

The moisture fixation in water repellent treated concrete was analyzed by the means of studying the sorption isotherms and comparing treated with untreated samples. Two different methods were used; the traditional way of climate boxes with saturated salt solutions and the DVS (Dynamic Vapour Sorption) - balance. These two methods are described in Paper V and Paper VI, respectively.

CHLORIDE INGRESS

Measurements of chloride content were carried out with an ion-selective-technique. In order to relate the content of chloride to the amount of cement gel, the results are expressed as percentage of cement weight. The mass of cement was calculated after a Ca-titration with EDTA (EthyleneDiamineTetraAcetate). This method is used in Paper VII.

CHAPTER 4 - THE PENETRATION PHASE

This chapter describes the factors affecting the outcome of a water repellent treatment in terms of concentration or depth. When a non reactive fluid such as water is applied on concrete the capillary rise can be described as a function proportional to the square root of time. This relation can be derived from a circular pore model with laminar flow [27]. If the fluid is reactive, such as a silane or siloxane on concrete, the capillary rise is almost proportional to the square root of time in the first few hours, but later on a deviation from a straight line can be noted [15]. This is explained by the polymerisation which increases the molecular weight and thereby the viscosity of the fluid. The capillary rise, which refers to the transportation during the treatment, is not same as the visual penetration depth.

The visual and effective penetration depth of the water repellent agent is not always the same in terms of water absorption, which is pointed out in [28], but closely correlated. However, the effective penetration depth is defined as a visual penetration depth in the European standard EN 1504-2 [29]. The distance from the treated surface to the sharp line between dry and wet concrete after it has been sprayed with water is the definition of the effective penetration depth. This is a measurement of the result of the treatment and it should be made after a few weeks when fully polymerised. The polymerisation rate of triethoxy(isooctyl)-silane was studied in [30] and the authors concludes that only 50 % of the theoretical amount of ethanol was liberated after 15 days. Figure 6 shows a photo of an effective penetration depth measurement.

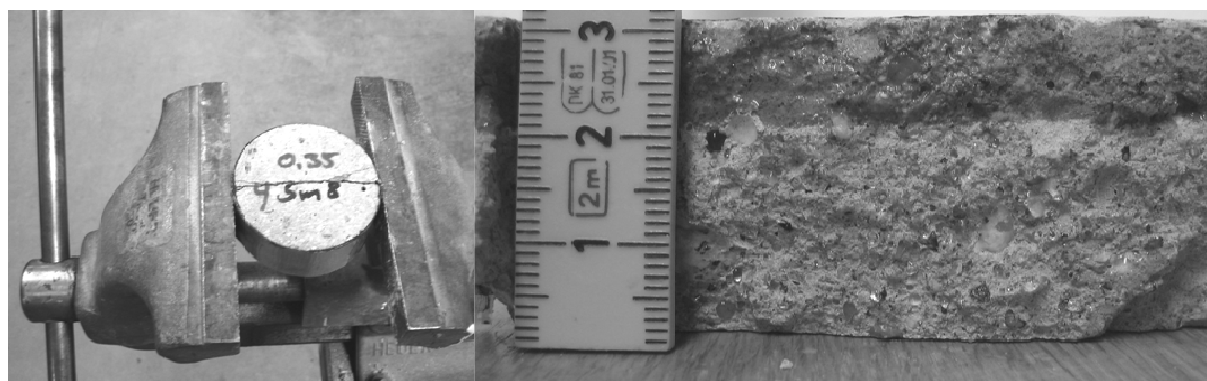


Figure 6: The effective penetration dept is the distance from the surface (bottom) to the sharp line between wet (dark) and dry (light) concrete. The penetration depth in this picture is 21 mm.

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 [31-35].

Among the results in [31] the ratio 30 should be mentioned as the relation between the highest penetration depth ($w/c = 0.70$ conditioned at 65% RH) and the lowest ($w/c = 0.40$ conditioned at 90 RH %). The combined 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. Paper I describes a laboratory study in which the influence of these three factors are quantified and expressed in an equation. Additional data to this paper is presented in Appendix X. A fourth factor is also considered, the influence of the water repellent agent itself. It can be concluded that the chemical reactivity and the molecule size of the water repellent agent also affect the penetration depth. All of these factors can of course be replaced by other similar and/or broken down into different subcategories, see for example [36].

Effect of porosity, degree of saturation and time

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 Figure 7 a clear time dependency is shown. 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/c is used initially as the parameter to represent the porosity of the concrete. Figure 7 (left) shows the difference between the four concrete types used in this experiment. While a water repellent treatment on concrete with $w/c = 0.8$ can show over 20 mm of effective penetration depth the equivalent treatment on $w/c = 0.35$ hardly shows any effect at all.

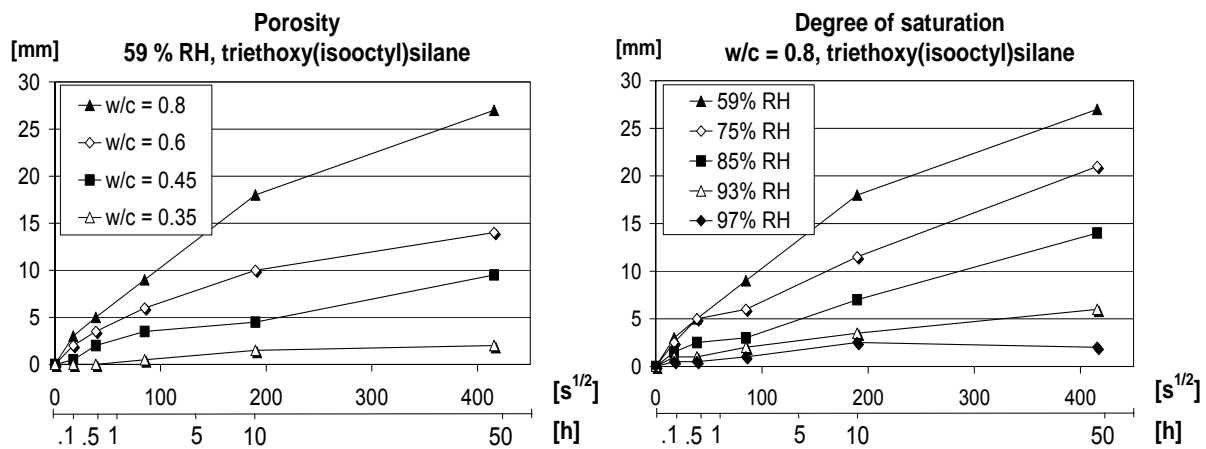


Figure 7: The influence of porosity, degree of saturation and time on the effective penetration depth. The time on the x-axis is the duration of contact for the treatment. The penetration depth is measured four months later (Paper I).

The third 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 7 (right) 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 approximately ten times higher if the RH is changed from 97 to 59 %.

Concentration profiles of water repellent treated concrete can be determined with FTIR (Fourier Transform InfraRed) – spectrometer. This instrument is used in Paper II and a full description of the method can be found in [37]. Figure 8 shows the penetration profiles for different durations of treatment. A longer duration of contact results in a higher concentration and depth. It can also be seen that a concrete with high porosity ($w/c = 0.8$) is easier to treat than one with a low porosity ($w/c = 0.45$).

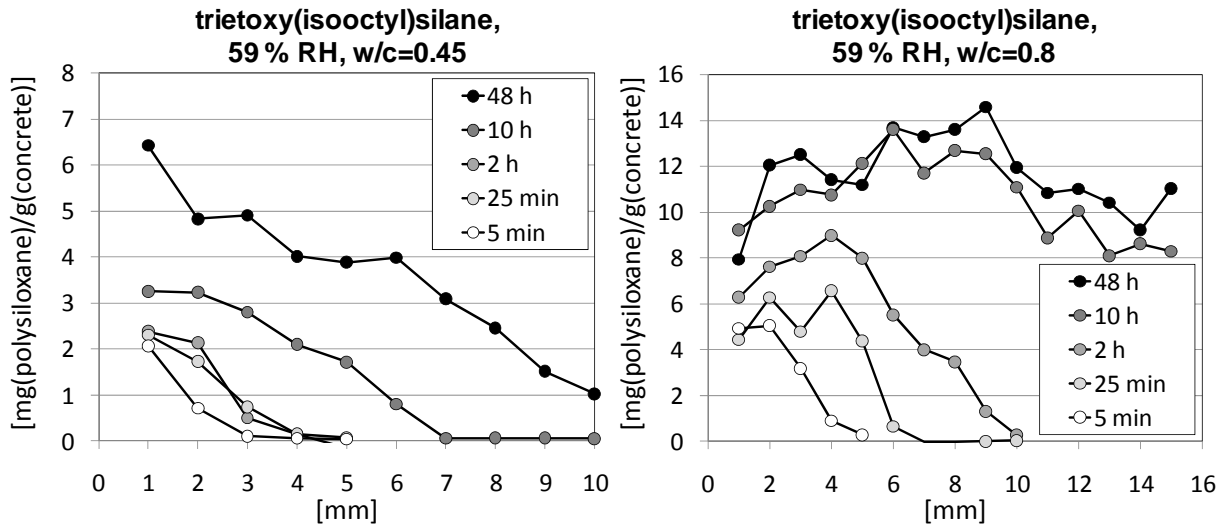


Figure 8: Penetration profiles of triethoxy(isooctyl)silane on concrete with $w/c = 0.45$ (on the left) and 0.8 (on the right) for different durations of treatment. The concrete samples were conditioned in 59 % RH before the treatment (Paper II).

The correlation between the visual penetration depth of the water repellent agent and the concentration is clear. The visual penetration depth of identically prepared samples in Paper II corresponds well to the approximate concentration of 1 to 2 mg polysiloxane/g concrete. In this experiment, the best correlation is given by 1.5 mg polysiloxane/g concrete. A slightly higher concentration is reported in [38], 2-4 mg polysiloxane/g concrete for triethoxy(n-octyl)silane in order to ensure a full effect in terms of reduction in water absorption.

Effect of different water repellent agents - silane

Figure 9 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.

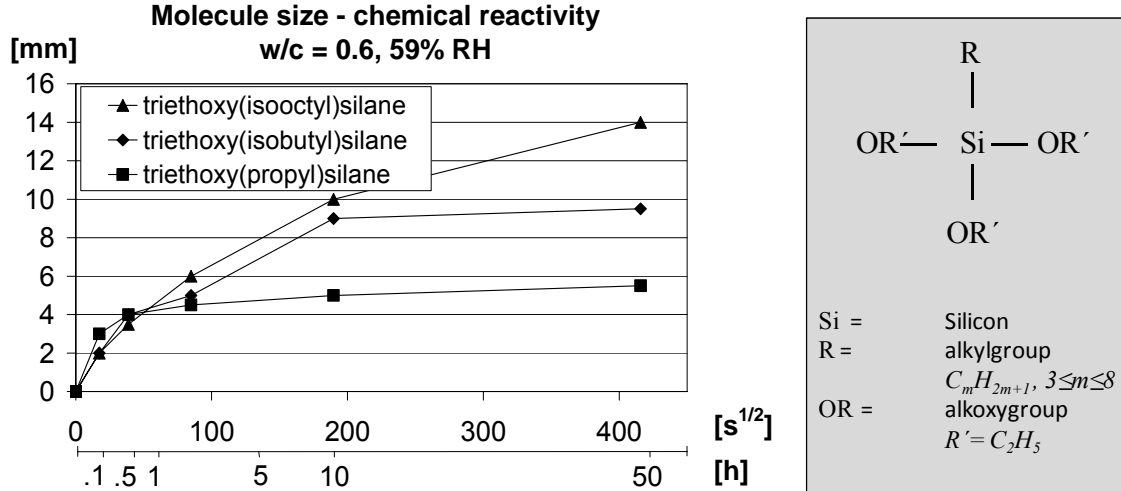


Figure 9: The penetration profiles of three different water repellent agents. The time on the x-axis is the duration of contact for the treatment. The penetration depth is measured four months later (Paper I).

Describing the effective penetration depth mathematically

Based on the results presented in Appendix X a semi-empirical equation is derived which describes how the efficient penetration depth depends on different factors. A full description of the derivation can be seen in Paper I.

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

where z [m] is the penetration depth; t [s] is the time; A [$\text{kg}/\text{m}^2\text{s}^{1/2}$] is the material property, called the sorption coefficient, used in this experiment to characterize the porosity of the concrete. The water cement ratio is a good way of estimating the porosity for most of the concrete types used today but there are still large variations especially for dense concrete with plasticizers. Since there are variations the choice fell upon using the sorption coefficient as a parameter to characterize the porosity of the concrete in the mathematical expression. C_1 and C_2 are empirically determined material parameters related to the water repellent agent used and they are presented in Table 1. It is important to emphasize that C_1 and C_2 in Equation 1 are evaluated at 20°C and for non carbonated concrete. If these two circumstance change they probably need to be modified. The degree of saturation is represented with the RH inside the concrete and numerically with the factor:

$[1 - \phi]$ where $\phi = v/v_s$ and v is the vapor content of air [kg/m^3]. Index s means saturated.

Table 1: C_1 and C_2 for different water repellent agents.

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

Concrete has a huge variation in material properties and the environmental conditions at the time for the treatment can change. It is difficult to derive an equation which can predict the penetration depth of a water repellent agent at every situation. Equation 1 should therefore just be used to illustrate how different factors affect the result and as a tool when choosing a suitable surface treatment. Table 2 shows some examples on how this can be done.

Table 2: Example of how Equation 1 can be used to evaluate the impact of different factors [39].

Factor	Change		Result (z)
	Before	After	
Time (t)	1 hour	5 hour	~double*
Porosity (A)	0.009**	0.018***	~double
RH	90 %	80 %	~double

*Only valid for triethoxy(isooctyl)silane.

**Corresponds to approximately $w/c=0.45$.

***Corresponds to approximately $w/c=0.55$.

It can be seen that by prolonging the treatment from one to five hours results in doubling the penetration depth which easily can be achieved for example by using an emulsion instead of a liquid [32]. It can also be noted that a decrease from 90 to 80 % RH would give the same result. Another example of the results from Equation 1 is shown in Figure 10. This mathematical description of the effective penetration depth need to be verified on field samples before it can be used as a general guideline but in current shape it still gives an idea of how much these parameters influence the penetration.

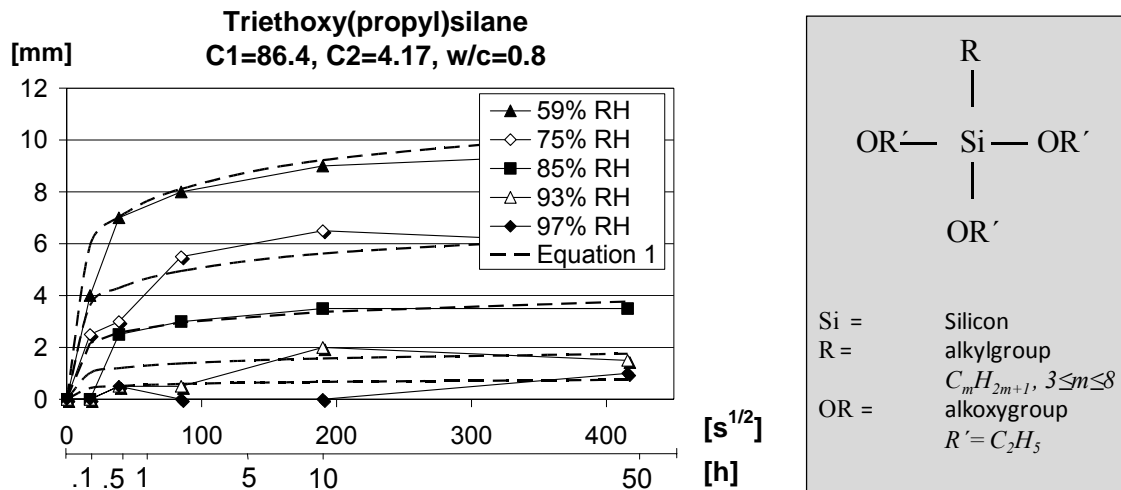


Figure 10: Example of how Equation 1 can be used with values from Table 1 on triethoxy(propyl)silane ($m=3$). The time on the x-axis is the duration of contact for the treatment. The penetration depth is measured four months later (Paper I).

THE IMPORTANCE OF REACHING A SUFFICIENT DEPTH

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. According to [40] a distance of 2 mm is required for a successful impregnation and according to [41] 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 [42] the authors conclude that 2-3 mm of penetration depth is not sufficient when narrow cracks of up to 0.2 mm are considered.

Figure 11 from Paper III presents the correlation between the effectiveness of the water repellent treatment and the penetration depth. It is clear that a high penetration depth means a good performance but it is not certain that a relatively low penetration depth means that the performance is poor but it is a clear risk. The spread in the results below 2-3 mm indicates this.

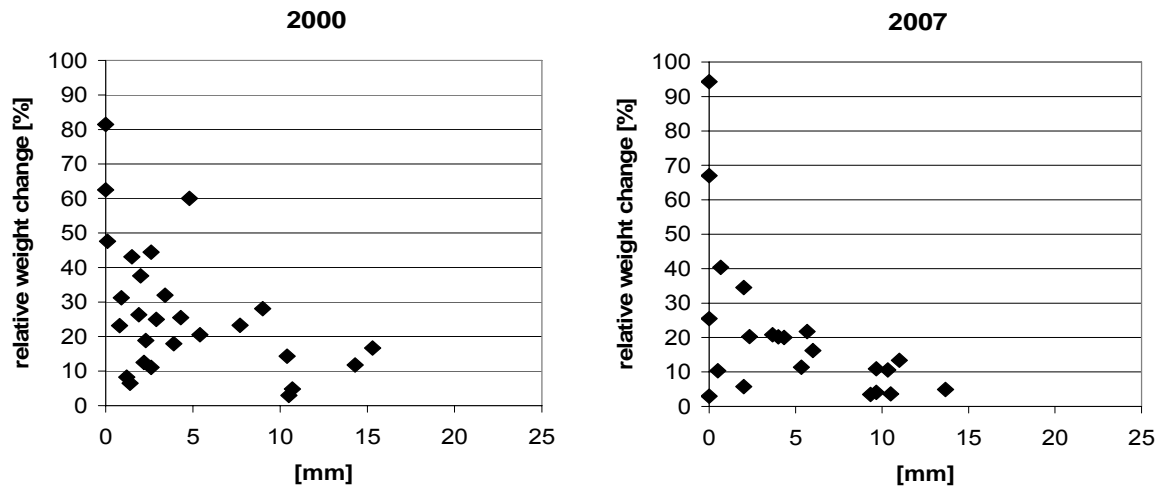


Figure 11: Results from Paper III based on water absorption tests on field objects in Stockholm. Average relative weight change for water repellent treated objects correlated to the penetration depth. Each point represents the average of three cores compared to its own reference.

CHAPTER 5 - MATERIAL PROPERTIES

This chapter concerns the change in material properties of concrete when it is treated with a silane based impregnation. It is important to state that the presented results and models in this chapter regard the material properties inside the hydrophobic layer and not a treated structure or structural member as a unity. Paper IV deals with the moisture transport through a hydrophobic layer, Paper V, Paper VI and Appendix XI deal with the moisture fixation inside a hydrophobic layer.

MOISTURE TRANSPORT

The material properties regarding moisture transport of untreated concrete are widely documented as can be seen in for example [43-46]. Several different mechanisms are involved in the transport of moisture in a porous material. A short summary of the basic theory of diffusion is given in [47]. For convenience in a hydrophilic material such as concrete it is often sufficient to describe the transport properties with the diffusion coefficient in Fick's first law in one dimension, steady state diffusion and isothermal conditions [48].

$$q = -\delta_v \frac{dv}{dx} \quad (2)$$

where q (kg/m²s) is the moisture flow, δ_v (m²/s) the diffusion coefficient and dv (kg/m³) the difference in vapour content over the distance dx (m). This diffusion coefficient is often presented as a function of RH. For low humidity levels the moisture flow is proportional to the potential difference in vapour content resulting in a constant diffusion coefficient. This is due to mainly vapour transport.

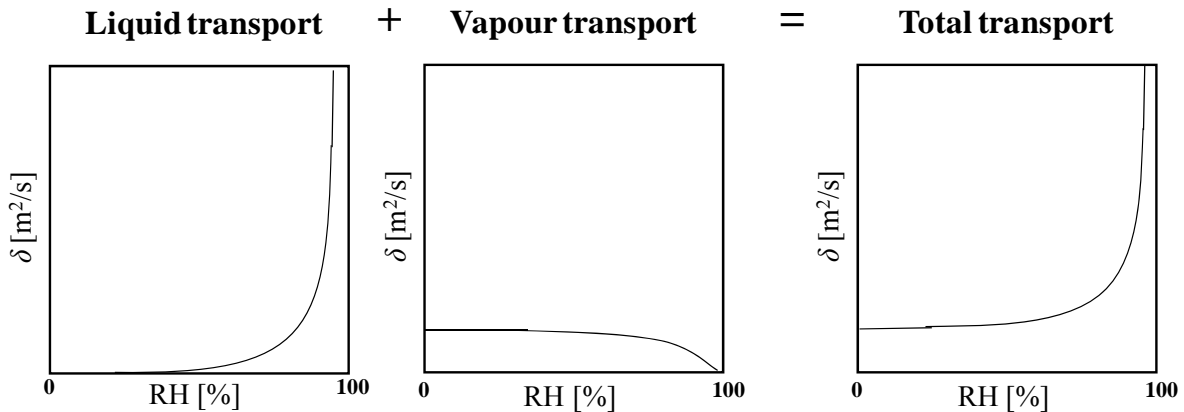


Figure 12: Simplified picture of the moisture diffusion coefficient for untreated concrete based on [49]. The total transport consists of a liquid and a vapour phase.

For high humidity levels where the concrete becomes close to saturation the main transport is in a liquid phase resulting in an exponential shape of the diffusion coefficient concerning its RH dependency. The exact shape of the curve varies with the pore structure and total porosity of the concrete. A simplified picture of the moisture diffusion coefficient or permeability, where the total transport is divided into a liquid and a vapour phase, is shown in Figure 12.

However, less research has been conducted to the influence of a water repellent treatment on the moisture transport mechanisms. Hence, in order to understand the mechanisms of water repellents it is important to study how the moisture diffusion coefficient is affected by a hydrophobic treatment. The moisture transport was measured with the cup method [43, 50]. The decision to use this method and not the drying and inverse method¹ [51] is that no assumptions are needed regarding the shape of the relationship between the coefficient and the RH. Figure 13 shows a drawing of the cup used in the experiments.

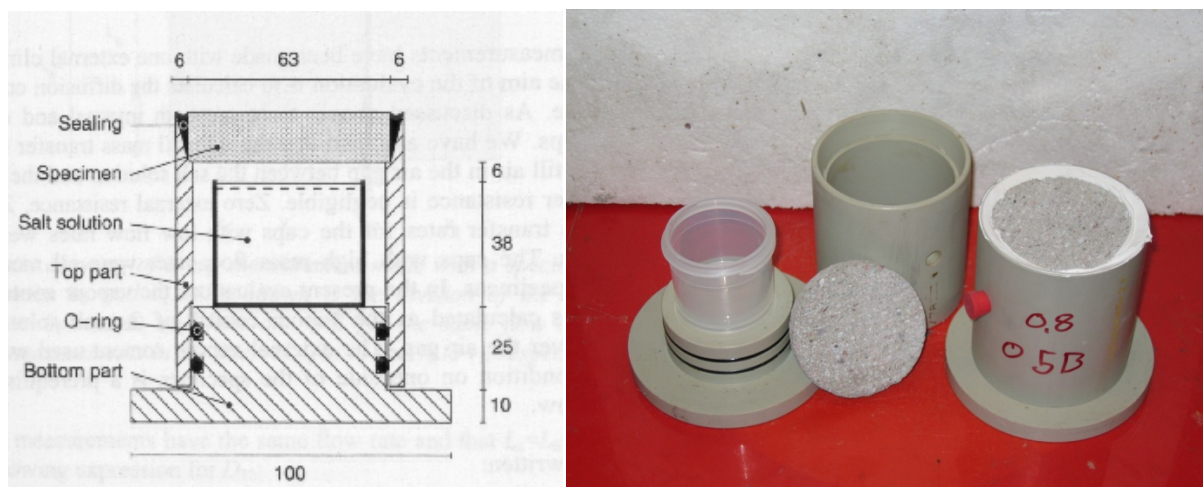


Figure 13: A drawing of the cup used in the experiments, measures given in mm [52] and a photo of the same.

With a saturated salt solution inside the cup and a controlled environment, regarding RH and temperature, outside the cup the result is a steady state uni-dimensional flow of moisture. Equation 2 can then be rewritten with a known thickness of the plate and known vapour content in the air:

$$q = -\delta_v \frac{\Delta v}{\Delta x} \quad (3)$$

The diffusion coefficient can then be calculated from the moisture flow. 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. 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 [43, 50] to obtain a continuous function of RH. The later was used in Paper IV.

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.

The approach in Paper IV is to create a so called two layer model. The first step is to establish the material properties of the untreated and the impregnated layer separately. In the discussion part of [15] a minimum amount of water repellent agent, necessary to obtain an efficient treatment, is defined based on the capillary water uptake and measurements of concentration with FTIR-spectroscopy. A similar experiment is presented in [35] but with an effect criterion instead of concentration. A possible way of interpreting these results are that, as long as a minimum amount of polymer siloxane/silicon resin is respected inside the specimen, the properties of the treated layer of concrete, regarding moisture transport, will remain approximately the same.

The second step is to verify the accuracy of the obtained results. In Paper IV, this is done for conditions of low relative humidity (RH) and a one dimensional isothermal steady state flow. The verification process is fully described in Paper IV. The deviations between calculated and measured values are within 8 % which indicates that the method works.

The results obtained and presented in Paper IV and [25] indicate that the moisture diffusion coefficient is almost constant for water repellent treated concrete on the contrary to the exponential behaviour of untreated concrete. This means that the liquid transport is reduced to almost zero. The field study in Paper III and Paper IX indicate that water absorption can be reduced up to 95 % in capillary transport under the right conditions which correspond well to this observation. The vapour transport is reduced as well but the hydrophobic layer is still open to diffusion and it is the governing transport mechanism even at high humidity levels. Figure 14 illustrates this.

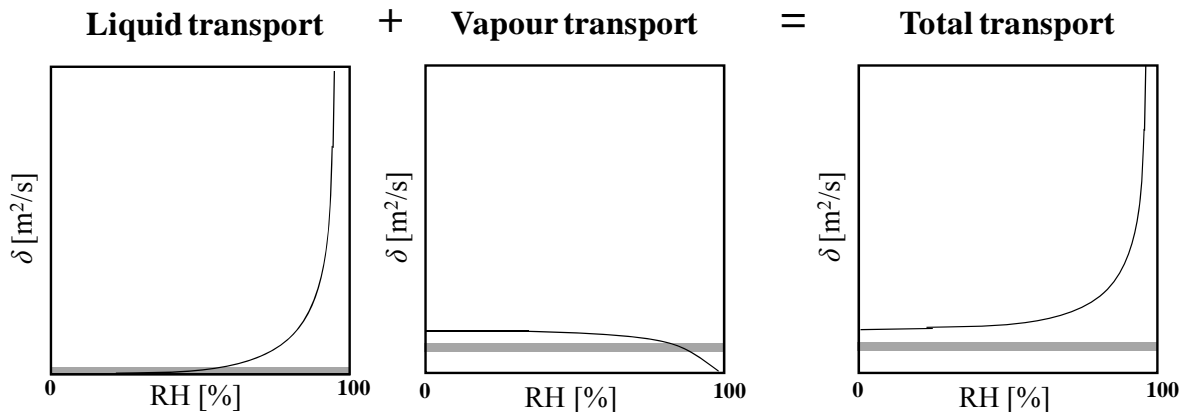


Figure 14: Simplified picture of the moisture diffusion coefficient for untreated concrete (black line) based on [49] and treated (grey line) based on Paper IV. The total transport consists of a liquid and a vapour phase.

MOISTURE FIXATION

Concrete is a porous and hydrophilic material. As such a material it contains a certain amount of moisture depending on the surrounding environment, regarding moisture content. 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, adsorption and capillary condensation inside the concrete. 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. Moisture fixation presented as sorption isotherms are well documented in the literatures for different types of concrete as can be seen in for example [54-58]. The isotherms however, are different depending on whether equilibrium is reached by absorption (involving both adsorption and capillary condensation) or desorption [27]. 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 15). 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.

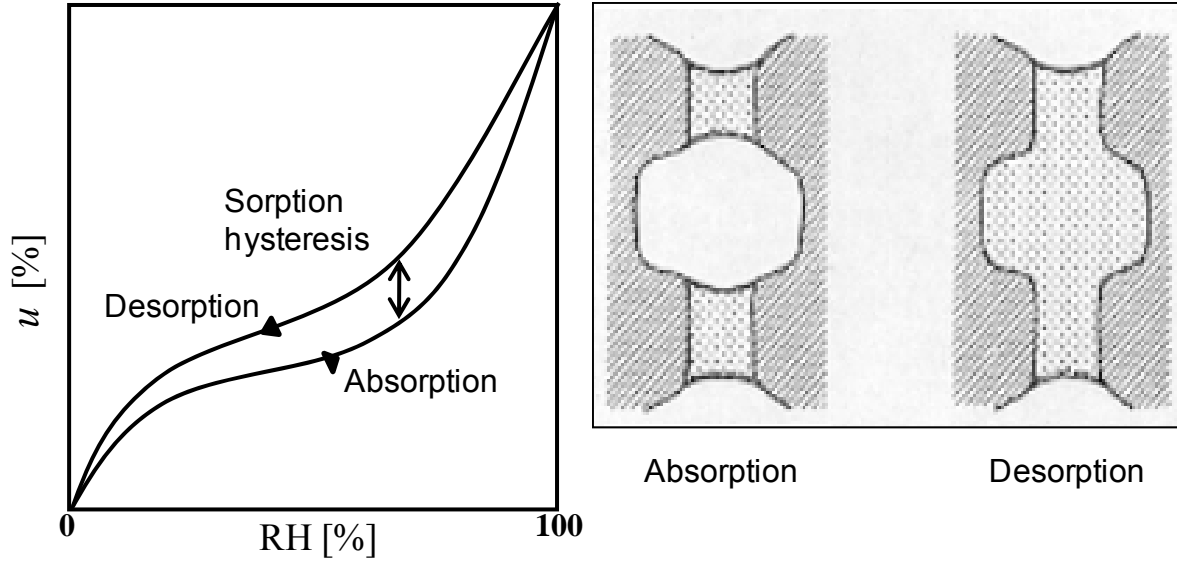


Figure 15: Principle shape of the sorption isotherms for concrete and a possible explanation to the gap between the absorption isotherm and the desorption isotherm referred to as the sorption hysteresis [27]. u is the moisture content in percent of dry concrete.

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 [53] (see Equation 12). 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 if we just consider the capillary condensation.

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

$$h = \frac{p_m}{\rho_f \cdot g} \quad (4)$$

where ρ_f is the density of the fluid [kg/m^3], g is the acceleration of gravity [m/s^2] and p_m [N/m^2] is the curvature pressure for the meniscus according to Laplace’s formula [59]:

$$p_m = \sigma \cdot \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (5)$$

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/m²] over the height Δz [m], i.e.,

$$\Delta p = -\rho_g \cdot \Delta z \cdot g \quad (6)$$

where ρ_g is the density of the gas [kg/m³]. With the use of the ideal gas law ρ_g can be expressed as

$$\rho_g = \frac{p_g \cdot M_g}{R \cdot T} \quad (7)$$

where p_g is the partial pressure of the gas [N/m²], M_g = molar mass of the gas [mol], R = molar gas constant [J/mol K] and T = temperature [K]. Combining Equation 6 and Equation 7 gives a differential equation which can be solved by separation assuming isothermal condition

$$\frac{dp}{dz} = -\frac{p_g \cdot M_g \cdot g}{R \cdot T} \quad (8)$$

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 8 becomes

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{M_g \cdot g \cdot h}{R \cdot T} \quad (9)$$

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 10

$$\phi = \frac{p_v}{p_{vs}} = \frac{p_2}{p_1} \quad (10)$$

Combining Equations 4 and 5 with 9 and 10 gives us the Kelvin equation

$$\ln(\phi) = -\frac{\sigma \cdot M_w}{R \cdot T \cdot \rho_w} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (11)$$

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 state when the meniscus forms for a specific pore radius as a function of the relative humidity in the surrounding air:

$$r = -\frac{2 \cdot \sigma_w \cdot \cos \theta \cdot M_w}{\ln \phi \cdot R \cdot T \cdot \rho_w} \quad (12)$$

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/m³]

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 $\theta = 0$ which is the usual simplification [53].

Figure 16 presents results from Paper V. On the y-axis the moisture content is presented as a function of the RH (x-axis). The sorption isotherms for the untreated concrete show a familiar shape while the water repellent treated shows a somewhat different shape. Below 50 % RH there is hardly any difference between the treated and the untreated isotherms. The size of a silane molecule is in the range of 10 Å (1 nm) [60]. Wittmann et al. [61] refer to a diameter slightly exceeding 2 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 12, 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 which also can be seen in Figure 16.

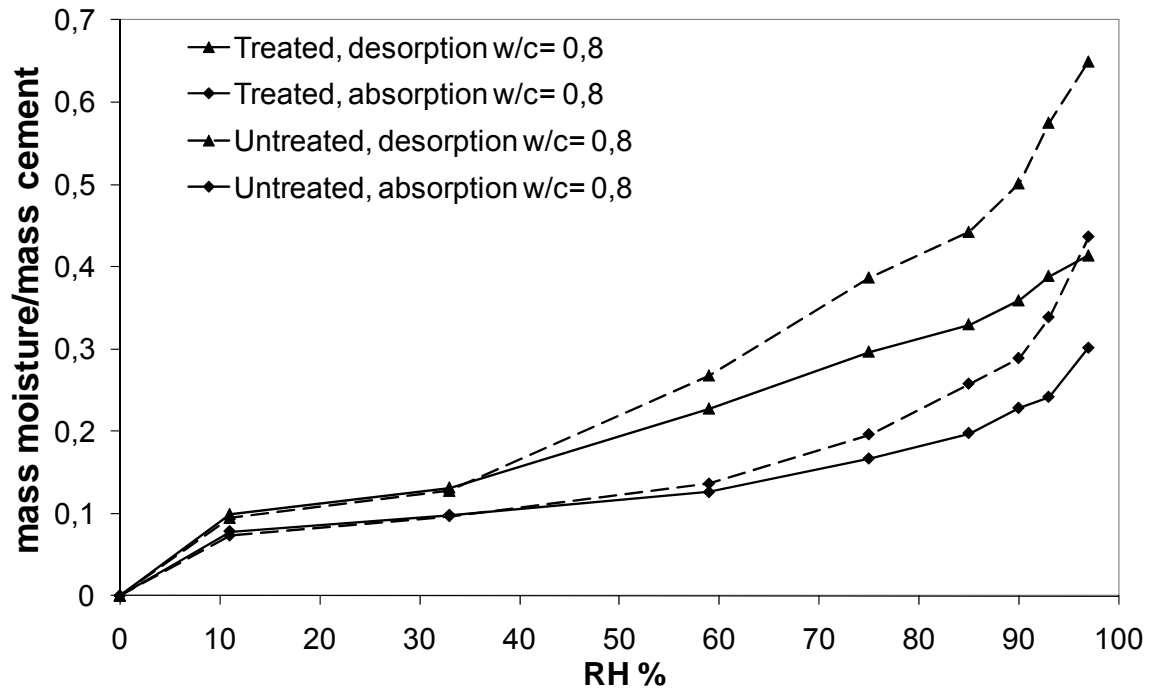


Figure 16: Sorption isotherms of concrete with $w/c = 0.8$, untreated and treated with a water repellent, triethoxy(isooctyl)silane. Samples were conditioned for one month in 70 % RH prior to the water repellent treatment.

Above 50 % RH where the capillary condensation is the dominant mechanism, the effect of the water repellent treatment is clear and a significant portion of the absorption of the moisture is prevented. Similar conclusions are drawn in [61] and [62].

Figure 17 illustrates an example of what happens when a water repellent agent is applied to concrete conditioned at different relative humidities. 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 Figure 17). The one exception corresponds to the concrete conditioned at 97 % RH, where the deviation starts at around 80 % RH and that can be attributed to boundary effects which are described in Paper VI. 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.

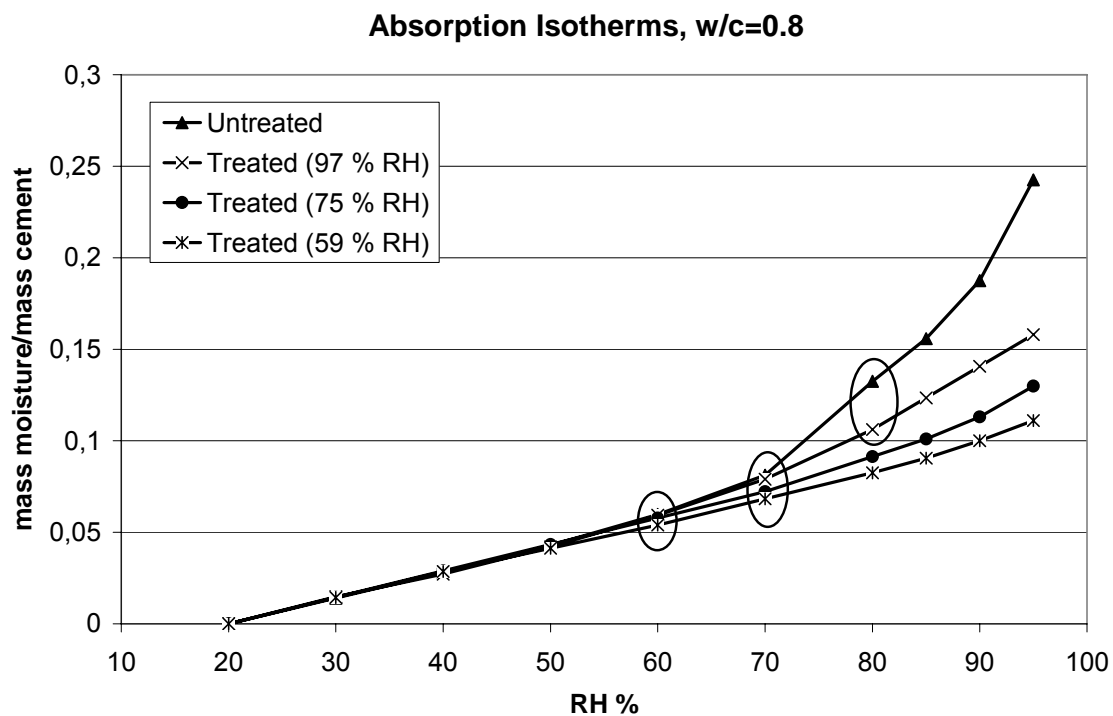


Figure 17: Sorption isotherms of the concrete with $w/c = 0.80$, untreated and treated with a water repellent, after the adjustments. The rings show where the isotherms separate. The isotherms are adjusted in accordance with the description in Paper VI.

Paper I shows that it is almost impossible to impregnate a saturated concrete. This means that the silanes will not enter a pore filled with water. If we use the correlation between the pore radius and the relative humidity in Equation 12, then it is possible to determine which part of the pore system that can be reached, given the humidity level inside prior to the treatment. Combining this with the knowledge about the interaction radius of the silane described above makes it possible to draw up a hypothesis which is shown in Figure 18. It is based on Equation 12 which describes capillary condensation and a cylindrical pore model. The sorption isotherms are not affected by the water repellent treatment below 50 % RH and the point where the deviation from an untreated sorption isotherm occurs correspond approximately to the RH inside the concrete at the time of the treatment.

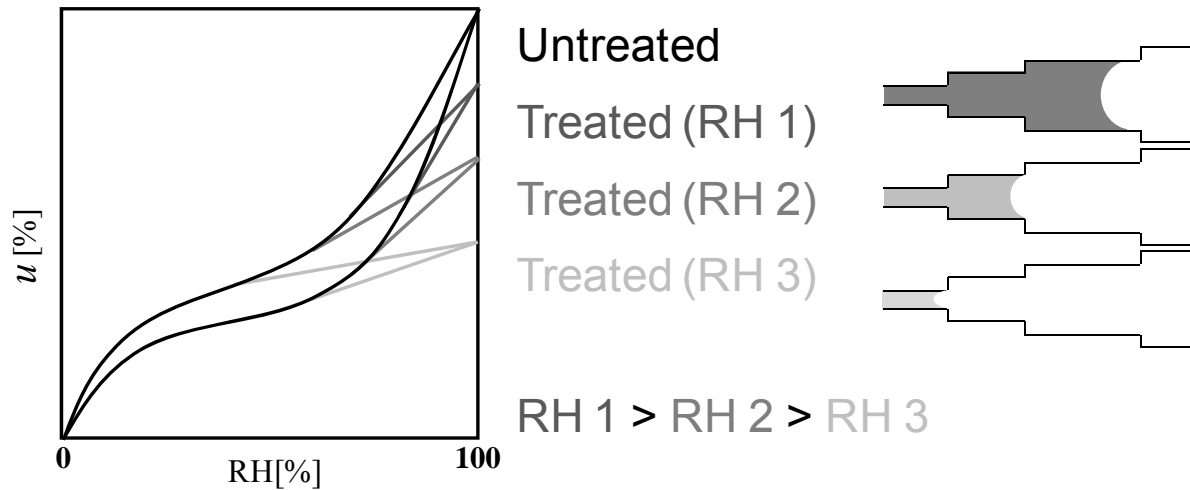


Figure 18: Model on moisture fixation based on the results in Paper V and Paper VI and the correlation between relative humidity and pore radius presented in Equation 12. The capillaries on the right hand side illustrate the pores in which a meniscus has formed at a certain relative humidity (RH).

The amount of moisture inside the treated layer is an important factor when the water repellent treatment's effect on the transport mechanisms in concrete is analyzed. In some models the assumption of totally dry or very low moisture content is used for the calculation of carbonation [63] and drying [51]. This seems to be the general view as well. The results presented Paper V suggest that the moisture content in the treated layer is higher than previously believed. However, the result does not give any information about the mobility of the moisture and whether there is a continuous fluid phase or not inside the treated layer of concrete. If the results presented regarding moisture fixation are compared with the results regarding moisture transport in Paper IV it is clear that the transportation of moisture is affected more than the fixation of moisture by a water repellent treatment. A possible explanation for this is that there is a significant amount of moisture present inside the treated layer but there is not a continuous fluid phase. This fact prevents the capillary suction inside the concrete and the only transportation that takes place is gaseous diffusion, which also explains why the transport would be reduced.

CHAPTER 6 - EXPERIENCES

The application and the factors affecting the outcome of a water repellent treatment in terms of concentration or depth are described in CHAPTER 4. The change in moisture transport and fixation which explains the different behaviour of water repellent treated concrete, as compared to untreated, is described in CHAPTER 5. This chapter on the other hand deals with the practical experiences of different surface treatments in field as well as in laboratory regarding the actual effects of water repellent treatments. A major part of the research conducted on water repellent treatments of concrete and natural stone can be found in the proceedings of the series of Hydrophobe conferences [64-68]. Based on these, the papers presented in this thesis and a literature survey the following topics are identified and described: (i) water absorption and desorption, (ii) chloride ingress, (iii) changing humidity, (iv) carbonation and finally (v) durability of water repellent treatments.

It is also important to emphasize that the evaluation of hydrophobic impregnations should be divided in to either the absence or the presence of active agent. This should always be verified by measurements of depth or concentration which are of great importance for the function of the treatment, see for example Paper III. It is difficult to achieve a sufficient penetration of active agent in some situations but the evaluation should not start with the question; do hydrophobic impregnations work, but rather; did this hydrophobic impregnation succeed (measured by depth or concentration)? If so, how did it perform?

WATER ABSORPTION AND DESORPTION

Reduction of water absorption is the main feature of hydrophobic impregnations and also one of the most evaluated properties when considering the effectiveness of the treatment. These tests can be performed in several different ways and in the literature one can find reduction percentages between 70 and 99 % depending on a number of different parameters as for example in [69-72]. In Paper III, with a few exceptions, 3 mm of penetration depth meant that the water absorption was reduced with more than 70 %. These samples were conditioned in 65 % RH prior to the test which suggests that the percentages would be even higher if a dryer conditioning environment would have been used.

As described previously the main transport through a hydrophobic layer is gaseous diffusion. This means that the transport is reduced in both directions (from the surface to the interior part and the opposite). This is also well documented in the literature. A significant reduction in drying rate due to a water repellent treatment is reported in [73] and [74] for example.

CHLORIDE INGRESS

A closely related property to the reduction in water absorption is the reduction in chloride ingress. Deicing salts containing chlorides are used all over the world whenever there is a risk for temperatures below zero and many concrete structures are exposed to sea water. The needs for preventive measures against chloride ingress are therefore immense. 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 PhD-project. The first aim is to measure if, and if so how, the properties of a water repellent treatment changes over time. The second aim is to evaluate the short term effect for a treatment which just barely meets the requirements of the Swedish Road Administration [75]. The 75 mm cubic concrete samples with $w/c = 0.45$ were treated with triethoxy(isooctyl)silane in liquid form on the exposed surface. The remaining five sides were sealed with neoprene film. The effective penetration depth was measured to 2-3 mm on two samples. Chloride profiles are evaluated continuously since 2005. Figure 19 shows pictures from the tunnel and the samples placed there. The field exposure site is located some 50 m from the entrance of the tunnel. The first samples were placed in the tunnel in November 2004.



Figure 19: 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.

Figure 20 shows the penetration profiles after exposure in the tunnel. The water repellent treatment reduces the chloride ingress significantly. It can also be seen that the so called “wash out”-effect, normally caused by rain but inside this tunnel caused by splashing water from the cars, has no apparent effect on the treated samples. The chloride concentration reaches its maximum closest to the surface for the treated samples while the peak for the untreated is shifted some five millimeters inside. Measurements with phenolphthalein as a pH-indicator gave no indication of carbonation. The visual effect of the water repellent treatment on the surface had disappeared already after one year of exposure due to dust and particles. When the samples were analyzed, however, it was easy to see the hydrophobic effect just below the surface. It appears to be the same still after five years in the harsh environment of the tunnel. The chloride ingress is significantly reduced by the water repellent treatment. A simple integration of the area below the chloride penetration profiles indicates that the treatment has reduced the ingress by 70-80 %. Similar results are presented in for example [76, 77] and [78]. The later is based on an extensive literature survey in which the correlation between water absorption and chloride ingress also is mentioned.

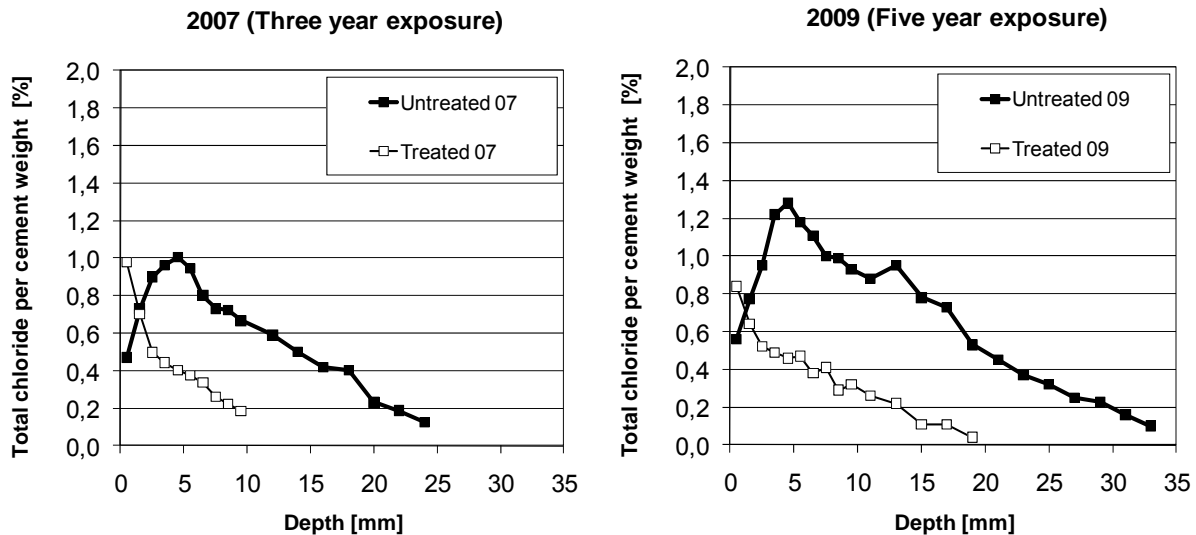


Figure 20: Chloride profiles after three and five years of exposure in the Eugenia tunnel, Paper VII. The samples are analyzed in the first part of autumn and the tunnel is washed twice every year as a part of a maintenance program according to the Swedish Road Administration.

A higher ratio weight gain/chloride ingress for silane and siloxane treated concrete surfaces is reported from a laboratory study presented in [79] when compared to other surface treatments. This is an effect of their high breathability. The chloride ingress is reduced while still open to gaseous diffusion resulting in a measurable weight gain. The effect of crack formation on the effectiveness of the surface treatment is studied in [42] and [80] and their main conclusion is that a crack forming after the treatment and with a depth that exceeds the thickness of the hydrophobic layer is a risk which has to be taken into consideration.

CHANGING HUMIDITY

Changing humidity inside concrete can affect several processes as described in the CHAPTER 1.



Figure 21: Photo of the 81 m high “Tax Scraper” in Stockholm (<http://sv.wikipedia.org>).

A water repellent treatment can change the humidity but it is important to know the source of the moisture before the water repellent agent is applied in order to predict the outcome. A reduction in humidity can for example reduce the corrosion rate in a specific situation while an increase might speed it up. The “Tax Scraper”, see Figure 21, described in Paper VIII is an illustrative example on how different situations can affect the outcome of the treatment. Figure 22 illustrates the difference between the north and the south side of the building. The dominant wind direction is southwest for Sweden. However, Stockholm is situated on the east coast and the wind direction is not as pronounced as on the west coast giving all the facades of the building a similar wind exposure. There is a difference in sun exposure though especially during spring which could explain the difference between the north and the south side. The south side illustrates the potential reduction in humidity which can be achieved with a hydrophobic impregnation. The north side on the other hand illustrates how important it is to analyze the situation before a decision on a surface treatment is taken. Especially the source of the moisture is pointed out in [81].

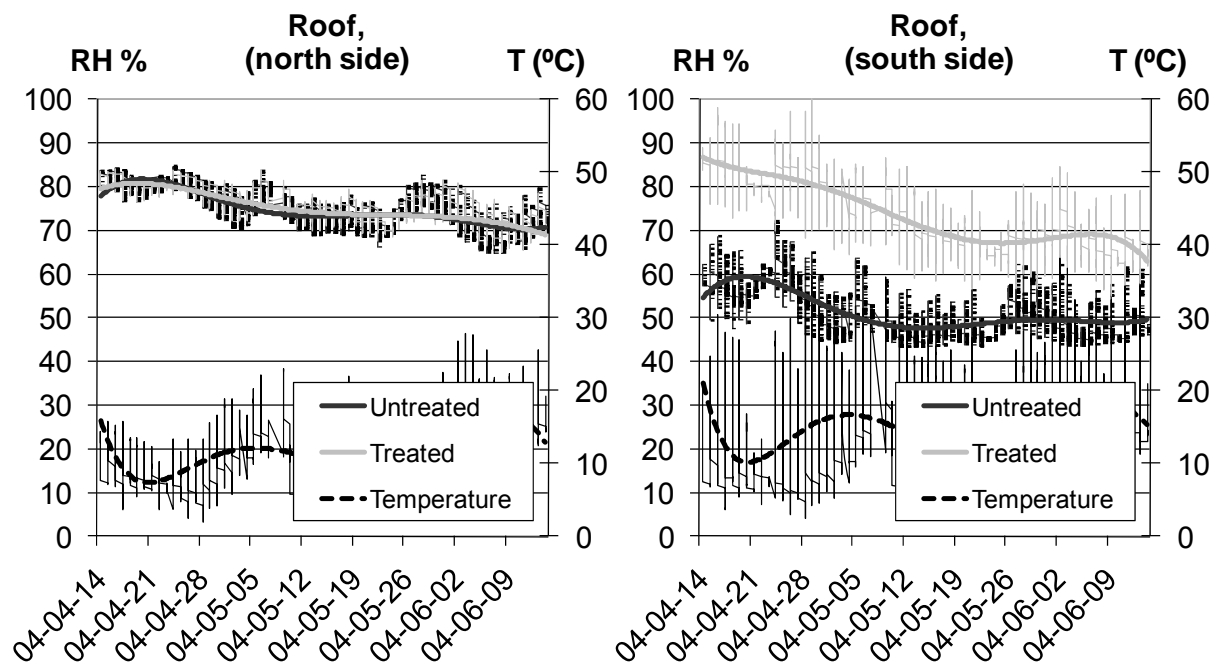


Figure 22: Measurements on relative humidity on the “Tax Scraper” in Stockholm, Paper VIII. The difference was not as pronounced during a manually performed test period a year earlier.

A dry out effect similar to the one seen on the south side of the “Tax Scraper” is reported on brick masonry in [82]. The mean moisture content of 13 % was reduced to 3 % by a water repellent treatment. In a laboratory study on reinforcement corrosion with 2 % chlorides in the mixing water a significant reduced rate of corrosion was observed during wet and dry-cycles. The authors explain the results with a dry out effect caused by the triethoxy(isobutyl)silane.

The risk for entrapment of water is of course present and as reported in [73] and [74] the drying is slowed down by a hydrophobic treatment which means that with a moisture source behind the hydrophobic layer, the humidity level can increase.

CARBONATION

The carbon dioxide diffusion through a hydrophobic layer and the subsequent carbonation rate is not significantly affected by a water repellent treatment. This is the conclusion in a literature survey by Basheer et al. [78]. Hydrophobic impregnations do not offer any resistance to carbon dioxide diffusion or carbonation when a treated structure or structural member as a unity is considered. There is however a slight decrease in degree of carbonation inside the hydrophobic layer. Polder et al. [84] report from a study in various climate conditions where no increase in carbonation was noted due to the water repellent treatment.

Whether the carbonation will go faster or slower due to a hydrophobic treatment depends entirely on the humidity level inside the concrete and how it is affected by the treatment. In for example [85] an increased carbonation rate is observed in a field exposure site in a marine environment. After 12 year exposure, the treatments are functioning well and a significant reduction in chloride ingress is also observed. Among the conclusions of Schueremans et al. [85] one can find that the reduced moisture content has increased the carbonation rate.

In a situation where a surface treatment is considered it is wise to analyze the structure to determine if any side effects, such as increased carbonation rate due to a decrease in humidity, could cause problems. Figure 2 in CHAPTER 1 illustrates how a changed humidity level could affect the carbonation rate.

DURABILITY

The long term performance or durability of water repellent treatments is not well documented in the literature. Several reports exist where treatments are functioning well several years after the treatment but they are rarely compared with the function right after the treatment was applied. Material properties are often measured in laboratory conditions relatively short after the treatment or after several years of exposure in harsh environment. The combination is difficult to find in the literature which means that it is almost impossible to determine whether the performance changes over time or not.

In order to avoid confusion regarding the topic durability it is divided into surface and in depth effects:

The surface effect in terms of visual effects or measurements of contact angle disappears within a few years, normally within the first year after the treatment. This is due to several reasons such as dust and particles, UV-light and abrasion. The rate depends on the environmental and mechanical loadings. Klugt and Koek [86] report that the surface effect disappears after a few years. This was also noted in Paper VII and Paper IX whereas no water repellent effect could be seen on the surfaces after field exposure. The effect in terms of reduction of chloride ingress and water absorption, however, was still there. The effect of UV-light on the treatment is reported to be negative in [87] and [78]. Büttner and Raupach [88] conclude that the UV-light has a negative effect in terms of contact angle based on an accelerated test method and also that there is no correlation between the reduction in contact angle and the water absorption.

Questions about the combination of graffiti protection and hydrophobic impregnation were studied by Stockholm Konsult and the results were presented in an article by Nyman [89]. 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 treatment, the

penetration depth was decreased. The effects of graffiti removal on concrete was recently studied in [90] 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 in depth effect is not sensitive to the same factors as for the surface effect described above. As a matter of fact, most reports in the literature indicate that if the surface treatment performs well right after the treatment and if it has a sufficient penetration depth (different requirements in different situations) the effect will be long lasting. The experiences in Stockholm of hydrophobic impregnation as a protection against salt and water are good according to [87]. Paper VII and Paper IX indicate the same. If the concrete is protected from external water and salt, the risk for damages can be significantly reduced. Specially exposed parts of the structure should therefore be treated with a water repellent agent on the surface [87]. This corresponds with the recommendations of the Swedish Road Administration [91]. The hydrophobic impregnations in the Eugenia tunnel, reported in Paper VII, show no indication of reduced function after five year exposure. In a field exposure site in a marine environment [85] the same observation is made after 12 year exposure. The treatments are functioning well and a significant reduction in chloride ingress is observed. Great Britain has a long experience and skill within the area of repairs and maintenance of concrete structures. According to [86] silanes and siloxanes have been used with success as breathable surface protection systems 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) [93-95].

Hoppe and Varkevisser [96] report on the monitoring of an alkali- aggregate reaction in which the reaction rate was reduced, when checked ten years after the water repellent treatment. The penetration depth of the treatment was measured to 1-4 mm. The results can probably be explained with a reduced humidity inside the concrete even though not measured in this study.

In a summary presented in [97] the durability of surface treatments is discussed. Reports of 36 year old treatments that function well is mentioned but also problems related to the entrapment of water and surface aesthetics. The high porosity of brick, masonry and certain natural stones in combination with the high demands on aesthetics on many old buildings and monuments offer a totally different set of problems. These are topics which seldom are relevant for reinforced concrete structures though the active agent in the water repellent treatments often is the same.

The long term properties have been studied by Nyman and León [40] and they show that impregnation with silane and/or siloxane can have a major impact on the water absorption still nine years after the treatment. Paper IX extends that period to 15 years. Today most of the water repellent agents for concrete 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.

CHAPTER 7 - CONCLUSIONS

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

- **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 I gives an idea on how much these factors affect the effective penetration depth of the water repellent agent. When the “real situation” is considered, the duration of contact is relatively easy to prolong by repeated applications and/or different emulsions. The porosity is a fact which cannot be changed for the concrete structure when designed and constructed. The last factor, the humidity is probably responsible for the major part of failed water repellent treatments. In order to get a high penetration and long lasting effect, it is essential to allow the concrete to dry a sufficient time before the hydrophobic impregnation is applied.

The chemical reactivity and the molecule size of the water repellent agent also 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.

- **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 action plays an important role for the moisture transport, the vapour transport is the dominant transport mechanism even at high RH for water repellent treated concrete, see Figure 14. It can also be concluded that the vapour transport in water repellent treated concrete is highly reduced when compared with untreated concrete (see Paper IV).

A first step of verification, presented in Paper IV, 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 V and Paper VI. 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 by the use of the Kelvin equation and the sorption isotherms in Paper V. However, to what degree this is likely to happen before the polymerisation starts is identified as a task of future research.

It is well documented that the RH affects the penetration depth which can be seen in Paper I. A hypothesis based on the results from Paper V and Paper VI is presented which suggests that the RH also affects in which range of pore radii the water repellent agent is present and active. The theory behind the hypothesis is based on a circular pore model and the relation between the pore radius and the humidity at which a meniscus forms. This relation is given by the Kelvin equation. The model is illustrated in Figure 18.

- **Durability of water repellent treatments**

The long term performance of hydrophobic impregnations can be divided into surface effects and in depth effects:

The surface effect in terms of visual effects or measurements of contact angle disappears within a few years, normally within the first year after the treatment. This is due to several reasons such as dust and particles, UV-light and abrasion. The rate depends on the environmental and mechanical loadings.

The in depth effect is not sensitive to the same factors as described above. As a matter of fact, most reports in the literature indicate that if the surface treatment performs well right after the treatment and if it has a sufficient penetration depth (different requirements in different situations) the effect will be long lasting. Paper VII and Paper IX indicate this. A good function can then be expected for at least 15 years.

It is also important to emphasize that the evaluation of hydrophobic impregnations should be divided in to either the absence or the presence of active agent. This should always be verified by measurements of depth or concentration which are of great importance for the function of the treatment, see for example Paper III. It is difficult to achieve a sufficient penetration of active agent in some situations but the evaluation should not start with the question; do hydrophobic impregnations work, but rather; did this hydrophobic impregnation succeed (measured by depth or concentration)? If so, how did it perform?

CHAPTER 8 - FUTURE RESEARCH

The main work in this project has been experimental. 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. Some suggestions for future research are listed below:

- **Hydrophobic impregnations, are they cost-effective?**

Bridge maintenance contains several measures, e.g., removal of de-icing agents through an annual cleaning, crack repair, vegetation removal, and checks and restoration of drainage function [26]. Mattsson [98] have studied how these measures are purchased and fulfilled currently in Sweden and proposed improvements. In order to improve the durability of bridge members subjected to harsh environment and de-icing agents, the Swedish Road Administration [91] requires that these members should be impregnated. The question is how efficient such a measure is. According to approximate life cycle cost calculations, Silfwerbrand [99] has concluded that impregnation is cost-effective on old concrete bridges but hardly on modern ones with high performance concrete and thick concrete covers. However, more thorough investigations are needed.

- **Is there an aging factor which has to be considered?**

Prediction models are often used to estimate the service life for concrete structures. These models are based on carbonation rate or chloride ingress 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 VII and Paper IX deal with the durability of water repellent treatments on concrete. Is it possible to use material data obtained in laboratory and in field right after the treatment or is there an aging factor on the treatment which has to be taken into consideration? The field exposure site in the Eugenia tunnel will hopefully give valuable input to this topic during the following years but more research is needed.

- **Transportation and fixation of moisture...**

This was the subtitle of the licentiate thesis [100] and also the main focus during the first part of this project. Numerical simulations of moisture flow and moisture fixations in water repellent treated concrete were discussed as an important alignment. However, it requires more material data and verifications regarding the models presented in this thesis, before it can become a useful tool for prediction of for example chloride ingress. It is still an interesting topic for future research.

- **Is carbonated concrete a problem for silane based impregnations?**

All the laboratory work presented in this thesis was done on non carbonated concrete. The pH-value has a major effect on the polymerisation rate as discussed in the

introduction. Is this a problem or an advantage? The positive side of a water repellent treatment on carbonated concrete is that the slow reaction enables the silanes to reach further inside the structure before it reacts, in theory giving the treatment a high penetration depth. The negative side is that the polymerisation rate might be too slow, resulting in evaporation or wash out before it has fully polymerised. If the second scenario is the more likely to happen, it might be wise to investigate accelerators or different alkoxygroups on carbonated concrete.

CHAPTER 9 - REFERENCES

CITATIONS IN THE EXTENDED SUMMARY

- [1] P.J. Koblischek, (1995) *Protection of Surfaces of Natural Stone and Concrete through Polymers*. Proceedings, Surface Treatment of Building Materials with Water Repellent Agents, Delft University of Technology, Delft, Netherlands, pp. 2.1-12.
- [2] A.J. Forbes, (1986) *Comparative Evaluation of the Water Proofing and Durability of Concrete Sealers*, Alberta Transportation, Report No. ABTR/RD/RR-86/09. Edmonton Alberta, Canada.
- [3] H.F.W. Taylor, (1997) *Cement Chemistry*. Second edition, Redwood Books, Wiltshire, Great Britain.
- [4] L-O. Nilsson, (1997) *Betong-handbok, Concrete Handbook, Material, Chapter 14, Moisture and Concrete*, Second edition, Svenskt Tryck AB, Stockholm, Sweden. (In Swedish)
- [5] A.M. Neville, (1995) *Properties of Concrete*, Fourth edition, Longman Group Limited, Harlow Essex, England.
- [6] R. N. Swamy, (1992) *The Alkali-Silica Reaction in Concrete*, Blackie and Son Ltd., Bishopsbriggs, Glasgow, Scotland.
- [7] K. Tuutti, (1982) *Corrosion of Steel in Concrete*, CBI Research fo 4.82. Swedish Cement and Concrete Research Institute, Stockholm, Sweden.
- [8] F. Hunkeler, (2005) *Corrosion in Reinforced Concrete Structures, Chapter 1, processes and mechanisms*, Woodhead Publishing Limited, Cambridge, England.
- [9] P. Utgenannt, (2004) *The Influence of Aging on the Salt-frost Resistance of Concrete*. Report TVBM-1021, Doctoral-thesis, Division of Building Materials, Lund Institute of Technology, Lund, Sweden.
- [10] E.P. Nielsen and M. Geiker, (2003) *Chloride Diffusion in Partially Saturated Cementitious Material*. Cement and Concrete Research, Vol. 33, pp. 133-138.
- [11] A.V. Satta, R.V. Scotta and R.V. Vitaliani, (1993) *Analysis of Chloride Diffusion into Partially Saturated Concrete*, ACI Materials Journal, Vol. 90, No 5, pp. 441-451.

- [12] E.P. Plueddemann, (1991) *Silane Coupling Agents*, Second Edition, Plenum Press, New York, USA.
- [13] B. Arkles, (1977) *Tailoring Surfaces with Silanes*, Chemtech, Vol. 7, pp. 766-778.
- [14] H. De Clercq, (2008) *Function of Silane Type on Its Reactivity for Surface and In-Depth Applications to Different Substrates*, Proceedings, Hydrophobe V - 5th International Conference on Water Repellent Treatment of Building Materials, Brussels, Belgium, April 15-16, Aedificatio Publishers, pp. 261-271.
- [15] A.H. Gerdes, (2001) *Transport und chemische Reaktion siliciumorganischer Verbindungen in der Betonrandzone*, Doctoral-Thesis, Eidgenössische Technische Hochschule (ETH), Building Materials Reports No. 15, Zürich, Switzerland.
- [16] S. Giessler, B. Standke and M. Büchler, (2005) *A New Silane System for Corrosion Reduction of Steel Reinforced Concrete*, Proceedings, Hydrophobe IV – 4th International Conference on Water Repellent Treatment of Building Materials, Stockholm, April 12-13, Aedificatio Publishers, pp 17-26.
- [17] H. De Clercq and E. De Witte, (2001) *Reactivity of Silicon Based Water Repellent Agents at Different Application Conditions*, Internationale Zeitschrift für Baueninstandsetzen und Baudenkmalspflege, Vol. 7, Heft 1, pp. 63-78.
- [18] A. Gerdes, (2005) *Preventive Surface Protection of Concrete Structures*, Proceedings, International Workshop on Service Life of Concrete Structures. Sapporo, Japan, February, pp. 31-40.
- [19] B. Arkles, J.R. Steinmetz, J. Zazyczny and P. Metha, (1992) *Factors Contributing to the Stability of Alkoxysilanes in Aqueous Solution*, Journal of Adhesion Science Technology. Vol 6, No. 1, pp. 193-206.
- [20] J. Suessmuth and A. Gerdes, (2008) *Computational Chemistry to Investigate the Chemical Behavior of Silanes and CSH-Gel*, Proceedings Hydrophobe V – 5th International Conference on Water Repellent Treatment of Building Materials, Brussels, Belgium, April 15-16, Aedificatio Publishers, pp. 233-244.
- [21] F.D. Osterholtz and E R. Pohl, (1992) *Kinetics of the Hydrolysis and Condensation of Organofunctional Alkoxysilanes: A Review*, Journal of Adhesion Science. Vol. 6, No. 1, pp. 127-149.
- [22] The Concrete Society, (1997) *Guide to Surface Treatments and Enhancement of Concrete*, Concrete Society Technical Report No. 50, Slough, Berkshire, UK.
- [23] H. De Clercq and E. De Witte, (2001) *Effectiveness of Silicon Based Water Repellent Agents at Different Application Conditions*, Internationale Zeitschrift für Baueninstandsetzen und Baudenkmalspflege, Vol. 7, Heft 6, pp. 641-654.
- [24] A. Johansson, (2005) *Impregnate Concrete with a System Open to Diffusion (Impregnera betong med diffusionsöppet system)*, The Journal Husbyggaren, No. 4, September, pp. 18-20. (In Swedish).

- [25] A. Johansson, M. Janz, J. Silfwerbrand, and J. Trägårdh , (2005) *Moisture Diffusion Coefficient of Impregnated Concrete*, Proceedings, Hydrophobe IV – 4th International Conference on Water Repellent Treatment of Building Materials, Stockholm, Sweden, April 12-13, Aedificatio Publishers, pp. 79-90.
- [26] J. Silfwerbrand, (2002) *Active Bridge Maintenance – A Pilot Study (Aktivt brounderhåll – en förstudie)*, Report No. 65, Chair of Structural Design & Bridges, Department of Structural Engineering, Royal Institute of Technology (KTH), Stockholm, Sweden, 65 pp. (In Swedish).
- [27] L. E. Nevander and B. Elmarsson ,(1994) *Handbook of Moisture, Practice and Theory (Fukthandbok, praktik och teori)*, AB Svensk Byggtjänst, Stockholm, Sweden. (In Swedish).
- [28] E. McGettigan, (1992) *Silicone-Based Weatherproofing Materials*, Concrete International, Vol 14, No. 6, pp. 52-56.
- [29] SS-EN 1504-2, (2004) *Products and Systems for the Protection and Repair of Concrete Structures- Definitions, Requirements, Quality Control and Evaluation of Conformity- Part 2: Surface Protection Systems for Concrete*, Swedish Standard Institute, Stockholm, Sweden.
- [30] A. Gerdes, D. Oehmichen, B. Preindl and R. Nüesch, (2005) *Chemical Reactivity of Silanes in Cement-Based Materials*, Proceedings, Hydrophobe IV – 4th International Conference on Water Repellent Treatment of Building Materials, Stockholm, Sweden, Aedificatio Publishers, April 12-13, pp 47-58.
- [31] M. Bofeldt, (2001) *Effects of RH, w/c-ratio and Absorption Time on Penetration Depth for Impregnated Concrete (Inverkan av RH, vct och absorptionstid på inträngningsdjup för impregnerad betong)*, Master Thesis no. 165, Chair of Structural Design and Bridges, Department of Structural Engineering, Royal Institute of Technology, Stockholm, Sweden. (In Swedish).
- [32] M. Bofeldt and B. Nyman , (2001) *Penetration Depth of Hydrophobic Impregnating Agents for Concrete*, Proceedings, Hydrophobe III- 3rd International Conference on Water Repellent Treatment of Building Materials, Hannover, Germany, September 25-26, Aedificatio Publishers, pp. 133-141.
- [33] S. J. Meier and F. H. Wittmann, (2001) *Influence of Concrete Quality, Its Age and Moisture Content on the Penetration Dept of Water Repellent Agents*, Proceedings, Hydrophobe III- 3rd International Conference on Water Repellent Treatment of Building Materials, Hannover, Germany, September 25-26, Aedificatio Publishers, pp. 123-131.
- [34] S. Krii (1996), *Hydrophobic Impregnation - Penetration Depth in Brick, Limestone and Mortar (Vattenavvisande impregnering - inträngningsdjup i tegelsten, kalksandsten och morbruk)*, Master Thesis TVBM-5031, Division of Building Materials, Lund Institute of Technology, Lund, Sweden. (In Swedish).

- [35] S.Meier, (2002) *Grundlagen und Möglichkeiten einer Hydrophobierung von Betonbauteilen*, Doctoral-Thesis, Eidgenössische Technische Hochschule (ETH), Diss. ETH No. 14811, Zürich, Switzerland.
- [36] A.M.U.B. Attanayaka, O. Dyar, X. Liang, H.M. Aktan and K.Y.S Ng, (2003) *Fundamentals of Use of Penetrating Sealants for Concrete Deck Protection*, TBR 2003 Annual meeting (CD-ROM), Paper No. 03-2575.
- [37] A.H. Gerdes, S. Betschart and F. H. Wittmann, (1998) *Quality Control by FT-IR-Spectroscopy*, Proceedings, Hydrophobe II- 2nd International Conference on Water Repellent Treatment of Building Materials, Zürich, Switzerland, September 10-11, Aedificatio Publishers, pp. 237-244.
- [38] A. Gerdes and F.H. Wittman, (2001) *Requirements for the Application of Water Repellent Treatments in Practice*, Hydrophobe III – 3rd International Conference on Water Repellent Treatment of Building Materials, Hannover, Germany, September 25-26, Aedificatio Publishers, Freiburg, pp. 155-168.
- [39] A. Johansson, M. Janz, J. Silfwerbrand, and J. Trägårdh, (2008) *Protection of Concrete with Water Repellent Agents-What Is Required to Achieve a Sufficient Penetration Depth?*, Proceedings, ICCRRR 2008, Capetown, South Africa, Taylor & Francis Group, pp. 287-288.
- [40] A. León, and B. Nyman, (2001) *The Effectiveness of Water Repellent Treatments (Effektiviteten hos utförda impregneringar)*, The Journal Bygg & teknik, No. 7, pp. 34-36. (In Swedish)
- [41] H. Zhan, F.H. Wittmann and T. Zhao, (2005) *Relation between the Silicon Resin Profiles in Water Repellent Treated Concrete and the Effectiveness as a Chloride Barrier*, International Journal on Restoration of Buildings and Monuments, Vol 11, No. 1, pp 35-46.
- [42] P. Lunk and F. H. Wittmann, (1998) *The Behaviour of Cracks in Water Repellent Concrete with Respect to Capillary Water Transport*, Proceedings, Hydrophobe II- 2nd International Conference on Water Repellent Treatment of Building Materials, Zürich, Switzerland, September 10-11, Aedificatio Publishers, pp. 63-75.
- [43] G. Hedenblad, (1996) *Material Data for Moisture Transport Calculations, (Materialdata för fuktransportberäkningar)*, T19:1996, Byggforskningsrådet, Stockholm, Sweden. (In Swedish)
- [44] G. Hedenblad, (1993) *Moisture Permeability of Mature Concrete, Cement Mortar and Cement Paste*, Report TVBM-1014, Doctoral-thesis, Division of Building Materials, Lund Institute of Technology, Lund, Sweden.
- [45] L-O. Nilsson, (1980) *Hygroscopic Moisture in Concrete- Drying, Measurements & Related Material Properties*, Report TVBM-1003, Doctoral-thesis, Division of Building Materials, Lund Institute of Technology, Lund, Sweden.

- [46] L. Ahlgren, (1972) *Moisture Fixation in Porous Building Materials*, Report 36, Doctoral-thesis, Division of Building Technology, Lund University of Technology, Lund, Sweden.
- [47] K. Thorvaldsson, (1998) *Diffusion of Water in Foods during Heating*, Doctoral-thesis, Department of Food Science, Chalmers University of Technology, Gothenburg, Sweden.
- [48] C. Nordling and J. Österman, (2004) *Physics Handbook for Science and Engineering*, Seventh Edition, Studentlitteratur, Lund, Sweden.
- [49] L-O. Nilsson, (2005) *Moisture Transport in Cementitious Material – Theory and Some Experimental Results*, Knut Højgaard Conference on Advanced Cement-Based Materials – Research and Teaching, DTU, Lyngby, Denmark, June 12-15.
- [50] A. Arfvidsson, (1998) *Moisture Transport in Porous Media: Modelling Based on Kirchhoff Potentials*, Report TVBH-1010, Division of Building Physics, Lund Institute of Technology, Lund, Sweden.
- [51] H. Sadouki and F. H. Wittmann, (1998) *Influence of Water Repellent Treatment on Drying of Concrete*, Proceedings, Hydrophobe II- 2nd International Conference on Water Repellent Treatment of Building, Zürich, Switzerland, September 10-11, Aedificatio Publishers, pp.177-188.
- [52] A. Anderberg, (2004) *Moisture of Self-levelling Flooring Compounds*, Report TVBM-3120, Division of Building Materials, Lund Institute of Technology, Lund, Sweden.
- [53] M. Janz, (2000) *Moisture Transport and Fixation in Porous Materials at High Moisture Levels*, Report TVBM-1018, Doctoral-thesis, Division of Building Materials, Lund Institute of Technology, Lund, Sweden.
- [54] E. Atlassi, L-O.Nilsson and A. Xu, (1989) *Moisture Sorption Properties of Concrete with Admixtures and Industrial By-products – Implications for Durability*, BFR Document:1989, Svensk byggtjänst, Stockholm, Sweden.
- [55] K. Norling-Mjörnell, (1994) *Self-desiccation in Concrete, Chapter 3, Physical Binding of Water*, Report P-94:2, Building Materials, Chalmers University of Technology, Gothenburg, Sweden.
- [56] E. Helsing-Atlassi, (1994) *Influence of Silica Fume on the Pore Structure of Mortar as Measured by Water Vapour Sorption Isotherm*, NATO/RILEM Workshop: The Modeling of Microstructures and its Potential for Studying Transport Properties and Durability. St Remy-les-Chevreuse, France, July 10-13, pp 257-270.
- [57] A. Xu, (1992) *Structure of Hardened Cement-fly Ash Systems and Their Related Properties. Section 3.3 to 5.2*, Report P-92:7, Building Materials, Chalmers University of Technology, Gothenburg, Sweden.

- [58] V. Baroghel-Bouny, T. Chaussadent, (1994) *Texture and Moisture Characterization of Hardened Cement Pastes and Concretes from Water Vapour Sorption Measurements*, NATO/RILEM Workshop: The Modeling of Microstructures and its Potential for Studying Transport Properties and Durability. St Remy-les-Chevreuse, France, July 10-13, pp 241-255.
- [59] C. Nordling and J. Österman, (2004) *Physics Handbook for Science and Engineering*, Seventh Edition, Studentlitteratur, Lund, Sweden.
- [60] K. Sandin, (1996) *Water Repellent Impregnation of Facades, (Vattenavvisande fasadimpregnering)*, Report T15:1994, Byggforskningsrådet, Stockholm, Sweden, (In Swedish).
- [61] F.H. Wittmann, F. Beltzung and S.J. Meier, (2006) *Shrinkage and Swelling of Concrete without Capillary Condensed Water*, International Journal on Restoration of Buildings and Monuments, Vol. 12, No. 1, pp. 35-42.
- [62] F.H. Wittmann, Y.Z. Xian, T.J. Zhao and S. Giessler-Blank, (2008) *Moisture Diffusion and Siloxane in Integral Water Repellent Concrete*, International Journal on Restoration of Buildings and Monuments, Vol. 14, No. 1, pp. 15-26.
- [63] J. Heinrichs, St. Schmeiser, and A. Gerdes, (2005) *Numerical Simulation of the Influence of Water Repellent Treatment on Carbonation of Concrete*, Hydrophobe IV – 4th International Conference on Water Repellent Treatment of Building Materials, Stockholm, Sweden, April 12-13, Aedificatio publishers, pp 27-44.
- [64] F.H. Wittmann, T.A.J.M. Siemes and L.G.W. Verhoef, Editors (1995) *Proceedings, Surface Treatment of Building Materials with Water Repellent Agents*, Delft, Netherlands, November 9-10, Aedificatio Publishers, Freiburg, Germany.
- [65] F. H. Wittmann, Editor, (1998) *Proceedings, Hydrophobe II – 2nd International Conference on Water Repellent Treatment of Building Materials*, Zürich, Switzerland, September 10-11, Aedificatio Publishers, Freiburg, Germany.
- [66] K. Littmann and A.E. Charola, Editor, (2001) *Proceedings, Hydrophobe III – 3rd International Conference on Water Repellent Treatment of Building Materials*, Hannover, Germany, September 25-26, Aedificatio Publishers, Freiburg, Germany.
- [67] J. Silfwerbrand, Editor, (2005) *Proceedings, Hydrophobe IV – 4th International Conference on Water Repellent Treatment of Building Materials*, Stockholm, Sweden, April 12-13., Aedificatio Publishers, Freiburg, Germany.
- [68] H. De Clercq and A.E. Charola, Editor, (2008) *Proceedings, Hydrophobe V – 5th International Conference on Water Repellent Treatment of Building Materials*, Brussels, Belgium, April 15-16., Aedificatio Publishers, Freiburg, Germany.
- [69] R.S. Gislason and K. Erlingsson, (1989) *Combined Application of Water Repelling Agents and Surface Coatings on Concrete and Rendering*, NI-Projekt P86050, Reykavik and Oslo, Iceland and Norway.

- [70] H. Zhan, F.H. Wittmann and T. Zhao, (2003) *Penetration Depth of different Water Repellent Agents*, Proceedings, 6th International Conference on Material Science and Restoration, MSR-VI, Aedificatio Publishers, pp.183-194.
- [71] H. Geich, (2001) *Protecting Concrete with Cream – Practical Aspects*, Hydrophobe III – 3rd International Conference on Water Repellent Treatment of Building Materials, Hannover, Germany, September 25-26, Aedificatio Publishers, pp. 287-298.
- [72] R. Hager, (1998) *The Revolution in Concrete Protection-Impregnation with Cream*, Proceedings, Hydrophobe II – 2nd International Conference on Water Repellent Treatment of Building Materials, Zürich, Switzerland, September 10-11, Aedificatio Publishers, pp. 205-216.
- [73] K. Sandin, (1998) *Surface Treatment with Water Repellent Agents*, Proceedings, Surface Treatment of Building Materials with Water Repellent Agents, Delft, Netherlands, November 9-10, Aedificatio Publishers, Paper 18.
- [74] F. H. Wittmann, (1998) *Influence of a Water Repellent Treatment on Drying of Concrete*, Proceedings, Proceedings, Surface Treatment of Building Materials with Water Repellent Agents, Delft, Netherlands, November 9-10, Aedificatio Publishers, Paper 31.
- [75] BRO 2004, Appendix 4-9.46, *Surface Products for Concrete*, (Ytbehandlingsprodukter för betong), Borlänge, Sweden. (In Swedish)
- [76] K.E.G. Hassan, (1998) *Short and Long Term Performance of Silane Treated Concrete*, Proceedings, Proceedings, Surface Treatment of Building Materials with Water Repellent Agents, Delft, Netherlands, November 9-10, Aedificatio Publishers, Paper 33.
- [77] J. De Vries, R.B. Polder, (1997) *Hydrophobic Treatment of Concrete*, Construction and Building Materials, Elsevier, Vol. 11, No. 4, pp. 259-265.
- [78] P.A.M. Basheer, A.E. Long and F. Roy Montgomery, (1992) *Durability of Surface Treated Concrete*, Report No. SMRG-03-1992, The Queen's University of Belfast, Northern Ireland, UK.
- [79] D.M. Thompson and M.B. Leeming, (1992) *Surface Treatments for Concrete Highway Bridges*, Research Report 345, Transport and Road Research Laboratory, Crowthorne, Berkshire, UK.
- [80] J. Dai, Y. Akira, F.H. Wittmann, H. Yokota and P. Zhang, (2010) *Water Repellent Surface Impregnation for Extension of Service Life of Reinforced Concrete Structures in Marin Environments: The Role of Cracks*, Cement & Concrete Composites, Elsevier, No. 32, pp. 101-109.
- [81] L.G.W. Verhoef, (1998) *Analysis of Facades*, Proceedings, Proceedings, Surface Treatment of Building Materials with Water Repellent Agents, Delft, Netherlands, November 9-10, Aedificatio Publishers, Paper 20.

- [82] H.M. Künzel and K. Kiessl, (1998) *Performance of Silane Impregnation for Exposed Brick Masonry*, Proceedings, Surface Treatment of Building Materials with Water Repellent Agents, Delft, Netherlands, November 9-10, Aedificatio Publishers, Paper 1.
- [83] A. Calder and P. Vassie, (2003) *Does the Application of Silane to Concrete Reduce Ongoing Reinforcement Corrosion?* Proceedings – Coatings for Masonry and Concrete, Brussels, Belgium, The Paint Research Association, Paper No. 21.
- [84] R.B. Polder, H. Borsje and J. de Vries, (2000) *Corrosion Protection of Reinforcement by Hydrophobic Treatment of Concrete*, Proceedings, Eurocorr 99, The European Federation of Corrosion, Publication No. 31, pp 73-84.
- [85] L. Schueremans, D. Van Gemert, M Friedel and S. Giessler-Blank, (2008) *Durability of Water Repellents in a Marine Environment*, Proceedings, Hydrophobe V – 5th International Conference on Water Repellent Treatment of Building Materials, Brussels, Belgium, April 15-16, Aedificatio Publishers, pp. 357-368.
- [86] L.J.A.R. van der Klugt and J.A.G. Koek, (1998) *The Effective Use of Water Repellents*, Proceedings, Proceedings, Surface Treatment of Building Materials with Water Repellent Agents, Delft, Netherlands, November 9-10, Aedificatio Publishers, Paper 19.
- [87] F. Karlsson, (1997) *Protection of Concrete against Salt and Water (Skyddsbehandling av betong mot salt och vatten)*, The Journal Betong, No. 3, pp. 10-13. (In Swedish)
- [88] T. Büttner and M. Raupach, (2008) *Durability of Water Repellent Treatment of Concrete Surfaces- Influences and Reasons*, International Journal on Restoration of Buildings and Monuments, Vol. 14, No. 1, pp. 27-38.
- [89] B. Nyman, (1998) *Graffiti on Concrete Surfaces (Klotter på betongytor)*, The Journal Betong, No. 1, pp. 8-11. (In Swedish).
- [90] A. Johansson, (2006) *The Condition of Concrete Surfaces Exposed to Graffiti (Temaundersökning: Klottersanerade betongytors tillstånd)*, Commission Report, Swedish Cement and Concrete Research Institute, Stockholm, Sweden, No. 2006-29. 22 pp. (In Swedish).
- [91] TK BRO, Swedish Road Administration 2009, *Allmänna tekniska beskrivningar för broar, (General Technical Regulations for Bridges)*, Publication No. 2009:27, Borlänge, Sweden, 230 pp. (In Swedish)
- [92] S.A. Hurley, (2001) *The British Experience of Impregnation and Surface Treatment of Concrete*, Betongrepartationsdagen 2001, Rebet, Swedish Cement and Concrete Research Institute, Stockholm, Sweden.
- [93] EN 13579, (2002) *Products and Systems for the Protection and Repair of Concrete Structures – Test Methods – Drying Test for Hydrophobic Impregnation*. European Committee for Standardization, Brussels, Belgium.

- [94] EN 13580, (2002) *Products and Systems for the Protection and Repair of Concrete Structures – Test Methods – Water Absorption and Resistance to Alkali for Hydrophobic Impregnations*. European Committee for Standardization, Brussels, Belgium.
- [95] EN 13581, (2002) *Products and Systems for the Protection and Repair of Concrete Structures – Test Methods – Determination of Loss of Mass of Hydrophobic Impregnated Concrete after Freeze-Thaw Salt Stress*. European Committee for Standardization, Brussels, Belgium.
- [96] G.E. Hoppe and J. Varkevisser, (1997) *Long-term Monitoring of the Effectiveness of the Silane Impregnation of a Concrete Arch Bridge to Inhibit the Further Effects of Alkali-Aggregate Reaction*, FIP symposium-The concrete way to development, Johannesburg South Africa, March 9-12, Concrete Society of Southern Africa, pp. 777-785.
- [97] A.E. Charola, (2001) *Water Repellents and Other “Protective” Treatments: A Critical Review*, Proceedings, Hydrophobe III – 3rd International Conference on Water Repellent Treatment of Building Materials, Hannover, Germany, September 25-26, Aedificatio Publishers, pp. 3-19.
- [98] H.-Å. Mattsson, (2008) *Integrated Bridge Maintenance – Evaluation of a Pilot Project and Future Perspective*, TRITA-BKN Bulletin No. 95, Doctoral Thesis, Chair of Structural Design & Bridges, Dept. of Civil and Architectural Engineering, School of Architecture and Built Environment, Royal Institute of Technology, Stockholm, Sweden.
- [99] J. Silfwerbrand, (2008) *Impregnation of Concrete Bridge Elements Exposed to Severe Environment – Is It Cost Effective?*, Proceedings, Hydrophobe V - 5th International Conference on Water Repellent Treatment of Building Materials, Brussels, Belgium, April 15-16, pp. 341-354.
- [100] A. Johansson, (2006) *Impregnation of Concrete Structures - Transportation and Fixation of Moisture in Water Repellent Treated Concrete*, Licentiate-thesis, TRITA-BKN Bulletin No. 84, Chair of Structural Design and Bridges, Department of Structural Engineering, Royal Institute of Technology (KTH), Stockholm, Sweden.

ADDITIONAL CITATIONS IN PAPERS I-IX

Coates, J. (2000) *Interpretation of Infrared Spectra, A Practical Approach*, Encyclopaedia of Analytical Chemistry, R. A. Meyers (Ed.) John Wiley & Sons Ltd, Chichester, West Sussex, UK, pp. 10815-10837.

De Vries, J., Polder, R. B. and Borsje, H., (1998) *Durability of Hydrophobic Treatment of Concrete*, Proceedings, Hydrophobe II- 2nd International Conference on Water Repellent Treatment of Building, Zürich, Switzerland, Aedificatio publishers, pp. 77-90.

Greenspan, L., (1976) *Humidity Fixed Points of Binary Saturated Aqueous Solutions*, Journal of Research of the National Bureau of Standards-A, Physics and Chemistry, Vol. 81A, No. 1, pp 89-96.

Gui-hong, Z., Wittmann, F.H. and Tie-jun, Z., (2008) *Surface Impregnation of Chloride-contaminated and Humid Concrete with Silane*, Int. J. Restoration of Buildings and Monuments, Aedificatio publishers, Vol. 14, No. 1, pp. 3-14.

Johansson, A., Janz, M., Silfwerbrand, J., & Trägårdh, J., (2008) *Long-term Measurements on Chloride Ingress in a Road Tunnel Environment*, Proceedings, Hydrophobe V, Brussels, Belgium, April 15-16, pp. 327-328.

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

Kus, H., (2002) *Long-Term Performance of Water Repellants on Rendered Autoclaved Aerated Concrete*, Doctoral-thesis, Centre for Built Environment, Materials Technology, University of Gävle, Gävle, Sweden.

Lide, D.R., (1994) *Constant Humidity Solutions, Handbook of Chemistry and Physics, Section 15*, 74th - Edition, CRC-Press, Boca Raton, Florida, USA.

Mörtstedt S-E., and Hellsten, G., (1999) *Data and Diagram, Energy- and Chemical-Technology Tables (Data och diagram, energi- och kemitekniska tabeller)*, Liber AB, Malmö. (In Swedish)

Nordström, E., (2005) *Durability of Sprayed Concrete – Steel Fibre Corrosion in Cracks*, Doctoral-thesis, no 2005:02, Division of Structural Engineering, Luleå University of Technology, Luleå, Sweden.

Nyman B., (2004) *Facade elements at the Student scraper in Stockholm (Fasadelement kv. Gamen, Studentskrapan, Stockholm)*, Commission report no. 2004-61, Swedish Cement and Concrete Research Institute, Stockholm, Sweden. (In Swedish)

Olsson, M. and Sjödin, J. (2002) *The Effect of Impregnation on Moisture Profile, Chloride Ingress, and Frost Resistance on Self Compacting Concrete (Impregneringens inverkan på fuktprofilen, kloridinträngningen och frostbeständigheten i självkompakterande betong)*. Master Thesis No. 182, Chair of Structural Design and Bridges, Department of Structural Engineering, Royal Institute of Technology, Stockholm, Sweden. (In Swedish).

Paulsson-Tralla, J., (2002) *Service Life of Repaired Concrete Bridge Decks*. Doctoral Thesis, Bulletin No 50. Chair of Structural Design and Bridges, Department of Structural Engineering, Royal Institute of Technology (KTH), Stockholm, Sweden.

Sjöberg A., (2002) *Properties and Function for Moisture- and Alkalibarriers on Concrete (Egenskaper och funktion hos fukt- och alkalispärrar på betong)*, Division of Building Materials, Chalmers University of Technology, Gothenburg, Sweden. (In Swedish)

SS-EN 197-1/A1:2004, (2004) *Composition, Specifications and Conformity Criteria for Common Cements*, Swedish Standard Institute, Stockholm, Sweden.

StoCryl HP 200, (2004) *Water repellent treatment*, Technical Specification, Edition 00.05/1, STO Scandinavia, Linköping, Sweden. (In Swedish)

VTI notat 30-2004, (2004) *Polishing of the Coarse Aggregate, Friction Measurements in Stockholm 2003 (Polering av asfaltbeläggning, Friktionsmätningar i Stockholm 2000)*, Väg och transport-forskningsinstitutet, Stockholm, Sweden. (In Swedish)

Wittmann, F. H., Zhan, H. and Zhao, T., (2005) *Chloride Penetration into Water Repellent Concrete Exposed to Sea Water in the Tidal Zone*, Hydrophobe IV – 4th International Conference on Water Repellent Treatment of Building Materials, Stockholm, Sweden, Aedificatio publishers, April 12-13, pp. 125-132.

Wittmann, F.H., Beltzung, F. and Meier, S.J., (2005) *Shrinkage of Water Repellent Treated Cement-Based Materials*, Hydrophobe IV – 4th International Conference on Water Repellent Treatment of Building Materials, Stockholm, Sweden, Aedificatio publishers, April 12-13, pp. 125-132.

www.temperatur.nu, 2009-09-01. (http://www.temperatur.nu/linkoping-egen_period.html?submit=yes)