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Hygrothermal Performance and Soiling of Exterior Building Surfaces

Eva B. Møller

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Front-page picture shows a droplet running down a hydrophobic roofing tile soiled with concrete dust. The set-up was constructed for this picture and does not reflect natural soiling and cleaning hereof. It is meant as a fictitious illustration of some phenomena dealt with in this thesis.

After the defence of the thesis, when the thesis was prepared for print, minor chances and corrections have been added in this edition.

PREFACE

This thesis is a part of the requirement for a Ph.D degree at the Technical University of Denmark. The research work represented was financed by Birch & Krogboe A/S and the Birch & Krogboe Foundation and has taken place at the Department of Civil Engineering, with associate professor Carsten Rode, DTU and Ph.D. Lars D. Christoffersen, Birch & Krogboe A/S as supervisors. A Reference group has also follow the project, the group consisted of Søren Svare, (business development manager), Birch & Krogboe A/S, Senior Lecturer Kenneth Sandin, Division of Building Materials, Lund University, Sweden, and the supervisors.

This project was only possible because of the generous grant by Birch & Krogboe, A/S and Foundation, for which I am very thankful. I especially want to thank the managing director Lars Holten Petersen for taking a personal interest.

Also special thanks to my two supervisors, who took the time for numerous fruitful discussions and had many ideas for experiments throughout the project.

The whole reference group is thanked. Despite of full appointment books you managed to meet with me every three months to discuss the project. This was very encouraging.

As an employee of Birch & Krogboe A/S it has been a privilege to be given these three years to do research on one single project. My colleges at Birch & Krogboe A/S have all been very understanding and helpful. Thank you! Special thanks to Peter Møller for taking the front page picture, Mads Jørgensen for computer support and John Berry, Arup for correcting my English in parts of the report.

Finally, I want to thank my colleagues at DTU who helped making my stay at DTU a good time with lots of more or less serious discussions and laughs, I am sure I will miss you. Thanks to my office-mates Ruut Peuhkuri, Lennart Østergaard and Lone Hedegaard in general making my stay a pleasure and in particular for being understanding when I struggled with Microsoft Word.

Lyngby, November 14, 2003
Eva B. Møller

SUMMARY

The hypothesis of this thesis is: "That by changing the exterior surface properties the hygrothermal performance of the whole building envelope can be improved". But it is only possible to preserve the improvements if the surface does not soil. To test this hypothesis decisive surface properties are described both as phenomena and by the physical chemistry of surfaces. That surface properties can be changed is unquestionable, but the aim here is to gain insight as to what mechanisms makes it possible to change surface properties. This knowledge should be helpful in the development and choice of surface treatments and towards more scientifically based decisions than the trial and error experiments of the past.

After an introduction to the subject the hygrothermal properties are described from a theoretical point of view with a focus on moisture transport and hydrophobic treatments plus heat, radiation and low emissivity/high absorptivity coatings.

Soiling affects surface properties and is the subject of Chapter 3. First a discussion of whether soiling is a failure, then a description of what soiling consists of, where it comes from, the impact on surfaces and how it adheres to surfaces. Soiling is differentiated in biological growth with a description of different genera of microorganisms and environmental dirt with its different compositions and sources. Possibilities in self-cleaning properties are outlined.

The consequences of changing surface properties are described in Chapter 4, which is seen from a more practical angle. Possible gains and risks in designing surface properties are described based on state of the art knowledge and simulations. Issues like application and cleaning methods are discussed with emphasis is on durability and energy consumption.

To test the hypothesis several experiments have been conducted, as described in Chapter 5. Two types of roofing tiles were used for the experiments; ordinary tiles and tiles with Lotus Effect i.e. tiles with a surface treatment which is supposed to be self-cleaning by a combination of hydrophobicity and a specific surface roughness.

The experiments showed:

- After almost 2½ years with natural exposure both tile types were soiled by algae growth, however the tiles with Lotus Effect soiled at a lesser rate.

- The treatment on the tiles with Lotus Effect was not hydrophobic. The water uptake in the Lotus tiles when exposed to natural weather was up to ten times higher than in the ordinary tiles.

- The bulk material of the two tile types was not similar; the pore size distribution was different.

- With SEM (Scanning Electron Microscope) it was possible to see the changed surface of the Lotus tiles. But the penetration depth and chemical composition could not be determined with SEM combined with EDX (Energy Dispersive X-ray spectrometer).

- XPS (X-ray induced Photoemission Spectroscopy) showed fluorine at the surface of the tiles with Lotus Effect.

- Both tile types passed a freeze-thaw test.

- Thermographical investigations indicated that the emissivity of the Lotus tiles was a little lower than the ordinary tiles.

The results of the experiments are used as starting point for a discussion in Chapter 6 of which surface properties have the most influence and which are realistic to change. The practical implications of the findings are outlined. The main issues and conclusions are:

- Hydrophobic treatments decrease the moisture content but no single treatment can be used for all porous materials. Chemical composition and molecule size of the treatment must be compared to pore size and composition of the substrate. The application must also ensure a sufficient penetration depth.

- Low surface free energy and non-polarity of a surface treatment reduces the soiling.

- Low emissivity increases the surface temperature and thereby inhibits algae growth. The effect on energy savings in the winter is negligible but the enhanced need for cooling in the summer could be a problem.

- Service life prediction of surfaces by the factor method is inadequate.

- Self-cleaning properties for porous surfaces have not been obtained yet.

Although not all the experiments had the expected outcome the main hypothesis still stands: The hygrothermal performance of the building envelope can be improved by changing the properties of the exterior surface. However, further research is needed. The most promising fields are:

- Fluorinated polymers for hydrophobic and self-cleaning treatment

- Low emissivity surfaces for porous materials

SAMMENFATNING

Den generelle hypotese i denne afhandling er, at ved at ændre overfladeegenskaberne på den udvendige overflade af en bygning kan de hygrotermiske egenskaber i hele klimaskærmen forbedres. Det er dog kun muligt at bevare forbedringerne, hvis overfladen ikke tilsmudses. For at teste hypotesen beskrives betydende overfladeegenskaber både fænomenologisk og ud fra en overfladefysisk og –kemisk tilgangsvinkel. Overfladeegenskaber kan utvivlsomt ændres, men det er hensigten at opnå mere indsigt i hvilke processer, der gør det muligt at ændre disse. Forhåbentlig kan denne viden anvendes til udvælgelse og videreudvikling af overfladebehandlinger, således at disse mere baseres på viden end som tidligere ved at prøve sig frem.

Efter en introduktion til emnet beskrives de hygrotermiske egenskaber teoretisk, hovedvægten er lagt på fugttransport og hydrofobering samt varme, stråling og lavemissive / højabsorptive belægninger.

Da tilsmudsning påvirker overfladeegenskaberne er dette emnet i kapitel 3. Først diskuteres det om tilsmudsning kan betragtes som svigt, herefter beskrives, hvad tilsmudsning består af, hvor det kommer fra, hvorledes det påvirker overfladen og hvordan det hænger fast på overflader. Der adskilles mellem biologisk vækst, hvor forskellige slægter af mikroorganismer beskrives, og miljøbetinget tilsmudsning, med forskellige kemiske sammensætninger og kilder. Muligheder indenfor selvrensende egenskaber gennemgås.

Følgevirkningerne af at ændre overfladeegenskaber beskrives i kapitel 4, hvor emnet belyses fra en mere praksisbetonet side. Mulige fordele og risici ved at anvende kunstigt skabte overfladeegenskaber beskrives udfra den eksisterende viden og simuleringer. Emner som påførings- og afrensningsmetoder diskuteres, men hovedvægten er lagt på holdbarhed og energiforbrug.

Som beskrevet i kapitel 5 er adskillige eksperimenter blevet udført for at teste hypotesen, hertil er der anvendt to typer tegltagsten; almindelige sten og sten med Lotus Effect, dvs. sten med en overfladebehandling, der forventes at være selvrensende ved en kombination af at være hydrofob og have en bestemt ruhed.

Eksperimenterne viste følgende:

- Efter at have været placeret udendørs i næsten 2½ års var begge teglstens typer algebegroet. Opstillingerne med Lotus Effect var dog lidt forsinket i deres tilsmudsning.

- Overfladebehandlingen på Lotus tagstenene var ikke hydrofob. Når teglstenene var udsat for almindeligt vejrlig, optog Lotus stenene op til 10 gange mere vand end de almindelige sten.

- Det bagvedliggende materiale i de to teglstenstyper var ikke ens; porestørrelsesfordelingen var forskellig.

- Med SEM (Scanning Electron Microscope) analyse var det muligt at se, at hvordan overfladen var forandret af Lotus Effecten, men det var ikke muligt at bestemme indtrængningsdybde eller kemisk sammensætning med SEM i kombination med EDX (Energy Dispersive X-ray spectrometer).

- XPS (X-ray induced Photoemission Spectroscopy) analyse viste, at overfladen på Lotus stenene var fluorholdig.

- Begge teglstenstyper holdt til en accelereret frostprøvning

- Undersøgelser med termografering viste, at emissiviteten af Lotus overfladen var lidt lavere end for almindelige sten.

Resultaterne fra eksperimenterne er blevet brugt som udgangspunkt for en diskussion i kapitel 6 af hvilke overfladeegenskaber, der er betydende og hvilke, det er realistisk at ændre. De praktiske betydninger af resultaterne er belyst. De vigtigste emner og konklusioner er:

- Hydrofobering nedsætter fugtindholdet, men der findes ikke en enkelt behandling, der kan bruges til alle porøse materialer, det er nødvendigt at vurdere behandlingens kemiske sammensætning og molekylestørrelse i forhold til sammensætningen og porestørrelsen af det materiale, der skal behandles. Endvidere skal påførelsesmetoden vurderes, således at der sikres en tilstrækkelig indtrængningsdybde.

- Lav overfladespænding og lav polaritet af overfladebehandlingen nedsætter tilsmudsningen.

- Lav emissivitet øger overfladetemperaturen, hvilket hæmmer algevæksten. Den energimæssige besparelse om vinteren er ubetydelig, men det øgede behov for køling om sommeren kan blive problematisk.

- Levetidsbestemmelse af overflader ved brug af faktormetoden er utilstrækkelig.

- På nuværende tidspunkt er der ikke udviklet metoder til at skabe selvrensende overflader af porøse materialer.

Selvom ikke alle eksperimenter fik det forventede udfald, så er hypotesen uforandret; at klimaskærmens hygrotermiske egenskaber kan forbedres, hvis de udvendige overfladeegenskaber ændres. Der er dog behov for yderligere forskning inden for området. De mest lovende perspektiver findes indenfor:

- Fluorholdige polymerer til behandlinger der er hydrofoberende og selvrensende.

- Lavemissive belægninger til porøse materialer.

LIST OF CONTENTS

STRUCTURE OF THESIS

The thesis is divided in eight chapters, which fall in different categories:

Introduction:

Chapter 1. Introduction. Presentation of the subject with hypothesis, goal, definitions and delimitations, but also a philosophical discussion of what science and scientific working methods are. Finally are simplifications in experimental work addressed.

State of the art:

Chapter 2. Hygrothermal properties and 3. Soiling. Theoretical chapters describing different surface properties based on the work of others.

Influence on structures:

Chapter 4. Consequences of changing surface properties. The chapter is a connection between the theoretical properties and more practical consequences on structures. Descriptions are based on work of others but also some own simulations i.e. theoretical findings.

Experiments:

Chapter 5. Experiments. Thorough description of own experiments with hypotheses and results.

Discussion and conclusion:

Chapter 6. Discussion and 7. Conclusion. The results of the experiments are evaluated and explained and used as starting point for a discussion of a broader field. The results are compared to findings of others and conclusions drawn as a combination of old and new findings. The conclusions are formed as scientific based results useful for practical application and development.

Literature:

Chapter 8. Literature. The literature used for the thesis is listed alphabetically.

NOMENCLATURE

A	Surface area	m^2
a	Constant	
b	Constant	
d	Thickness of material	m
F	Force	N
G	Gravity	N
g	Acceleration of gravity	m/s^2
g	Vapour flux	kg/m^2s
h	Height above water surface	m
h	Coefficient of heat transfer	W/m^2K
I	Irradiance	W/m^2
m	Mass	kg
P	Pressure	Pa
p	Partial water vapour pressure	Pa
Q	Water uptake per suction area	kg/m^2
q	Heat flux	W/m^2
R	Gas constant	J/kg K
r	Pore radius	m
r_a	Ratio of actual to projected area	
T	Temperature	K
t	Time	s
W	Work	Nm
W	Load	N
x	General 1- dimensional space coordinate	m
α	Absorptivity	
$δ_p$	Water vapour permeability	kg/m·s·Pa
ε	Emissivity	
γ	Surface free energy = surface tension	N/m
$γ_c$	Critical surface tension	N/m
θ	Contact angle	°
ρ	Dry density	kg/m^3
ρ	Porosity	
ρ	Reflectivity	

σ_S	Stefan-Boltzmann constant	W/m^2K^4
τ	Transmittance	
μ	Frictional coefficient	

Indices:

A	Advancing
a	Adhesion
c	Cohesion
I	Indoor
L	Liquid
O	Outdoor
R	Receding
S	Solid
sky	Sky and surroundings
sol	Solar
ssd	Saturated surface dry condition
sur	Surface
sw	Weighed under water
V	Vapour

Abbreviations and factors in service life estimation:

ESLC	Estimated service life of a component
RSLC	Reference service life of a component
A	Quality of components
B	Design level
C	Work execution level
D	Indoor environment
E	Outdoor environment
F	In-use conditions
G	Maintenance level

1. INTRODUCTION

The outer surface of a building envelope is important to the visual appearance, performance, durability and cost of the whole building. Yet there is only little scientific knowledge of how a desired quality is obtained and why the behaviour of a surface changes when it is subjected to treatments, which experience show, have the desired quality. This thesis will describe some of the effects that can be obtained, not only as phenomena but also going further and explaining *why* it is possible to acquire these properties.

1.1 Hypothesis and goal

Whether the surface influence is decisive or almost negligible depends on the material behind the surface. This thesis will focus on materials where the surface has the most influence on hygrothermal performance of the building parts i.e. especially porous materials. The overall hypothesis is:

> *By changing surface properties the hygrothermal performance of the building envelope can be improved.*

The goal is not only to test the hypothesis but also to determine how the obtained surface properties are preserved. A quality once obtained can diminish if:

- The surface is exposed to natural weather. Artificially obtained properties can decompose and have to be renewed if possible.
- The surface is covered with soil or biological growth. The initial properties might be suppressed by a new surface layer that probably has other properties.

By favouring self-cleaning surfaces the second point would be countered. Therefore soiling of surfaces has become a substantial part of the thesis.

1.1.1 Delimitations and definitions

When choosing the outer surface of a building envelope the following parameters should be considered:

- *Aesthetics*. How does it look? This is guided by individual taste and therefore difficult to discuss.

- *Performance.* The effect the surface has on the hygrothermal behaviour of the whole building envelope.

- *Durability.* How does the surface change with time, whether it has to be renewed and whether it continues to protect the materials behind the surface.

- *Economics.* Initial costs are not the only consideration, performance and durability must be a part of an economical calculation.

- *Environmental issues.* Sustainability and working environment can be decisive. Many treatments have become unacceptable after society has become more aware of environmental factors.

Which parameters have the highest priority depends on the actual project. In this thesis the focus will be on performance, durability and, to some extent, aesthetics. Economics and environmental issues will only briefly be considered.

In this thesis the term "surface" describes the outer layer of the external building envelope. From a theoretical point of view the surface layer is at an atomic scale i.e. tenth of nanometers. In crystals this is best illustrated by the area where a translational periodicity of the structure no longer exists, and a "free" side of the lattice is accessible for other molecules. Figure 1.1 illustrates how the surface of a solid is accessible for other molecules. In fact it is not the layer itself that is interesting but the interface between two phases; the solid and either another solid, liquid or gas.
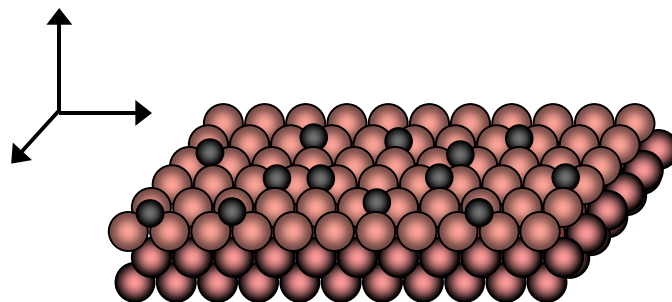
Figure 1.1:   Most solids are crystals consisting of molecules with a translational periodicity of the structure, however, at the surface there is a "free" side of the lattice where other molecules (here represented by the dark molecules) might adhere to the solid. The dark molecules could represent soiling (solid), water (liquid) or a surface treatment.
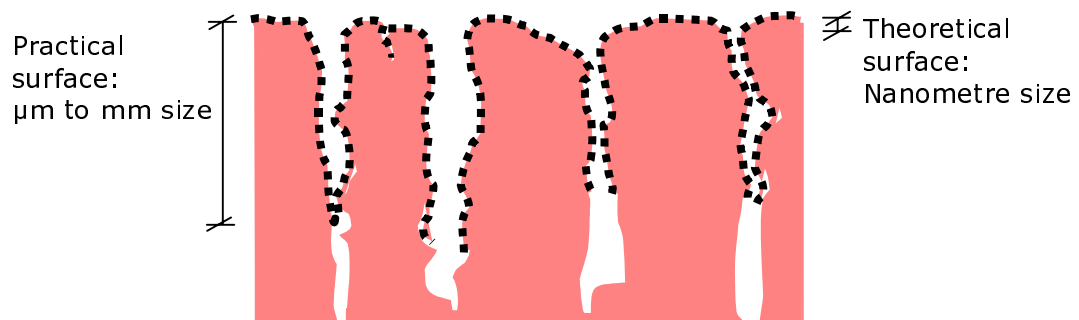
Figure 1.2: The surface is theoretically the outermost few atomic layers of the building envelope. For practical reasons thicker layers are also described as surface, e.g. the layer of a porous material where the surface of the pores are treated.

However, for practical purposes and phenomenological descriptions a surface layer will be much thicker for instance in porous materials with a surface treatment where the surface of the pores are treated until a few millimetres inside the material the treated area will be considered as being a part of the surface layer as shown at Figure 1.2.

As surface properties are defined at an atomic scale and given by physical and chemical binding there is in principle no difference between a "natural" surface and an "artificial" surface obtained by a treatment. However, as the thesis describes how surface properties can be *changed*. The focus will be on treatments and how they interact with the parent material (solid), take over the surface properties and changes the interface with water (liquid) or soil (solid) and the susceptibility to biological growth.

1.2 Test of hypothesis – a science philosophical problem

Test of a hypothesis is often used in statistical analysis. Provided that a suitable test has been chosen we generally acknowledge that a hypothesis can be either accepted or rejected by the test on a given level of significance. This method is very useful from a practical point of view, because it is possible to give a clear statement. Many theories are based on the inductive method: From a series of observations a general theory is formed. But if a hypothesis is accepted in a statistical sense then it only states that in this special case the hypothesis is true. It does not prove that the hypothesis in general is true; as we cannot know for sure,

that it always will be true. On the other hand just one experiment can prove a theory to be false.

The philosopher Karl Popper has pointed out, that there is this asymmetry in verification and falsification (Jessen et al. 1999). Instead of the inductive way he claims that theories should be tested in a hypothetical deductive way: The theory is just a hypothesis (temporary theory) that has to be falsified. The boldest consequence of the hypothesis should be tested. If the experiment gives the expected outcome the hypothesis is neither verified nor proven but only corroborated; it makes the hypothesis stronger but not true. If the hypothesis fails we know some of its limitations and have to revise the hypothesis. According to Popper this does not mean that the truth is relative. He points out instead, that because it is possible to make mistakes (errors are absolute) there must be a truth which does not depend on the expectation. Popper's thoughts on epistemology are schematically shown in Figure 1.3.
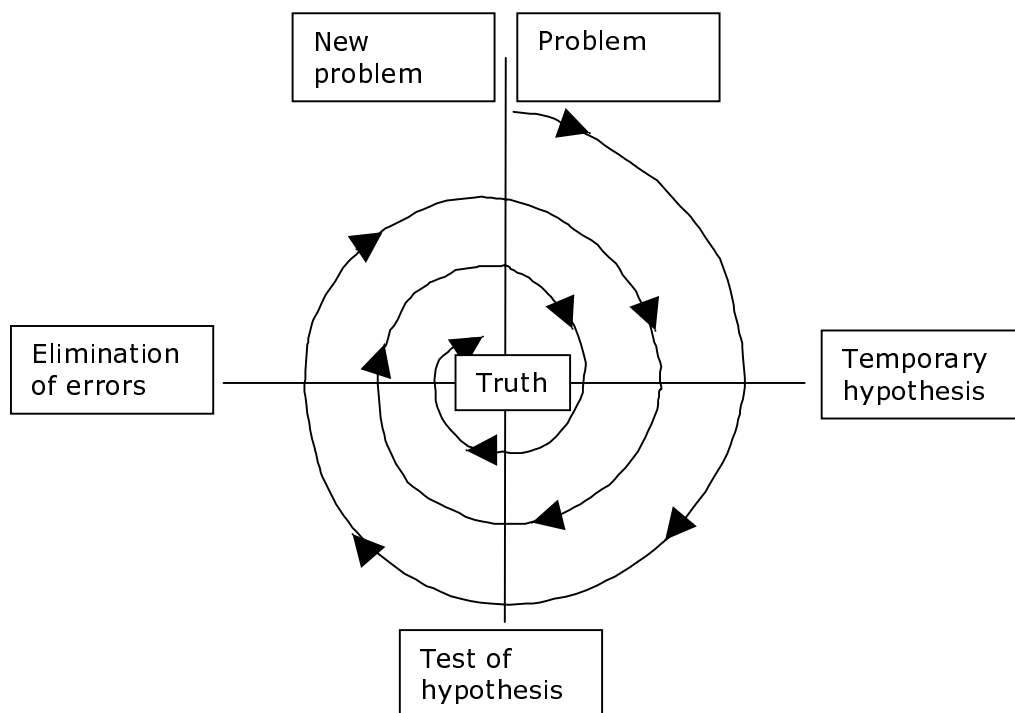
Figure 1.3: Schematic picture of Popper's thoughts on theory of knowledge. By piecemeal engineering mistakes can be adjusted and the hypothesis improved towards the truth. There is a truth but it is impossible to know if it has been found.
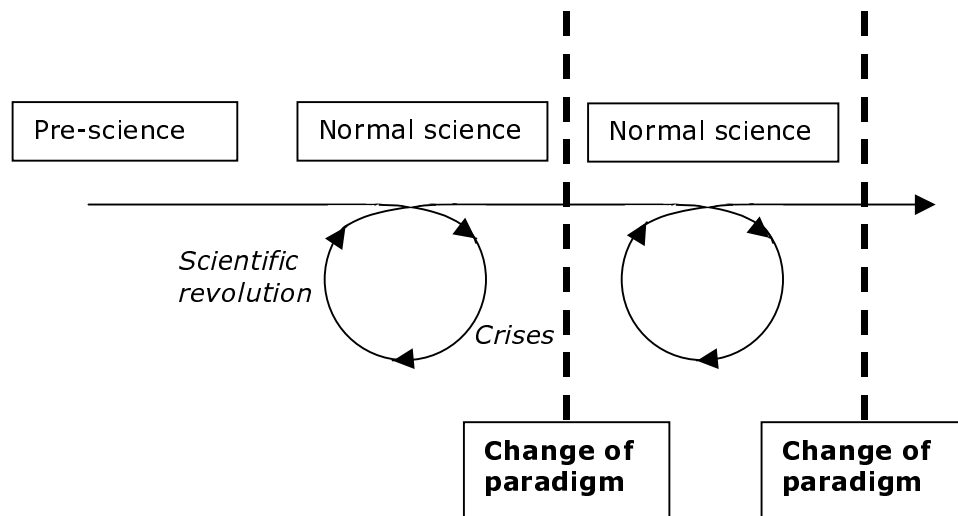
Figure 1.4: Development of science according to Kuhn. Most scientific work takes place as normal science. But when too many crises arise a scientific revolution takes place and a new paradigm is established. Scientist are now working in the new normal science. There is no absolute truth.

Another science philosopher Thomas Kuhn does not agree with Popper that there is a truth (Jessen et al. 1999). He claims that it all depends on which paradigm we work in. In "normal science", where by far the most scientific work takes place, the scientist work in a context of discovery which is known and accepted by him and his peers. Only if too many unsolved problems arise can a new theory take over; there has been a shift in paradigm, a scientific revolution. In that case the scientist does not only interpret his results differently, the facts are different, the scientist now sees other details he could not see before.

1.2.1 Verification or falsification

Most scientific work consist of trying to match theory and experiments but both Popper and Kuhn find it much more interesting when experiments do not show the expected outcome, because an unexpected result forces the scientist to review the hypothesis. However, one should not give up theories too easily. Popper (Jessen et al. 1999) and Kuhn (Madsen & Werner 1990) both warn against accepting unexpected results. Kuhn points out that most abnormalities are dissolved with normal means; most suggestions for new theories turn out to be wrong. Popper says that if a defeat is too easily accepted the possibility to see that something was almost right might be wasted.

1. Introduction

Although Kuhn agrees with Popper that science should have its background in problems not observations (Madsen & Werner 1990), he criticises the idea, because the tradition in science is not falsification but verification. In a scientific community where scientists share the same values and context of discovery and where the tradition is to verify hypothesis it can be problematic to falsify. Many scientists would therefore prefer to verify hypothesis instead of falsifying.

Popper claims that it is easy to find collaboration for a theory if you look for it. Falsification however, is the essence of testing (Madsen & Werner 1990). However, in some cases the question of falsifying versus verifying is just semantics. Popper made a famous example with the hypothesis "All swans are white" which cannot be verified just by only observing white swans, but could be falsified by the discovery of just one black swan. If he had changed the hypothesis into "Swans can have other colours than white"; the hypothesis could be verified but not falsified. The important part is therefore not whether a hypothesis can be falsified or verified but that it can be <u>tested</u> in a way that rules out the other.

Popper has tried to define the difference between scientific theories and pseudo theories (Madsen & Werner 1990). His result is that only hypothesis which theoretically can be falsified are scientific. Some theories are very broad and it would be impossible to imagine how they could fail, in that case the theory is no better than a myth (Madsen & Werner 1990).

These philosophical considerations, inspired by Popper and Kuhn, lead to a few criteria for scientific work:

1. Hypothesis should be based on problems not observations
2. A hypothesis should be testable
3. It should be possible to define criteria for failure and success of a hypothesis

These criteria do not imply that the hypothesis should be true; it is possible to start with wrong assumptions and still work scientifically. According to Popper scientific work would lead the scientist towards the truth, but to Kuhn there is no absolute truth.

1.2.2 Theory versus practise

The philosophical approach is very theoretical. In engineering science, however, the research is often justified by having a practical goal. Söderfeldt (1985) describes scientism and pragmatism as two poles of how to relate science to practical work and although his examples are from the medical world, this also applies for engineering science. Hypothesis should be based on problems, but problems from practice are very complex. Considering all parameters influencing an actual case is not possible and a problem can therefore be handled from two different angles:

- – Scientific approach: In order to *understand* a problem a model of the case must be created leaving out the supposed minor effects. Traditionally the aim is to devise a theory that explains a phenomenon, but the problem from practice must be simplified otherwise too many parameters will blur the picture of the "truth". If a problem is fully understood, then solving the problem should be the easy part. This is the search for *why*.

- – Pragmatic approach: Understanding a problem is not necessary to *solve* it. Solutions that work are more important than why they work. Explanations of the simplified problem are only of interest if they can also explain the more complex reality. Success in solving a problem in a truly pragmatic manner increases with experience. This is the search for *how*.
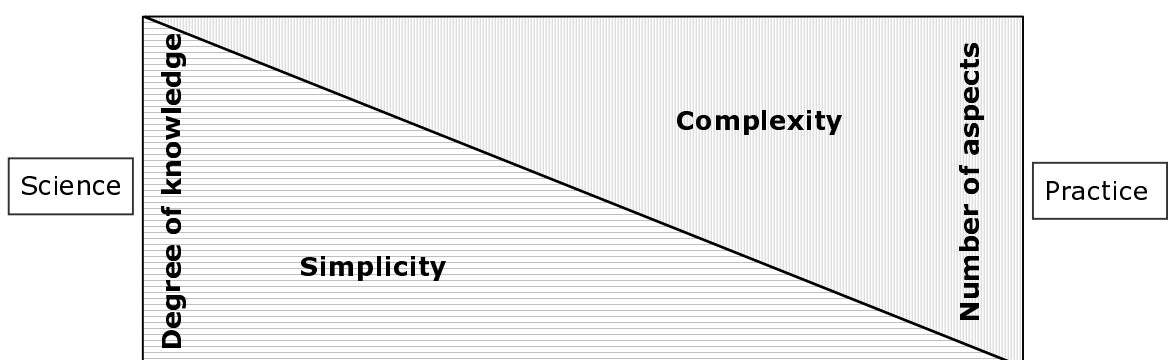
Figure 1.5: In pure science there is a high degree of knowledge about a very narrow subject; many simplifications have been made. In pure practice the world is accepted with all its complexity, a lot of aspects are therefore considered but the degree of knowledge on each subject is small.

A combination of the two methods can often be helpful when solving a problem; an example is trial and error experiments, which basically is a pragmatic approach. Although a theory of *why* things react as they do helps when deciding which parameters should be changed in the next experiment. Figure 1.5 show how there is a continuum between science and practice.

1.3 Science in this project

This thesis is not strictly scientific. Engineering science projects rarely are. Although the ideas of Popper and Kuhn have been considered practical issues have made it difficult to follow them to the letter and only work at the left side of Figure 1.5. However, by giving the thesis a practical angle it becomes more useful.

1.3.1 Induction versus hypothetical deduction

Traditionally the subject of surface treatments have been based on trial-and-error methods. In applying surface treatments to buildings "short-cuts" have been used instead of following the prescribed protocol for testing, documentation and evaluation (Charola 2001). This means that much data has been obtained over the years but there is still a lack of knowledge of *why* some treatments succeed while others fail.

In Section 1.2 it was described how hypothesis should not be based on induction but on hypothetical deduction. However, often the first hypothesis will be based on observations. Tests are designed to corroborate the hypothesis rather than falsifying. After some time, when knowledge has grown, elaboration of the hypothesis can make it more scientific and testing more demanding. As a result the evaluation of the hypothesis becomes a combination of induction and hypothetical deduction.

1.3.2 Falsification of hypothesis

In Chapter 5. Experiments, the hypothesis for each experiment is listed. When the experiments were initiated the assumption was that many of them would corroborate the hypothesis. There was no attempt to make bold assumptions and thereby try to falsify the hypothesis. However, the hypothesis fulfils the criteria for scientific work as given in Section 1.2.1. As it turned out many of the results did not corroborate with the hypothesis but as stated in Section 1.2.1 this does not mean that the hypothesis has to be rejected immediately. The results still have to

be carefully examined to rule out explanations other than the hypothesis was wrong. This examination is a part of Chapter 6. Discussion.

1.3.3 Experiments – scientific or practical approach

In the theoretical chapters 2. Hygrothermal properties and 3. Soiling, the practice related traditional phenomenological approach has been left for the benefit of a more scientific approach by analysing the matters one level deeper. Explanations are sought at an atomic scale by considering how molecules interact and forces act on fluids. Because the descriptions are based on generally accepted theories in physics and chemistry they do not only apply in specific cases but are generally valid.

Chapter 4 represents a movement from the left of Figure 1.5 toward the right. The possible effects of the theoretical aspects in the previous chapters are analysed and illustrated with examples from practice. Truly hand-on experiments, designed for this work, are not explained before Chapter 5.

Some of the experiments described in Chapter 5. Experiments are based on observations at an atomic level (XPS and SEM analysis with EDX). While others are of a more phenomenological nature (e.g. how much water runs off a set-up). The combination of working at the problem from a scientific and a practical level is recurrent in the thesis. It is hoped that the thesis will not only give scientific insight but also be applicable in practice.

Testing full-scale materials in real time is a typical practical approach. The full complexity of the problem (right side of Figure 1.5) is considered but it is very difficult to separate the different parameters which influence the outcome. Experiments of this kind describe the outcome as a phenomenon; focus is on *how* things react, not why. The testing of soiling of roofing tiles by exposing them to natural weather for two years is an example. However, as described in Chapter 5. Experiments, some of the factors are varied (two orientations, two slopes and two surface treatments, resulting in 2 x 2 x 2 = 8 set ups) while others are the same for all tiles (the weather, the bulk material). In this way the experiment also becomes a test of specific controlled factors which moves the experiment to the left in Figure 1.5.

Testing objects in fully controlled environments under conditions that only occur in laboratories increases the simplicity, as there cannot be many confounders. An example is the testing of water vapour transmission properties where test specimens are subjected to well defined relative humidity above and below the specimens until the moisture transport has reached equilibrium. The problem of the water vapour transmission through the specimen is simplified by making the conditions static, which is extremely rare in practice.

Simplifying experiments does not necessarily mean simpler experiments, but limiting the parameters. The experiments in this thesis are conducted on tiles. Simplifying the experiments may have meant using a less complex material, e.g. roll off properties of surface treatments could have been investigated with inert materials like glass or metal with the relevant surface treatment. This would mean that effects from pores in the tile or other uncertainties about the bulk material were effectively eliminated.

2. HYGROTHERMAL PROPERTIES

When testing whether the surface properties can change the hygrothermal performance of the building envelope, the hygrothermal properties, responsible for the performance, must be known. With this chapter it is not the intent to give a thorough description of heat and moisture transport with a detailed exposition of essential parameters. The descriptions will be limited to mechanisms that are important when considering interfaces between solid and liquid or thermal conditions at the surface.

2.1 Surface treatments in a historic perspective

That water can lead to deterioration of buildings has been common knowledge for centuries, probably longer, which can be seen from the shape of buildings from medieval times and how archaeology describes prehistoric houses. Buildings were designed to give shelter and divert water to areas where it could not harm the building (Verhoef, 2001). As building skills were improved, the constructive protection methods such as extensive eaves were combined with better materials or improvement of the materials e.g. by applying surface treatments.

Over time the use of surface treatments at building envelopes evolved; from sacrificial surface treatments, which were demanding in their maintenance, to more sophisticated treatments with longer lifetime and more environmental friendly composition. However, the purpose of applying a surface treatment is basically the same: To protect the underlying material from deterioration and for decoration purposes.

2.1.1 Limewashing and its progenies

A typical example is limewashing of facades; a method that has an over 1000 year tradition. Lime is burnt and slaked in a lime pit, afterwards it is mixed with water and applied to the facade where it reacts with air and is transformed to lime, the original material. The new surface adheres to the facade (often made of clay) and become an extension of the envelope, a sacrificial layer, which is white and antiseptic. When executed correctly, with lime that has been prepared right, the limewashing lasts up to 10 years (Jessen et al. 1980). Unfortunately, limewashing is difficult; preparing the lime is a process of years and when the lime and water mixture is applied, the weather conditions have to be stable (moist but no rain or

direct sunlight, temperatures between 10ºC and 25ºC) for a period of up to 14 days. These conditions are rare in the Nordic countries and as a result limewashing has an average service life of 2 years. (BYG-ERFA 1993)

During the last century new paints have been invented, trying to improve the properties of e.g. limewashing. The intention has been to make the surface treatment more durable (requiring less maintenance) and improve the appearance (larger variety in colour and lustre etc.). Some of these paints did not fulfil the expectations in the long run, instead some treatments were damaging to the facade; large areas peeled off.

Product development seemed to be guided by trial-and-error methods and as it is difficult to mimic real weathering in artificial ageing processes, standardised test have been rare (Charola, 2001). The result has been that the real test came after the product became commercially available, which exposed the failures even more and made the users sceptic to new developments.

2.1.2 Water repellents

Surface treatments that actively divert the water from the substrate by repelling it have a long history. The ancient Greeks and Romans used oils and greases and the Mayas improved the durability of painted stones by adding cactus milk (Wittmann, 1996).

Year	Surface treatment
1820	The term "Water glass" is for the first time used in chemistry to describe NaSiO
1845	Ethyl silicate was developed
1872	The first silicone fluids were developed
1912	Hydride of silicon was identified
1943	Production of silicon products started in the U.S.
1950s	Water repellents for the protection of buildings were commercialised
1963	Silicone resin paints were developed
1990	Water-dispersions of water repellents were introduced
1994	Impregnation gel was developed

Table 2.1: Historic overview of the development of water repellents during the last 200 years. Based on Charola (2001) and Schultze (1997).

But since the 19th century different chemicals have been developed and used as water repellents at building surfaces, silicon-based treatments have been the most successful. A historical overview of the evolution in water repellents in the last 200 years is given in Table 2.1.

In resent years other water repellents have evolved e.g. fluorine-containing polymers, which promise to be good alternatives to the more common used silicone-based treatments (Charola, 2001).

2.2 Moisture transport

Water repellent surface treatments can be applied to virtually every building material and have two major functions:

– Make water run off the surface.

– Prevent water from entering the bulk material.

While the first purpose is valid for most materials, the latter only applies to porous materials. There is a large variety of porous materials used as the exterior of building envelopes. In this section only moisture transport in porous material will be addressed. Moisture transport by water runoff is seen as a surface property and will be treated in Section 2.3.

Phase	Transport mechanism
Liquid (water)	**Capillary suction** Gravity Wind pressure Water pressure
Gas (vapour)	**Diffusion** Convection Thermo diffusion Effusion

Table 2.2: Moisture transport mechanisms, categorised after moisture phase. The mechanisms in bold are the most important when discussing surface treatments. Based on Nevander & Elmarsson (1994).

To understand how surface treatments can affect the moisture content in the bulk material, some of the basic principles of moisture transport in porous materials will be outlined. The transport mechanisms depend highly on the phase of the moisture, Table 2.1 give an overview of the different the different mechanisms.

However, not all of these mechanisms are relevant in this thesis, as some of them have very little practical influence in porous materials. Capillary suction and diffusion are often the most important mechanisms in the surface-near area of the building envelope. Furthermore they are the most affected mechanisms when surface properties are changed and will therefore be described.

The descriptions are kept simple with a minimum of formulae, much more detailed descriptions have been given by others. But the aim here is not to calculate moisture transport but to explain the physical phenomena, which are important when discussing how surface treatments affect moisture transport.

2.2.1 Capillary suction

When porous materials are in contact with a liquid, a solid-liquid-gas system arises. As a result of interactions between the solid and the liquid, which will be explained in Section 2.3.2, the liquid surface in the pore will form a meniscus. Furthermore, in combination with gravity it means that in a vertical system the liquid surface in the pore and a free surface will not be at the same level. A simplified system with a cylindrical pore is shown in Figure 2.1.
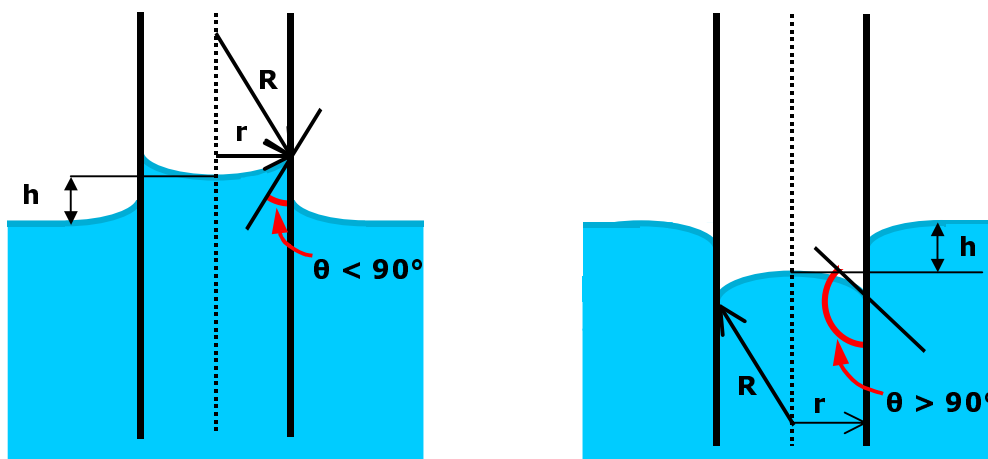
Figure 2.1: In capillary pores with radius r, the pressure difference across a meniscus will lead to either capillary rise (left) or capillary depression (right), depending on whether the contact angle θ is smaller than 90° or not.

The pressure acting on the surface can be described as:

$$\Delta P = \frac{2\gamma}{r}\cos\theta$$

(2.1)

where ΔP = the pressure difference across a surface in a cylindrical capillary pore with radius = r and a contact angle = θ and surface tension = γ. This pressure difference has to be equal to gravity forces and the total equation can be expressed by:

$$\Delta P = \frac{2\gamma}{r}\cos\theta = \Delta\rho \cdot gh \Leftrightarrow h = \frac{2\gamma \cdot \cos\theta}{r \cdot \Delta\rho \cdot g}$$

(2.2)

where $\Delta\rho$ = difference in density between the liquid and the gas phase; g = acceleration due to gravity, h = height of meniscus above a flat liquid surface.

The approximation $\theta = 0$ is often made when calculating capillary rise. An example could be clear water (γ = 73 mN/m) rising in a capillary with atmospheric air above ($\Delta\rho \cong 1000$ kg/m^3) and g = 9.81 m/s^2. Equation (2.2) would be:

$$h = 1.5 \cdot 10^{-5} \cdot \frac{1}{r}$$

(2.3)

from this it can be calculated, that the theoretically possible capillary rise in cylindrical pores with a radius of 10 μm is 1.5 m, if the pores have a radius of 1 μm it is 15 m and in small pores, with a radius of 0.1 μm it is 150 m.

As shown at Figure 2.1 the height can be positive or negative, leading either to capillary rise i.e. the substrate absorbs liquid, or capillary depression where water is repelled. The "natural" condition in virtually all porous materials will be a capillary rise of water into the material. The transport of liquid by capillary rise is relatively fast compared to the transport of vapour, however, it does depend on the pore size of the material; large pores fill fast but the water rises higher in small pores (Krus, 1995). See Figure 2.2.
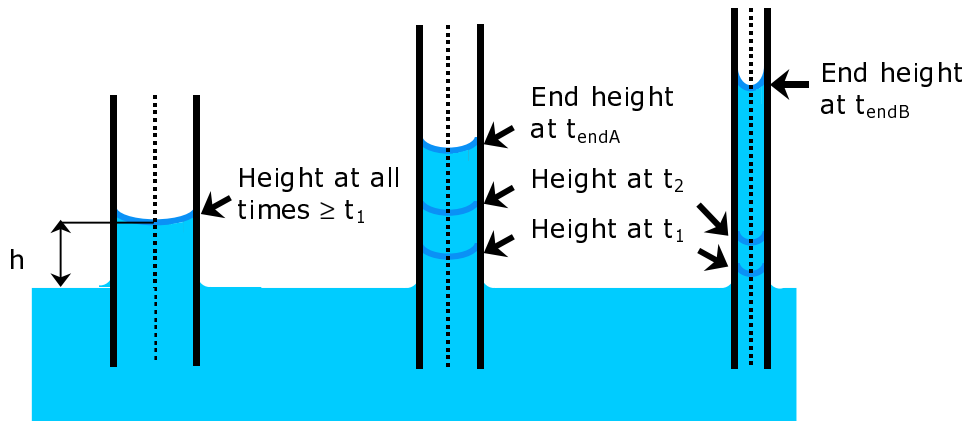
Figure 2.2: Capillary rise at different times t, where $t_1 < t_2 < t_{endA} < t_{endB}$. Water rises faster in pores with larger radius than in smaller pores. But the end height is larger in the small pores. Figure inspired by Krus (1995).

2.2.2 Diffusion

Vapour pressure is an expression for the density of water vapour molecules in a given space. Many molecules mean high vapour pressure. If there is a difference in vapour pressure the molecules will move to the space with less molecules until equilibrium is reached. In porous materials with different vapour pressure over the two sides, moisture will be transported from the area with high pressure through the pores to the area with low pressure. The principle is depicted in Figure 2.3.

The moisture transported through the porous material can be expressed by:

$$g = \delta_p \frac{p_1 - p_2}{d} \qquad (2.4)$$

where g = vapour flux, δ_p = water vapour permeability, d = thickness of material and p = vapour pressure, indices 1 and 2 refer to the two sides of the material, see Figure 2.3. More generally Equation (2.4) can be given as:

$$g = -\delta_p \frac{dp}{dx} \qquad (2.5)$$

which is also known as Fick's first law (Hagentoft, 2001).

Moisture transport
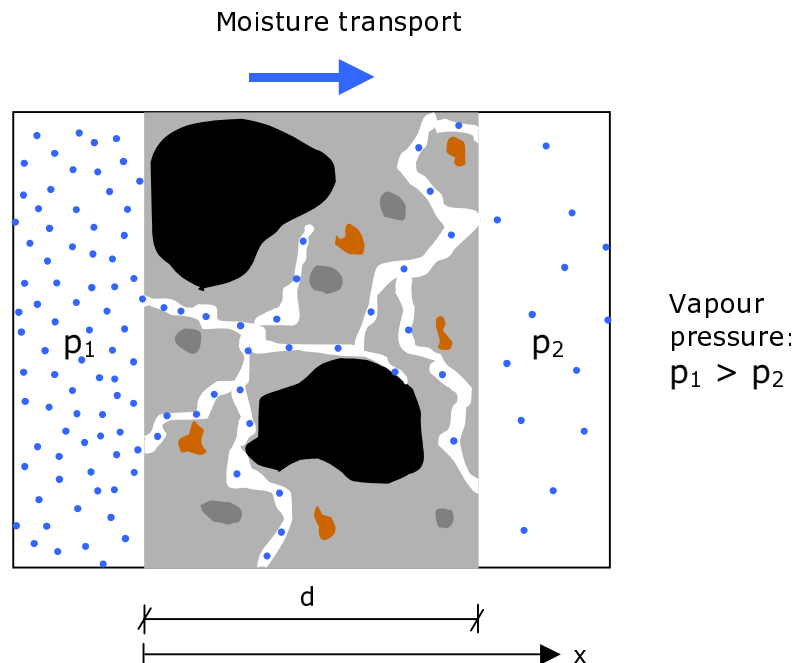
Figure 2.3:   Principle of diffusion through a porous material. Because of the higher vapour pressure p_1 at the left-hand side, molecules will move through the pores to the right. How water molecules might adhere to the walls of the pores is not illustrated here.

The water vapour permeability δ_p is given by the material but varies with temperature and moisture content. It increases with higher temperature or higher moisture content. There are different theories to why the permeability depends on the moisture content (Krus 1995):

–   The bridge theory: Pores are seldom cylindrical as shown in Figure 2.1, but will have cross sections of different sizes. As the moisture content increases, still more water will be adsorbed at the walls of the pores. In the narrower parts the water layers will meet and form a short cut for moisture transport as it has shifted from diffusion to the much faster liquid transport.

–   The surface diffusion theory: At higher moisture content more water molecules are adsorbed at the surface of the pores. As the sorption layer gets thicker it becomes more mobile. The solid in porous materials are crystals, therefore the walls of the pores will not be round but more in the shape of a polygon. In the corners the sorption layer will be thicker, enhancing the moisture transport.

Bridge theory   Surface diffusion theory
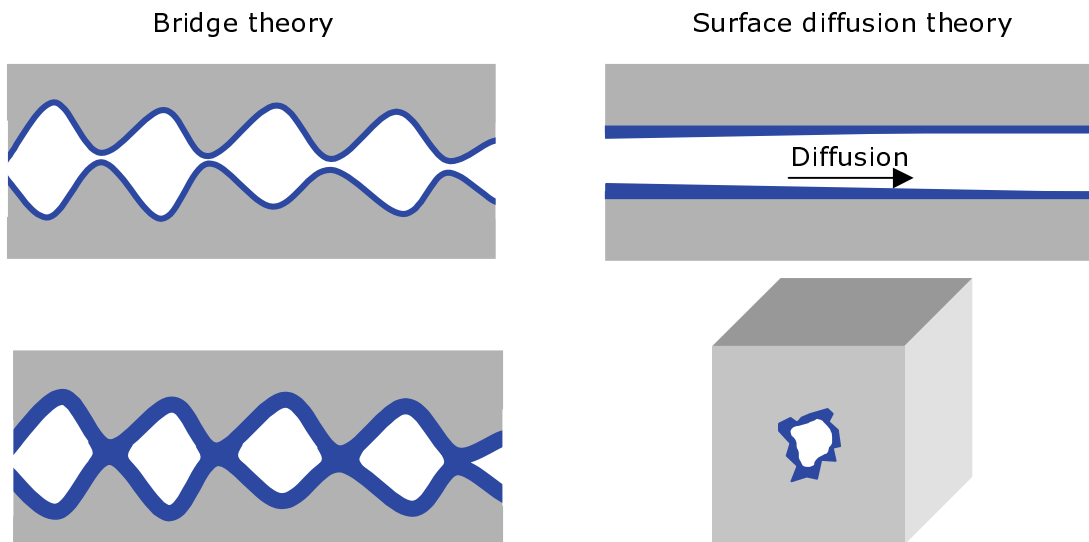
Figure 2.4:   Different theories on why water vapour permeability depends on
                moisture content. Left: the bridge theory; as the moisture
                content increases the narrow gaps become water-filled, allowing
                liquid transport. Right: surface diffusion theory, the adsorbed
                water molecule layer is mobile, as the pores are not round more
                liquid might be transported in the corners of the pores.

The principles in the two theories is shown in Figure 2.4. Both theories originate
from the fact, that in porous, hygroscopic materials water molecules are adsorbed
at the pore walls. The higher the vapour pressure the thicker is the adsorbed layer.

Whether one or the other theory is correct, or a third explanation is needed, is
unimportant to this project. The main point is, that vapour permeability increases
with moisture content and that diffusion at higher vapour pressures involves an
adsorbed layer of water molecules.

When water has been transported through a porous material, either by capillary
suction or diffusion, and reaches the surface, e.g. the exterior surface of a building
envelope, convection will take over, as air movements will transport the moisture
away from the surface. Convection will not be discussed any further in this thesis.

2.3 Material and surface properties

Moisture transport is important for how water penetrates porous materials and dry
out, but hygroscopic porous materials can also retain water, an ability that can
influence the durability and thermal conductivity of the material. How specific

material and surface properties affect moisture transport and retention is presented in this section.

2.3.1 Porosity

Porosity is the ratio of volume of air in a dry material to the total volume and is often given as a characteristic material parameter. Porosity, in many cases, gives a fair idea of many properties of the material; especially strength but also dry density, thermal conductivity and possibly water content. However, porosity does not give any information on pore shape or size, which can be decisive for moisture transport and durability.

In Section 2.2.1 capillary rise was explained assuming that pores are cylindrical. However, this is rarely the case, instead they can have different shapes:

- Closed pores. Not part of the "active" pore system. As a result they will not be filled with water nor take part in moisture transport.

- Inkbottle shaped pores with a narrow opening and a large volume behind. Can influence the durability, as frost resistance is increased.

- Open pore system, where all pores are connected. In e.g. wood the pore system can be uniform with regular pores in one direction, but in most mineral materials the shape and size of the pore varies considerably, and the materials are often isotropic.
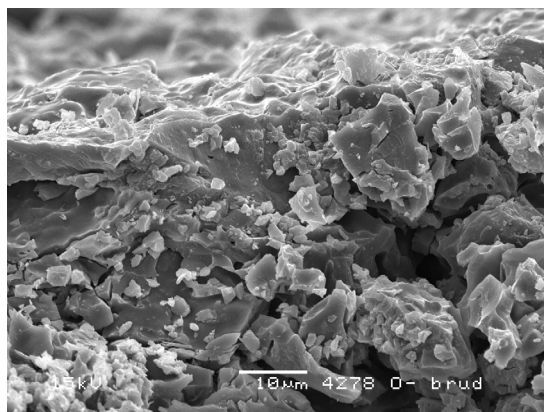
Figure 2.5:   SEM picture of a fractured roofing tile. The pores are not regular cylinders but simply the space between the solid material. The bar equals 10 μm.
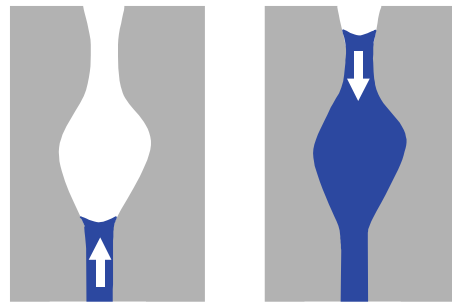
Figure 2.6: Wetting and drying through pores. The size of the meniscus determines the water content at equilibrium at a given RH. Left: wetting process. The water stops as the pore radius becomes too large. Right: drying process. The water in the large part of the pore is still filled.

Figure 2.5 shows a SEM picture of a fractured roofing tile. Instead of nice cylindrical pores, the pores appear as the voids between particles without any kind of regularity.

This irregularity has importance for the moisture transport as indicated in Figure 2.4. The size of a meniscus defines the capillary rise. In irregular pores this can result in different moisture content, as the meniscus might stop at a different place if a material is dried out than if it is wetted. Figure 2.6 illustrates the principle. As a result the equilibrium for wetting and drying processes is different: the phenomenon is called hysteresis.

As stated in Section 2.2.1 the pore size determines how far water can be transported and how fast the process goes. The smaller the pores the longer the transport, but at with decreasing rate. The material with fewer, but larger, pores will react relatively fast to changes in moisture content of the surroundings, while the other material will fill its pores slower but continue to transport for a longer time and over longer distances.

How porous materials take up water and dry out is depending on the accessible water in the surroundings. When the relative humidity in the air is lower than 95 - 98 %, the material is in the hygroscopic region; above this humidity level it is difficult to determine relative humidity and moisture content in the material accurately (Pedersen 1990). However, in the hygroscopic region the measurements are sufficiently accurate to determine reproducible curves describing how the

equilibrium moisture content in the material depends on the relative humidity of the surrounding air under isothermal conditions. These sorption isotherms are empirical, and are in principle only valid for the sample, which has been measured. However, in practice these curves have proven to be useful for simulation purposes, where the sorption isotherms are used as general descriptions for hygroscopic behaviour of the materials.

Sorption isotherms do not only depend on the material (e.g. wood, concrete or tile), but also on porosity and pore size distribution. Figure 2.7 shows examples of adsorption isotherms illustrating how pore size distribution influence has an influence on the curve. In Figure 2.7 only adsorption isotherms have been showen. As most porous materials exhibit hysteresis as shown in Figure 2.6, the drying curve, desorption isotherm, will be above the shown curves.

There are different shapes of sorption isotherms, but they are typically S-shaped, which the curves in Figure 2.7 probably also would have been, if measurements below 20 % RH had been available. The curves have to start in (0,0).
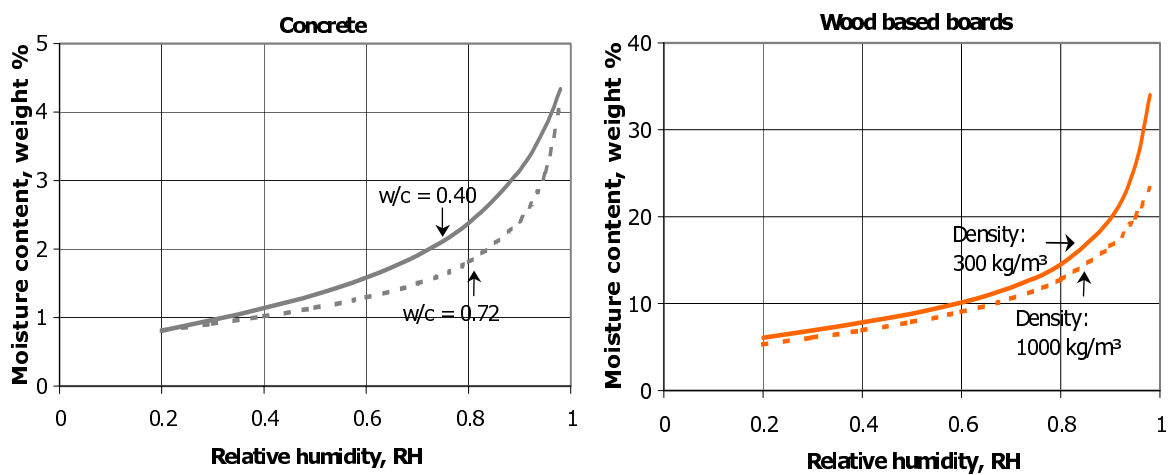
Figure 2.7: Adsorption isotherms for different materials. Left: concrete with different water cement ratio (w/c) but similar density (2300 kg/m^3). The pore size distribution is different in the two concretes. Concrete with w/c = 0.40 has finer pores than concrete with w/c = 0,72 and contains more water. Right: Wood based boards with different porosity, the boards with high porosity contains more water than the dense boards, pore size distribution is unknown for the two boards. Based on Hansen (1986)

The S-shape can be explained by how water molecules fill the pores: At low RH water molecules start forming a monolayer on the pore walls. At higher RH the layer is full, and multilayers are formed (relatively flat part of the sorption curve). At some point the layers meet and small pores are filled. From this point on capillary condensation take place and the curve becomes steeper.

Capillary condensation occurs because of the meniscus formed in the small pores, Equation (2.1) describes the pressure at the surface, as illustrated in Figure 2.8. The pressure P' under the meniscus will be smaller than the atmospheric pressure, reducing the free energy of the water and the saturation pressure is thereby reduced. (Gottfredsen & Nielsen, 1997).

The relative humidity just above a meniscus is given by the Kelvin equation (Pedersen, 1990), combined with Equation (2.1) it means:

$$\ln(RH) = \frac{-\Delta P}{\rho_w R_v T} = \frac{-2\gamma\cos\theta}{r \cdot \rho_w R_v T} \qquad (\ 2.6)$$

where ρ_w = density of water (kg/m^3), R_v= Gas constant for vapour = 461.5 J/kgK and T = absolute temperature (K), γ = surface free energy (N/m), θ = contact angle and r = radius of pore.
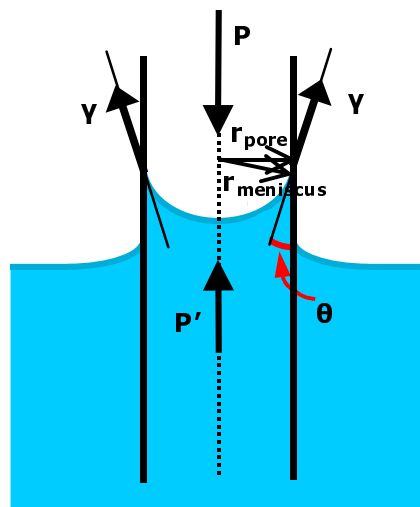
Figure 2.8:   Forces acting on a meniscus in an idealised cylindrical pore. (Gottfredsen & Nielsen, 1997)

Mostly it is a fair approximation to set the contact angle = 0. In that case the radius of the pore is equal to the radius of curvature in the meniscus. Equation (2.6) can then be rewritten as:

$$\ln(RH) = \frac{-2\gamma}{r \cdot \rho_w R_v T}$$

(2.7)

If the water vapour pressure in the air is higher than the reduced saturation pressure over the meniscus, condensation occurs.

Figure 2.9 illustrates the different steps in adsorption in porous materials. In materials with similar porosity but different pore size distribution, e.g. one material with many fine pores compared to a material with less but larger pores, the material with finer pores will have a larger surface and can therefore bind more water molecules at the same relative humidity. But also because capillary condensation occurs earlier in small pores. The multilayer is limited by the size of the pores, and capillary condensation will gradually take over (Chorkendorff & Niemantsverdriet, 2002).
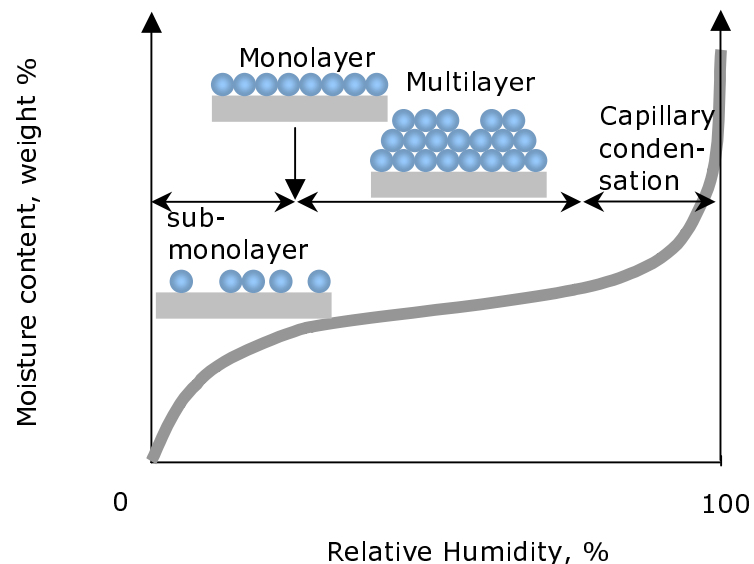
Figure 2.9: Schematic presentation of sorption isotherm, illustrating how pores gradually are filled with water, based on Chorkendorff & Niemantsverdriet (2002) and Hansen (1986).

Above the hygroscopic region, the capillary domain, pores are filled with liquid water, and the mechanisms described in Figure 2.1 and Equation (2.1) become important if in contact with a water reservoir.

The suction pressure -ΔP under the meniscus (see Figure 2.8) is a hydraulic pressure, water is sucked in the material. The Kelvin Equation is applicable and a general description is therefore:

$$\ln(RH) = \frac{-\Delta P}{\rho_w R_v T} = \frac{-2\gamma\cos\theta}{r\cdot\rho_w R_v T} \qquad (2.8)$$

which shows that contact angle and pore size are decisive for the water uptake in porous materials.

This expression is valid for all pressures and can therefore be used to describe a suction curve, which combine the hygroscopic region with the capillary domain. An example is shown in Figure 2.10.
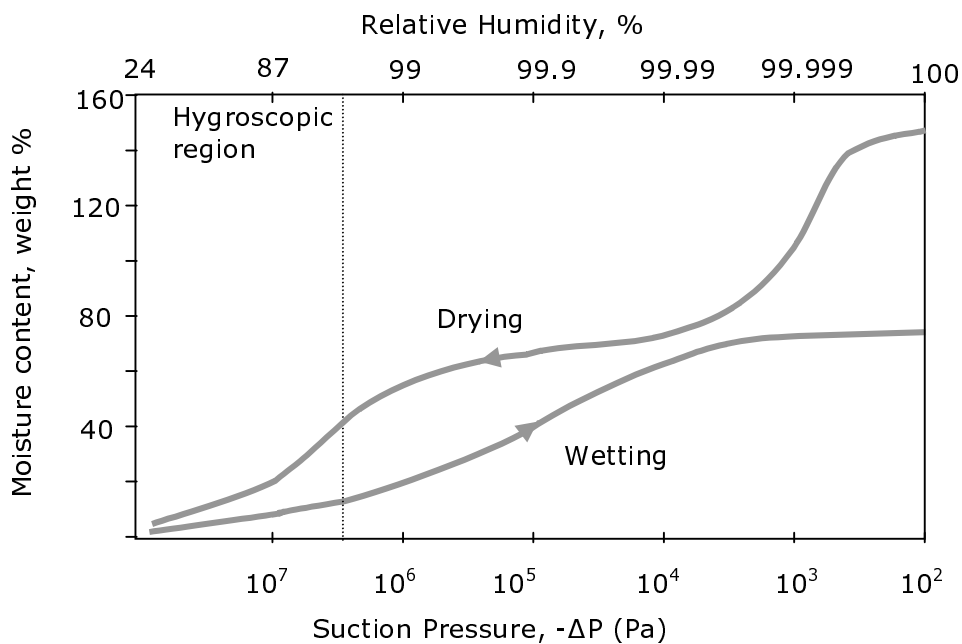
Figure 2.10: Example of suction curve. The curve combines the hygroscopic region with the capillary domain. The example is cellular concrete. There is a noticeable difference between drying and wetting. Based on Pedersen (1990) and Gottfredsen & Nielsen (1997)

2.3.2 Chemical composition

Pore shape and size are physical properties given by the substrate. Changing them would mean either choosing another material or blocking the pores. In new buildings one might consider the first and sealing of the surfaces might be seen as blocking of pores, but otherwise: except for narrowing are pores unchangeable.

If one wishes to change the moisture transport in the material, not the pores, but how the moisture moves in the pores should be changed. As stated in Section 2.2.1, moisture transport can be seen as a solid-liquid-gas interaction. In the case of moisture at exterior surfaces of building envelopes, the gas and liquid is given as water vapour and liquid water respectively, only the solid can be chosen. Focus of this section is therefore on properties of the solid and its interactions with water. This section is not limited to porous materials, because the attention here is at the interface between liquid and solid, which could be e.g. water and a pore wall or the surface of a glass panel.

2.3.2.1 Surface tension or surface free energy

Atoms and molecules in the bulk of a solid are placed in a lattice and interact with its neighbours and experience a uniform force, except for minor defects, which are unimportant for this illustration. If the bulk is divided, the lattice breaks up and some of the atoms or molecules loose their neighbours at one side; the field will no longer be uniform. Because of the neighbours inside the lattice, the free energy of atoms or molecules here is lower than when one side is free.

A   B
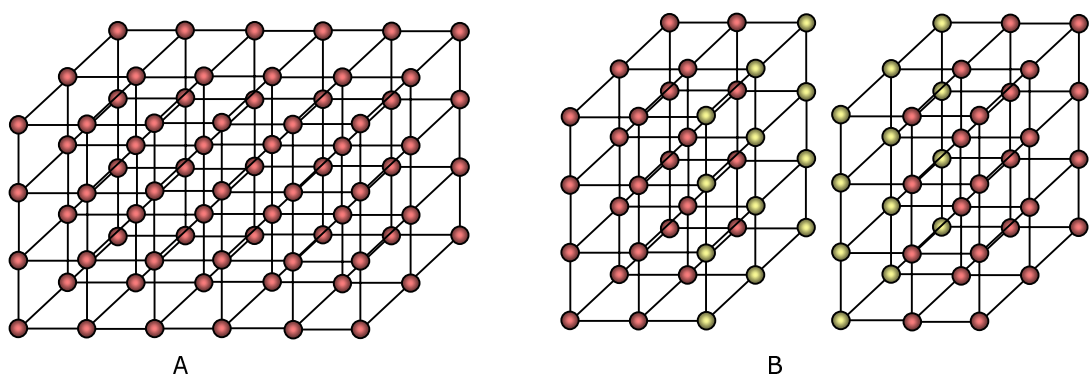
Figure 2.11: Changes in atomic forces when new surface is formed. A: in the bulk material all atoms are in a lattice, experiencing uniform force from neighbours (red atoms). B: if the surface is cleaved, the atoms at the new surface (yellow atoms) loose their neighbour and therefore increase their free energy.

Consequently the atoms or molecules that loose their neighbours, experience an increase in free energy (Myers, 1991). The principle is illustrated in Figure 2.11.

For a whole system the increase of free energy is proportional to the area A of the new surface. In terms of reversible work W needed to overcome the attractive forces between the molecules or atoms at the surface can be described as (Myers, 1991):

$$\Delta W = 2\gamma A \qquad\qquad (2.9)$$

where the proportionality factor γ = surface free energy or surface tension.

Historically the term surface tension was used before the term surface free energy was introduced, and surface tension is still more used when considering liquids, but the terms are interchangeable (Adamson, 1990).

In short: the surface free energy describes the energy needed to create new surface. The surface free energy is material specific but temperature dependent and is an important term in describing wetting of surfaces.

Given this explanation for surface free energy the terms work of cohesion and work of adhesion, as illustrated in Figure 2.12, can be described as:

- Work of cohesion W_c: The reversible work required to separate two surfaces of area A of *one* material:

$$W_c = 2\gamma A \qquad\qquad (2.10)$$
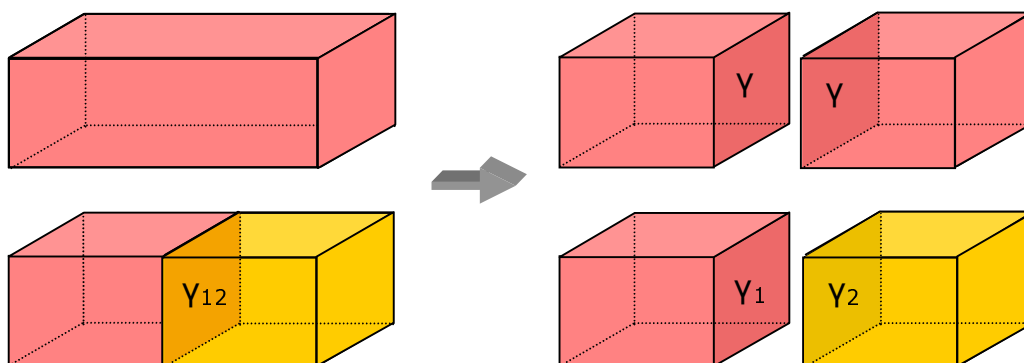
Figure 2.12: Work of cohesion and adhesion. Top: Work of cohesion; separation of two surfaces of one material with surface free energy γ. Bottom: Work of adhesion; separation of two surfaces of two different materials with surface free energies γ_1 and γ_2 respectively and γ_{12} as interfacial energy.

- Work of adhesion W_a: The reversible work required to separate two surfaces of area A of two *different* materials 1 and 2:

$$W_{a(12)} = (\gamma_1 + \gamma_2 - \gamma_{12})A \qquad (2.11)$$

γ_{12} is an interfacial energy, as illustrated in Figure 2.12.

Especially work of adhesion will be discussed later on as it has significance for soiling (see Chapter 3).

In general it is difficult to determine surface free energy by experiments. However there are different methods and a short description of two methods of measuring surface free energy of liquids will be given here:

- The capillary rise method. A clean glass capillary with a well-defied radius r is used in a set-up similar to the one shown in Figure 2.1. However, a receding meniscus should be used. The capillary rise (or depression) h is measured. Equation (2.2) can be rewritten and the surface free energy γ can be determined by:

$$\gamma = \frac{\Delta\rho \cdot g \cdot r}{2\cos\theta} \qquad (2.12)$$

where $\Delta\rho$ = difference in density in liquid and air, g =acceleration due to gravity and r= pore radius and θ = contact angle. As stated in Section 2.2.1 $\theta = 0$ is often a fair approximation which reduces Equation (2.12) to:

$$\gamma = \frac{\Delta\rho \cdot g \cdot r}{2} \qquad (2.13)$$

which is a quite simple way to determine the surface free energy. However, an exact solution, i.e. when $\theta \neq 0$, has been found, but in practise an iterative method is used, still only involving the parameters $\Delta\rho$, g, and r. This method is generally seen as the most accurate of all methods, but difficult to use in practice when $\theta \neq 0$. (Adamson, 1990)

- The drop weight method. A simpler method is by weighing droplets. Tate's law expresses the gravity W of a droplet as a function of surface free energy γ:

$$W = 2\pi r \cdot \gamma \qquad (2.14)$$

where r is the radius of the tip on which the drop is formed. However when a drop is formed, not the whole drop will fall, as up till 40 % of the liquid may still be attached to the tip. Therefore a correction factor most be introduced. By comparing measurements by the capillary rise method with this method, tables of correction factors have been developed. The factor depends on $r/V^{1/3}$, where V is the volume of the drop. When the gravity of the fallen droplet is determined as G, the right hand side of Equation (2.14) is simply multiplied by the correction factor. In this method the tip must be smooth, and the drops must form slowly (with a drop time of 1 min only a 0.2 % error is introduced). The method is good to 0.1%. (Adamson, 1990).

It is difficult to obtain absolute experimental values of surface free energy of solids. Instead measurements of the contact angle are widely used, see Section 2.3.2.2.

Tables with values for surface free energies or surface tension can be found in different handbooks of chemistry. Some general remarks and guidelines can be made on these values measured at ordinary temperatures (Baer, 1964):

- Except for liquid metals the surface free energy for all liquids, is less than 100 mN/m, e.g. the value for water is 73 mN/m.

- Soft solids like waxes and most solid organic polymers and compounds have surface free energy less than 50 mN/m. E.g. glycerine has the value 24 mN/m.

- Hard solids have surface free energies between 500 and 5000 mN/m, the greater the hardness and higher the melting point, the higher the surface free energy.

2.3.2.2 Contact angle

Water droplets at exterior building surfaces are typical examples of solid-liquid-gas systems. The angle θ between solid and liquid is called contact angle. Figure 2.13 illustrate how the contact angle can vary depending on the combination of solid-liquid-vapour.

Contact angle measurements can be done by direct measurement on a droplet resting on a surface. A goniometer can be used or by measuring the angle on a

photograph. Other methods using bubbles from a syringe where the bubbles are made to contact a solid below. The advantage is, that the bubble can be controlled, it can swell or shrink, which makes it possible to measure advancing and receding angles. The described methods have a precision of approximately 1°. (Adamson, 1990).

At solids where these methods are not applicable, like powders and soil other methods have been developed based on capillary pressures, sedimentation rates, wetting times etc. (Myers, 1991).

Wetting behaviour is guided by the size of the contact angle, as will be described in Section 2.3.3.1. Although different methods for measuring contact angles have been developed, the nature of the contact angle imply some difficulties in determination of a precise and reproducible angle for a given solid-liquid-gas system (see Figure 2.14):

- Time dependency. The contact angle diminishes with time. Houvenaghel & Carmeliet (2001) have reported this and offer an explanation: water molecules from the droplet are temporarily adsorbed at the surface, changing the forces between the molecules, favouring the long-range attraction forces. The result is spreading of the droplet and surface wetting i.e. decreased contact angle. In porous materials the wetting of the surface promotes water adsorption at the pore walls. As a result the water droplet will with time disappear from the surface as a combination of evaporation, adsorption at the pore walls and the intermolecular bonding forces.
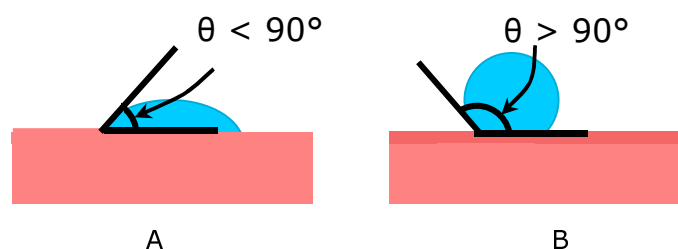
Figure 2.13: Different contact angles. A: Wetting behaviour, contact angle θ < 90°. B: Water repellent, contact angle θ > 90°. The contact angle is guided by the surface free energy as shown in Figure 2.16 and described in Equation (2.16).
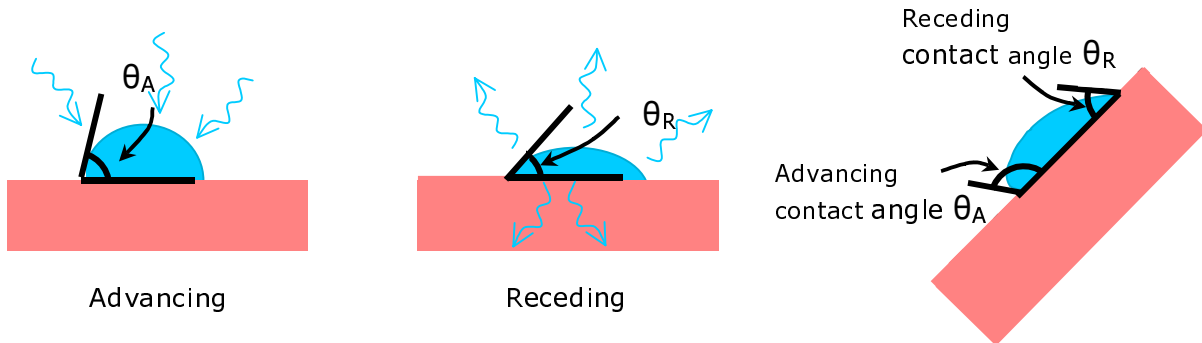
Figure 2.14: Inconsistency in contact angles. Left: a drop is placed at a surface, liquid is provided by e.g. condensation; the droplet grows, the contact angle is advancing. Middle: a drop is left at the surface; liquid evaporates or is absorbed in pores and the contact angle is receding. The difference in contact angle illustrates hysteresis. Right: the two different contact angles can be seen at a running droplet, however gravity is also responsible for the shape of the droplet.

However, the pictures given in Houvenaghel & Carmeliet (2001) do not show any signs of spreading on porous materials. The decrease in contact angle is only visible as a decrease in volume; the droplet becomes smaller. If the theory given above is correct, it must be a coincidence that spreading is neutralized by evaporation and adsorption in the pore walls. Alternatively the measuring technique might not be sufficiently precise to conclude whether any spreading occurs.

– Hysteresis, the contact angle depends on the history of the system. There is an advancing angle θ_A when a solid is wetted and a smaller receding angle θ_R when the liquid moves away. The reason for this behaviour is most likely, that when the droplet covers an area of the solid, pores and fissures in the solid trap liquid, and as the droplet moves away some areas will therefore still be wet (Baer, 1964).

– Roughness of the solid can enhance the contact angle. If the surface is rough in a way that the water can trap air between protrusions, the result is a composite surface with a larger contact angle θ_r than the true angle θ_{true} (Adamson, 1990):

$$\cos \theta_r = r_A \cdot \cos \theta_{true} \qquad (2.15)$$
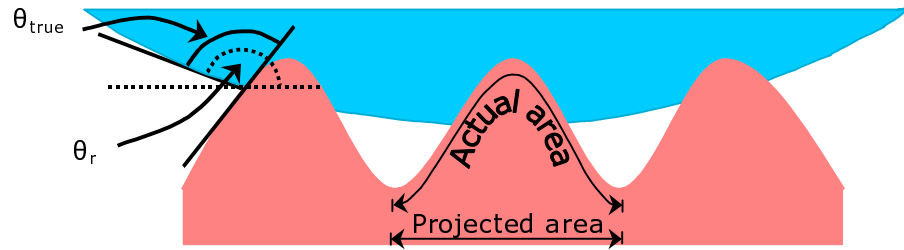
Figure 2.15: The contact angle is increased from θ_{true} to θ_r when the surface has sufficient roughness on the microscopic scale. (After Adamson 1990)

where r_A = ratio of actual (true) to projected (apparent) surface area, Which means that r_A describes a surface roughness factor. The phenomenon is illustrated in Figure 2.15. Roughening a surface will enhance the wetting / non-wetting behaviour of the original surface, not change from wetting to non-wetting or vice versa; the two angles θ_r and θ_{true} cannot be at each side of 90°. The contact angle can only be independent of the surface roughness, if the contact angle is 90°.

Measurements of contact angles can therefore be deceiving and the effects listed above can be very difficult to avoid in experimental work, especially when working with porous materials. Despite difficulties in determining its value, the contact angle is a very useful tool in describing how water is transported at the surface of materials. Its value is often given within a range.

The contact angle is closely connected to the surface free energies of the interfaces by Young's equation (Baer, 1964), this can also be seen from simple geometrical considerations in Figure 2.16:

$$\gamma_{SV} - \gamma_{SL} - \gamma_{LV} \cos\theta = 0 \Leftrightarrow \gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} \qquad (\ 2.16)$$

Where θ = contact angle and γ = surface free energy with subscripts L = liquid; S = solid; and V = vapour. The surface free energy, denoted γ, given in handbooks is mostly γ_{SV} or γ_{LV} values, depending on whether the material is a solid or liquid.
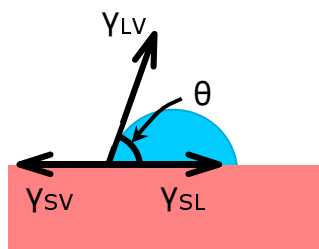
Figure 2.16: Surface free energies needed to describe the contact angle according to Young's Equation (2.16)

Work of adhesion W_a as given in Equation (2.11) can now be rephrased. If Figure 2.12 is used as illustration, the work of adhesion can be seen at the work needed to divide two materials, the liquid (L) and the solid (S) by vapour (V). When using the terms from Equation (2.11) the surface free energies correspond in the following way: $\gamma_1 = \gamma_{LV}$, $\gamma_2 = \gamma_{SV}$ and $\gamma_{12} = \gamma_{SL}$. Equation (2.11) now becomes:

$$W_{a(SLV)} = (\gamma_{LV} + \gamma_{SV} - \gamma_{SL})A \qquad\qquad (2.17)$$

Combining Equations (2.16) and (2.17) gives the Dupré equation (Adamson, 1990):

$$W_{a(SLV)} = A \cdot \gamma_{LV} (1 + \cos \theta) \qquad\qquad (2.18)$$

From Equation (2.18) it is clear, that low work of adhesion is obtained by enlarging the contact angle, as $\cos \theta$ decreases with increasing angle. From Equation (2.17) it can be seen, that lowering the surface free energy of the solid-vapour interface decreases the work of adhesion.

2.3.2.3 Critical surface tension

Measuring contact angles involves some uncertainties and as mentioned earlier it is very difficult to determine surface free energy for solids. Instead another term: critical surface tension γ_c, is often used e.g. in data sheets on solids. The term is widely used to describe wetting behaviour, as it defines the wettability of a solid as the lowest surface free energy a liquid can have and still form a contact angle on that solid (Thünemann, 2000). This means that if a liquid has a lower surface free energy than the critical surface tension of the solid, the liquid will wet the surface. Consequently, if the critical surface tension of the solid is very low, it is unlikely to be wet except by special liquids e.g. when detergents have been added.

The term is based in experiments, and a theoretical way to equating the critical surface tension with the surface free energy has not been found. However the term γ_c is from a practical point of view useful in understanding tendencies in adsorption at solids. Generally low critical surface tension indicates low surface free energy of the solid. (Myers, 1991; Adamson, 1990 and Thünemann, 2000).

The experimental background for the term critical surface tension was established by Zisman and co-workers based on the experience that at surfaces of solids with low surface free energy (γ < 100 mN/m), the contact angle formed by a drop on the solid surface is primarily a function of the surface free energy of the liquid (Myers, 1991). By using a homogenous series of non-polar liquids (e.g. alkanes, ethers etc.) on the surface of a solid, different lines could be obtained for the relationship between surface tension of the liquid and contact angle. By extrapolating each line to cos θ = 1 (theoretical total wetting), the lines met at about the same value, characteristic for the solid: the critical surface tension γ_c. The principle is shown in Figure 2.17. For polar liquids the method starts to break down. Although the method should be useful on solids with higher surface free energy, these are most likely to be covered with an adsorbed layer of fluids with a low surface free energy (Myers, 1991).
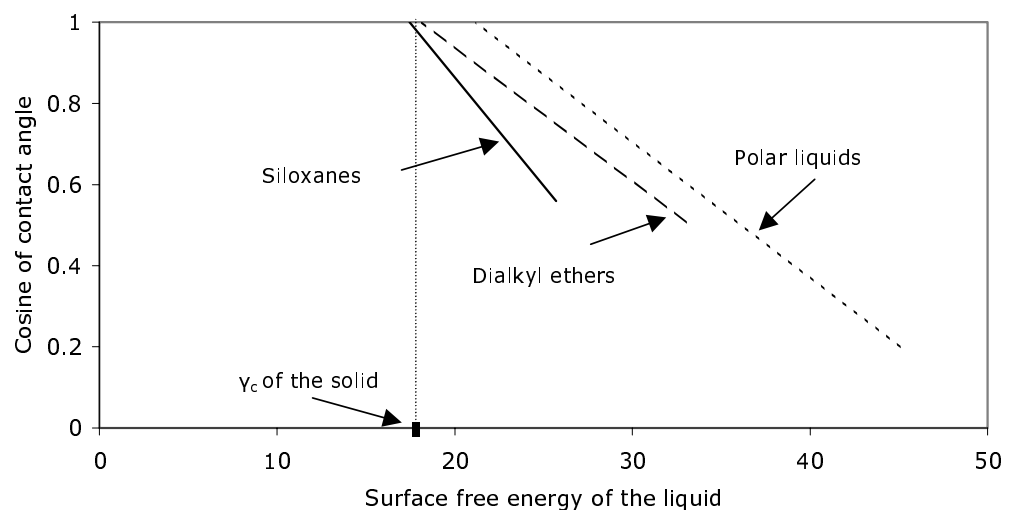
Figure 2.17: Principle of Zisman plots. The relationship between cosine of the contact angle and surface tension for several classes of liquids on teflon. For non-polar liquids the lines met at one point, the critical surface tension γ_c. (After Adamson, 1990)
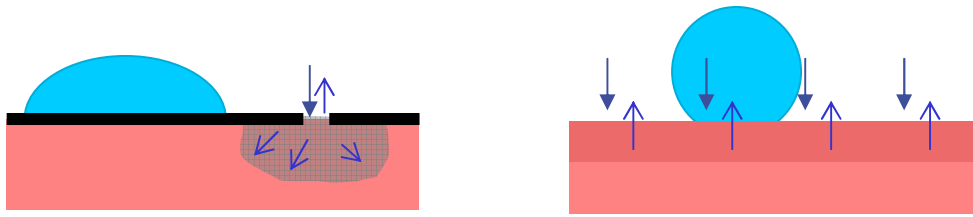
Figure 2.18: Water penetration into the building envelope can be stopped by sealing the surface; theoretically not allowing liquid in any form to penetrate the sealing. If there is a crack, the water can only dry out through the hole (left). Alternatively a hydrophobic layer (with a penetration depth) can be used; it prevents moisture in liquid form to penetrate, but allows diffusion (right).

2.3.3 Hydrophobic treatment

Moisture inside or at the surface of building envelopes is generally unwanted, as it can have a series of negative effects, see Chapter 4. A way to diminish the effect of moisture from the outdoor climate is to apply a surface treatment that prevents the moisture from penetrating the building envelope. Apart from a sacrificial layer two main types can be used:

– Sealing of a surface, making it *waterproof*. An impeccable sealing of a surface prevents moisture transport through the sealing.

– Coating of a surface, making it *water-repellent*. A coating that inhibits capillary suction but allows diffusion.

The difference of the two treatments is shown at Figure 2.18.

Sealing the surface is only effective if the sealing has no cracks, otherwise water will find the crack, penetrate the sealing, and the water will spread behind the crack. The only way moisture can dry out is through the crack, a time consuming process, and it is likely that during that time more water from the outside has found its way in. Therefore sealing of surfaces will not be treated any further in this thesis.

Water repellent treatments are more likely to succeed. Generally they enhance the run off effect and prevent capillary suction. If moisture still builds up behind the treatment e.g. through cracks in the treatment or internal moisture, it can escape

through diffusion. However, there is more to the broad field of hydrophobic treatments, the main subject of this section.

2.3.3.1 Wettability and hydrophobicity

Wetting of a surface occurs when the contact angle is so close to zero that the liquid spreads over the solid easily. Non-wetting is when the contact angle is larger than 90°, and the liquid tends to form spherical droplets that run off the surface easily (Adamson, 1990).

The definition of hydrophobicity can be even clearer: Water repellent or hydrophobic treatments are theoretically defined by the contact angle the material has after the treatment (Gottfredsen & Nielsen, 1997):

- A surface is hydrophobic if the contact angle θ > 90°

- A surface is hydrophilic if the contact angle θ < 90°

The theoretical impacts on a surface of a porous material when changed from being hydrophilic to hydrophobic are:

- <u>Capillary behaviour</u>. Instead of capillary suction, there will be capillary depression as seen at the right figure in Figure 2.1.

- <u>Contact area</u>. Because of the shape of the droplet, the covered area will be smaller. It is from this area e.g. capillary suction can occur.

- <u>Work of adhesion</u>. Not only is the contact area smaller, but with a large contact angle cos θ becomes negative, diminishing the work of adhesion according to Equation (2.18). Generally, hydrophobic surfaces have low surface free energies, decreasing the work of adhesion even further.

- <u>Droplet run-off</u>. As a consequence of the diminished work of adhesion, droplets will run off easier, maybe even removing particles in the process, see Section 3.4.1.

These theoretical considerations based on physical chemistry of surfaces all seem to favour hydrophobic treatments at exterior building surfaces. Unfortunately practical experiences have shown, that the risk of applying less successful or even harmful treatments is considerable. Choosing the right hydrophobic treatments, using the

right application and maintaining the treatment are essential to the success of
hydrophobic treatments.

2.3.3.2 Water uptake

Measuring the effectiveness of a hydrophobic treatment by measuring the contact
angle after application or after some time can be right in a theoretical sense. While
a high contact angle might be useful when the aim is an enhanced run-off effect
e.g. at non-porous materials, the aim in porous materials is more likely to prevent
water penetration, and the success criterion should therefore be decreased water
uptake.

Although a large contact angle should mean low water uptake several researchers
(e.g. Carmeliet, 2001 and De Clercq & De Witte. 2001) have found, that the contact
angle is not valid as a measure for the effectiveness of water repellent treatments,
as it does not correspond to the water uptake. De Clercq & De Witte. (2001) have
even shown results after ageing where the contact angle was intact but the
effectiveness was reduced and other results showing the opposite.

The reasons for this can be:

- <u>Difficulties in measuring</u> contact angle as mentioned in Section 2.3.2.2

- <u>Contamination</u>. If either the solid or the liquid is contaminated, θ might
  be altered. If a surface has been exposed to contaminants like oil or
  hydrophilic particles the surface free energy is changed and therefore also
  the contact angle. However, the contamination might only be superficial,
  within the pores the original treatment can still be active and the water
  repellency is intact. Biological growth might have the same influence.

- <u>UV-radiation</u>. UV-light decomposes polymers and is therefore likely to
  have an effect on hydrophobic treatments. However, only the exposed
  molecules are affected, within the pores the hydrophobic effect might still
  exist. The effect is questionable, as some studies even indicate that
  silicon-based compounds are not susceptible to UV-radiation (Charola,
  2001).

- <u>Cracks</u>. Larger cracks in the surface may cause water uptake. A critical
  width of cracks has not yet been established, but 0.3 mm seems to be

generally accepted when concerning hydrophobic treatments. However, Sandin (1999) has shown that 0.1 mm is a more reasonable limit, if water penetration cannot be accepted relatively often.

Measurements of contact angle are therefore more of academic interest. For practical purposes water uptake should be measured. In fact, standardized tests for hydrophobicity e.g. the German regulation ZTV-SIB 90 (1990) use the water uptake not contact angle to evaluate the efficiency of the treatment. Tests are described in ZTV-SIB 90 (1990). In these tests samples are immersed in the hydrophobic agent for 1 min. After 14 days the water uptake is tested by placing the samples in water and measuring the water uptake for the next 28 days. However, no requirements to water uptake are listed. Only British Standard and Dutch regulations have defined when a treatment can be called hydrophobic, their demands are respectively 50% and 80% reduction in water uptake (Gerdes, 2001).

In the laboratory the water uptake is often measured by weighing of smaller samples before and after exposure to water e.g. immersion, compared to similar weighing of non-treated samples. At larger building components, like walls, weighing is not possible. Instead water ingress by driving rain can be simulated and measured with the Karsten pipe in accordance with RILEM Recommendations (De Clercq & De Witte, 2001). The principle is shown in Figure 2.19. The Karsten pipe is sealed to a surface with a given area. Water is filled in the pipe to a given height, and in regular time steps the decrease in the height of the water is measured. To maintain a water column pressure of approximately 10 cm, it might be necessary to refill the pipe (Karsten, 1992).
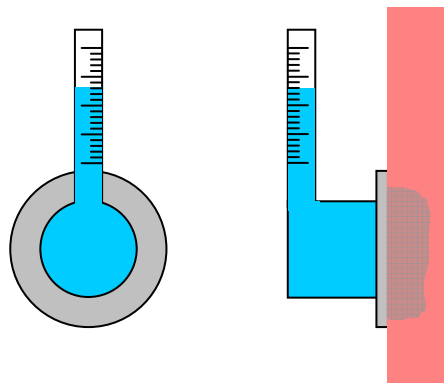
Figure 2.19: Measuring water uptake with Karsten pipe at a vertical surface. The height of the water column is measured at given times. A similar apparatus exist for horizontal surfaces. (After Pleyers, 1999)
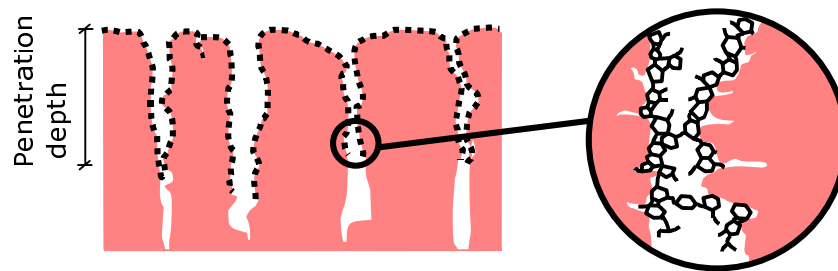
Figure 2.20: Penetration depth. The surface-near pore walls are treated with hydrophobic agent, but the depth of the penetration varies with pore size and shape. Penetration depth will be an average of penetration depth in the pores. The enlargement shows that not all pores are treated, and treatments with large molecules may clog up the pores.

2.3.3.3 Penetration depth

When a hydrophobic treatment is applied to a porous substrate the treatment will cower the top of the material and to some extent the surface-near pore walls. The thickness of the treated layer is called the penetration depth, and is illustrated at Figure 2.20.

The penetration depth is very important for the long-term performance of a hydrophobic treatment (Gerdes & Wittmann, 2001).

The size of the penetration depth is a result of many factors and combinations hereof, the most important parameters are:

- Porosity. Hydrophobic treatments are transported into the porous material by capillary suction. Its susceptibility to the treatment will be similar to how fast water will be sucked into the material. The faster, the larger penetration depths. I.e. brick and other relatively porous materials will have larger penetration depths than denser materials like concrete.

- Contact time. As a consequence of the capillary transport of the hydrophobic agent, the time the surface is in contact with the agent influences the penetration depth. Longer contact times means more time to transport the treatment into the material.

- Hydrophobic agent and solvent. Different hydrophobic agents would be effective at a given solid, but if the substrate has very fine pores there is

a risk of clogging up the pores if the molecule chains of the hydrophobic agent are too long (Carmeliet, 2001), see Figure 2.20. Whether the treatment is solvent-based or water-based seems to influence the penetration depths more than the protective properties of the treatment: water-based treatments show lower penetration depths (Charola, 2001). The subject is treated further in section 2.3.3.5.

– Application. The way the hydrophobic treatment is applied to the substrate and under what conditions affect the outcome. Aside from the contact time also the moisture content in the substrate prior to the application has an effect. Penetration depth decreases with initial moisture content (Meier & Wittmann, 2001 and Sandin 2003). Temperature, however, does not seem to be very important when it is in the range of 0-55°C (De Clercq & De Witte, 2001). To minimize the risk of defects in the application spraying or application with brush should always be from the bottom and upwards (Verhoef, 2001).

To increase the penetration depth in concrete one could imagine adding a hydrophobic agent to the concrete mixture but the hydration process in concrete takes place over a long period and would probably cover the hydrophobic agent, so changing the contact angle and the hydrophobicity can be lost. This is probably why – aside from the price – the method is not used in dense concrete structures, where it is very difficult to gain penetration depths in mm size. At least this is the reason why hydrophobic treatments should not be applied too early on concrete (Meier & Wittmann, 2001).

2.3.3.4 Silane and Siloxane

The most commonly used active agents in hydrophobic treatments are silane and siloxane. Other silicon-based compounds like siliconate and silicone resin have been used earlier but are inferior to the others either because they are limited to fewer materials, lower penetration depths or visible covers (Sandin, 1996 and Schultze, 1997). Both silane and siloxane are silicon-based and have low surface energies. The major difference is the length of the molecules: if a small part of the silane is replaced by another silane molecule, it becomes a siloxane (Gerdes, 2001). Figure 2.21 shows an example of silane/siloxane molecules.
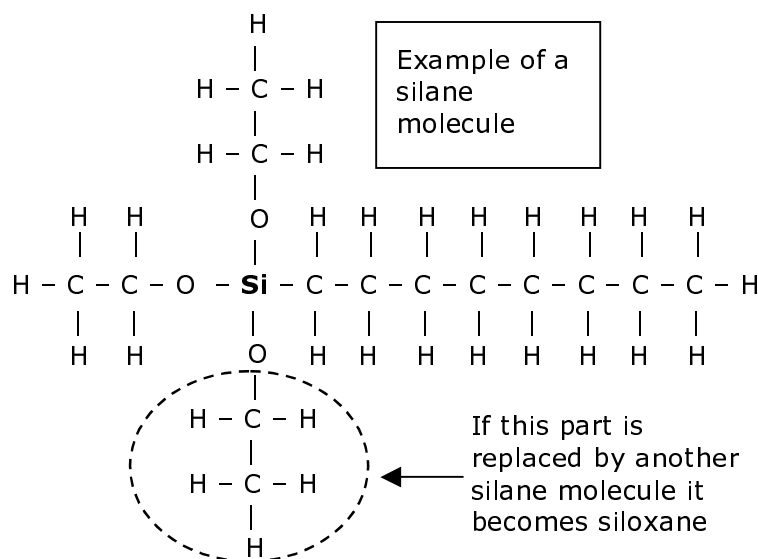
Figure 2.21: Schematic illustration of the silane n-octyltriethoxysilane $C_8H_{17}Si(OC_2H_5)_3$. If the encircled part is replaced by another silane molecule, the new molecule is a siloxane molecule.

When exposed to water silane and siloxane become instable and are very reactive, they will start to hydrolyze and afterwards condensate. The two step mechanism is depicted in Figure 2.22. Condensation can also occur directly with silicon in the substrate. How fast the reaction takes place is very dependent on the pH in the material; in acid environment step 1 is favoured, in alkaline environment, step 2 is favoured (Gerdes, 2001).

Responsible for the hydrophobic effect is the hydrocarbon group "R" or the alkyl, which is attached to Si. The main difference in many of the commercial available hydrophobic treatments is the length of this alkyl.

It has been suggested, that increased length and branching of the R group improves the performance of the water repellents. However, most of the available treatments have small groups, the silane depicted in Figure 2.21 has an octyl group, which is a relatively large group in water repellents used in practice (Charola, 2001).

Carmeliet (2001) has investigated how effective a water repellent with an octyl group was in treating two materials; ceramic brick with a coarse pore system and calcium silicate with a fine and midsize pore system. The length of the hydrophobic component was 10-100 nm, the pores in ceramic brick were 1-10 μm, and the
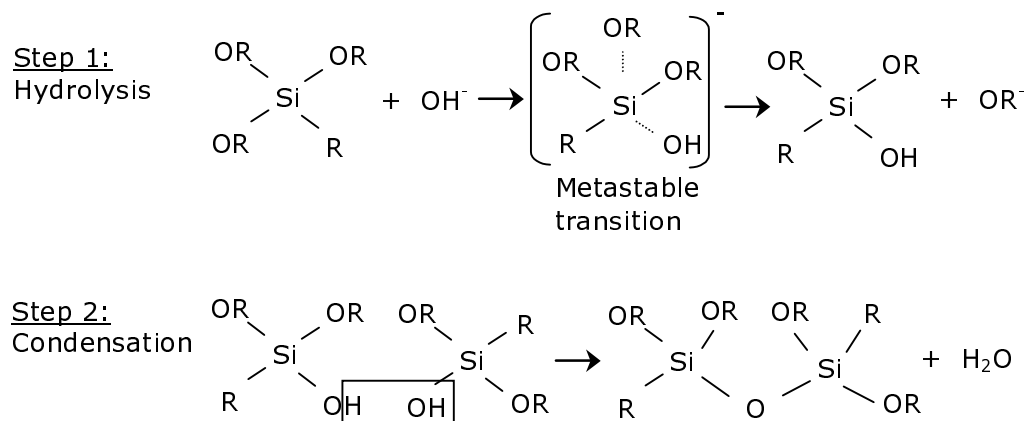
Figure 2.22: When exposed to water silane and siloxane transform in two steps: hydrolysis and condensation. R = Radical (water repellent hydrocarbon group, alkyl). (After Gerdes, 2001)

treatment worked perfectly. In calcium silicate a relatively high amount of pores are < 10 nm, and the treatment was less successful, probably because the polymer does not treat the fine pores, see Figure 2.20.

When applied to porous materials, the hydrophobic agent is transported into the material by capillary suction. Most porous building materials contain silicon, and when inside the material, hydrolysis and condensation continues.

Silane or siloxane can connect to the solid in basically different ways (Gerdes, 2001):

- By adsorption
- Through hydrogen bridges
- Through chemical bonding, see Figure 2.23.

Siloxane has the advantage, compared to silane, that the surface free energy is somewhat 10 % lower, the reaction rate in the siloxane is higher and siloxane does not evaporate from the surface like silane does, but stays on the surface until the conditions are right for forming polymers (Schultze, 1997).

2.3.3.5 Solvents, emulsions and gels

Silicon-based hydrophobic treatments are available as undiluted or diluted with different solvents. Solvents like alcohol or white spirit has for environmental reasons been superseded by water based emulsions and are now mainly used in connection with stone conservation (Gerdes, 2001).
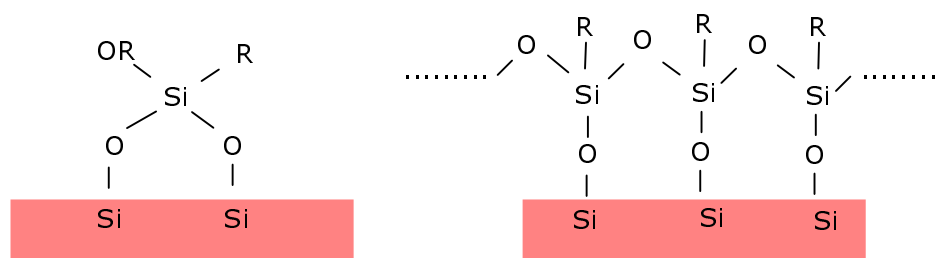
Figure 2.23: Silicon-based polymers can adhere to the Si-containing substrate through chemical bonding. The silane or siloxane reacts with the silicon in the substrate (After Gerdes, 2001)

Silicon-based compounds and water are not miscible. However, by intensive stirring the silicon-based compound will split up in small droplets and can be dispensed in the water. The dilution will not be stable and will after a short while return to two separate phases. But an emulsifier would lower the interfacial tension and thereby facilitate the formation of droplets, with the addition of a stabilizer, which prevent breaking of the emulsion i.e. separation in two phases, the dilution becomes stable (Myers, 1991).

Three different types of emulsions are used for hydrophobic treatments of buildings. These are shown in Table 2.3 based on Gerdes (2001).

The relatively high fraction of water in water-in-oil emulsions results in an increased surface free energy for the substance. E.g: The surface free energy for octyltriethoxysilane changes from 25.5 mN/m in a pure substance to 27.9 mN/m in a 50% solution in water and to 30.2 mN/m in a 10 % solution (Gerdes, 2001).

Water-in-oil emulsions tend to have a smaller penetration depth than solvents especially in concrete. Gerdes & Wittmann (2001) have a theory on why this is: Concrete has very fine pores and act as a filter; the droplets are too small to enter the pores. The emulsion breaks because of ions in the pore solution, organic compounds act as demulsifiers, or the emulsifier is adsorbed at the surface. In all cases the water in the emulsion will penetrate the substrate first, hindering the uptake of the hydrophobic agent.

Type of emulsion	Components	Droplet size	Solution on application
Water in oil	Water and Silan / siloxane	0.5 – 10 µm	10-25 %
Water in oil	Water, Silan / siloxane emulsifier and stabilizer	10-80 nm	10-25 %
Oil in water	Water and Silan / siloxane	No information	~ 80 %

Table 2.3:   Most common hydrophobic treatments in the building trade. (Gerdes, 2001)

Oil-in-water emulsions are creams or gels. They have a high viscosity, like skin cream. Like traditional hydrophobic treatments they can be applied by brush or spray, but instead of a contact time of 20 sec., which is the normal time for liquids at vertical surfaces, they stick to the surface prolonging the contact time significantly (Bofeldt, 2001). The treatment is invented for concrete where penetration depths normally are very small, but these treatments show higher penetration depths. However, the method is relatively new - from 1994 (Hankvist & Karlsson, 2001) - and results from other materials than concrete have not been reported yet.

2.3.3.6 Other hydrophobic agents

As stated in the beginning of Section 2.1.2 different liquids have been used for hydrophobic treatments, even linseed oil is used. Investigations have showed (Gerdes, 2001) that with a correct application this is comparable to treatments with silane or siloxane.

The history of water repellents shows many failures. But in stead of basing the search for improvement in hydrophobic treatments solely on trial-and-error methods and learning from the mistakes as the general tendency has been, one could use the gained knowledge to look for new possibilities. E.g. Tetrafluoroethylene (Teflon), shown at Figure 2.24, has the lowest reported surface free energy for solid homogeneous organic materials (Drummond & Chan 1996).

```
        F   F   F              F   F   F   F   F
        |   |   |              |   |   |   |   |
  F – C – C – C – ·············· – C – C – C – C – C –  F
        |   |   |              |   |   |   |   |
        F   F   F              F   F   F   F   F
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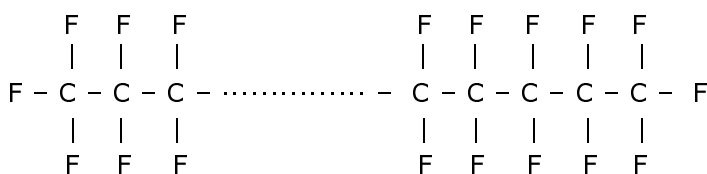
Figure 2.24: Principle structure of Teflon (Polytetrafluoroethylene)

Measurements of critical surface tension, γ_c show, that if perfluoromethyl groups are introduced as side chains the critical surface energy decreases even further. The closer the packing of exposed terminal CF_3 groups the lower the γ_c, e.g. from 18 mN/m in Teflon to 5.7 mN/m in a complex surface with enrichment of CF_3 groups, see section 3.4.2.3. This would probably mean very high contact angle. Although the results from using fluorine-containing polymers have been promising (Charola, 2001), the use is very limited.

The possibilities in using fluorine-based compounds for hydrophobic treatments are further discussed in Chapters 3 and 6.

2.4 Thermal conditions

When dealing with porous materials exposed to the outdoor climate heat, and moisture transport influence each other and the processes become inseparable. Accordingly, an analysis of how surface properties affect maintenance and operational costs would not be complete without a discussion of thermal conditions.
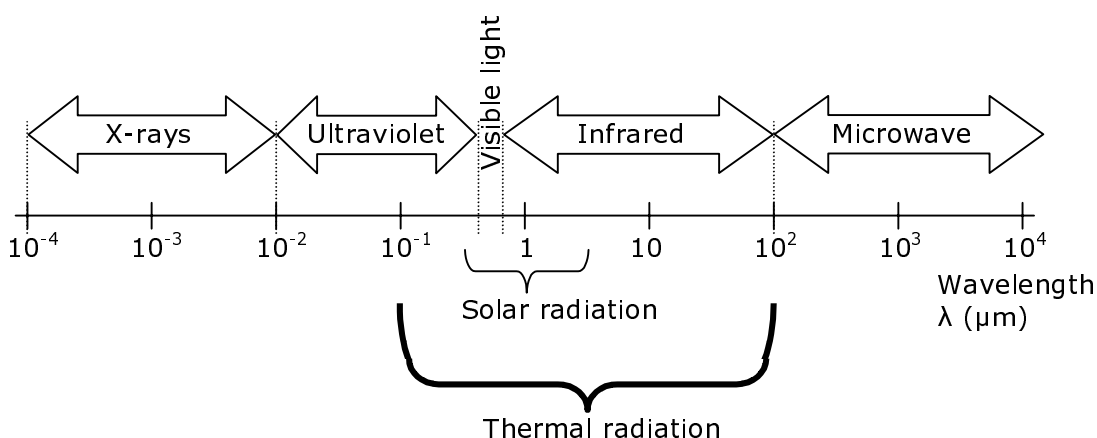
Figure 2.25: Part of the electromagnetic radiation spectrum. Thermal radiation (wavelengths between 0.1 and 100 µm) is of interest in this thesis. (After Hagentoft, 2001)

With basis in the Scandinavian climate where the outdoor climate in general is colder than the indoor climate, the fundamental idea in this section is: In a warm building envelope the moisture content will be low. As a result the moisture related problems like soiling and deterioration will be diminished and at the same time the thermal conductivity decreased.

Yet, a thorough description of heat transport is beyond the scope of this thesis, and only mechanisms important at the surface, primarily radiation, will be discussed.

2.4.1 Radiation

The spectrum of electromagnetic radiation is depicted in Figure 2.25. The wavelengths that are of interest here are those in the area of thermal radiation, which has wavelengths from 0.1 to 100 μm. Within the spectrum of thermal radiation different areas have special characteristics:

- Solar radiation: wave length of 0.3 − 3 μm

- Visible light: wave length of 0.4 − 0.7 μm

- Long wave thermal radiation
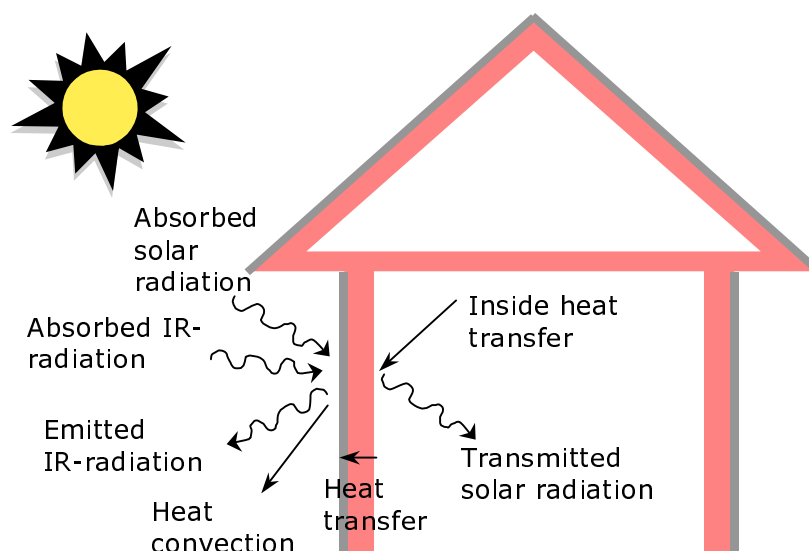
Figure 2.26: Heat fluxes at the building envelope in cold climates. Solar radiation is short waved (0.3-3 μm) while IR-radiation is long waved (3-40 μm). (After Zürcher et al. 1982)

Especially the distinction between short waved solar radiation and long wave thermal radiation is important. The heat fluxes at the building envelope can be described as shown in Figure 2.26. Radiant energy that meets a surface will partially be absorbed (α), reflected (ρ) and transmitted (τ) with the following relation:

$$\alpha + \rho + \tau = 1 \tag{2.19}$$

Transmittance for solar radiation through building envelopes is normally zero, except for glass (Hagentoft, 2001), and heat convection will at the moment be disregarded.

Although the possibilities of controlling heat gain by changing surface properties of the building envelope is used in warm climates e.g. by having white houses, probably due to the high reflectance of white, the idea has not been very used in cold climates where the problem is quite the opposite. Maybe because the gains are smaller in cold climates, as heating requires less energy than cooling. Furthermore, the effects are in the winter, where heat is needed, smaller because of lower sun angles, shorter day lengths and cloudy weather, on roof there might even be snow. Nevertheless, inspiration for cold climates can be found by inverting some of the findings from warm climates. Bretz & Akbari (1997) have reported how high-albedo (high reflection coefficient, for the whole spectrum of solar radiation) roof coatings can reduce the building cooling loads. Rewriting the requirements to cold climates where heating loads must be reduced, these are:

- Low solar reflectance, both in the visible and the near-infrared bands (wavelength of 0,3 – 3 µm)

- Low infrared emissivity (thermal radiation, wavelength of 4-40 µm)

- Maintain these properties for the service life of the coating

In walls or roofs where the transmittance equals zero, low reflectance seems to be incompatible with low emissivity according to Equation (2.19). However, the two terms consider different wavelengths and both requirements can be fulfilled. In general, throughout the thesis, is absorptivity restricted to radiation with short wavelengths and emissivity to radiation with long wavelengths. Solar collectors are an area where this is very important; the ratio between reflectance of solar

radiation and infrared emissivity generally determines the effectiveness of the collector (Chaudhuri et al. 1997).

The point of maintaining the properties is soiling-related in both climates; dirt decrease the reflectance and increases the emissivity. The first is unwanted in warm climates, the latter in cold climates. Consequently soiling should be avoided, a problem that will be addressed in the following chapters.

Figure 2.26 shows heat fluxes at the building envelope. At opaque envelopes no solar radiation is transmitted, and under stationary conditions the energy lost by emitted IR-radiation from the surface must be compensated by other energy fluxes (Zürcher et al. 1982):

$$0 = h_{sur,I}(T_I - T_{sur}) + h_{sur,O}(T_O - T_{sur}) + \alpha_{sol}I_{sol} + \varepsilon\sigma_S(T_{sky}^4 - T_{sur}^4) \qquad (\,2.20)$$

where:

$h_{sur,I}$ = coefficient of heat transfer through the envelope from exterior surface to indoor air

T_I = Indoor air temperature

T_{sur} = Exterior surface temperature

$h_{sur,O}$ = coefficient of heat transfer by convection at the outer surface

T_O = Outdoor air temperature

α_{sol} = absorptivity for solar radiation

I_{sol} = Global solar radiation on surface element at wavelength of 0.3 – 3 μm

ε = emissivity

σ_S = Stefan-Boltzmann constant = $5.67 \cdot 10^{-8}$ W/(m^{2}K^4)

T_{sky} = Effective radiant temperature of the ambient.

Disregarding the heat flux through the envelope, the surface temperature can be approximated to (Bretz & Akbari, 1997):

$$T_{sur} = T_O + \frac{1}{h_O}(\alpha_{sol}I_{sol} - \varepsilon I) \qquad (\,2.21)$$

Building material	a_{sol}	ε	a_{sol} / ε
Concrete smooth	0.55	0.96	0.57
Lime brick	0.60	0.96	0.63
Plaster White	0.36	0.97	0.37
Fir board	0.44	0.92	0.48
Plaster gray	0.65	0.97	0.67
Face brick	0.54	0.93	0.58
Roof tile brown	0.76	0.94	0.81
Aluminium anodised	0.33	0.92	0.36
Aluminium polished	0.20	0.05	4.00
Float glass	0.12	0.91	0.13
Glass with TiO_2/Ag(200Å)/TiO_2	0.11	0.03	3.67
Glass with Cu(100Å)/SiO_2(500Å)	0.34	0.05	6.80

Table 2.4: Averaged solar absorptivity, a_{sol} and IR-emissivity, ε and ratio a_{sol} / ε between them for different building materials. Normal incidence. From Zürcher at al. (1982).

Where

I = Net irradiance of surface element by thermal emission (atmospheric and from ground) at wavelength longer than 3 μm.

The two surface properties that can be changed are the absorptivity, a_{sol} and the emissivity ε, which are the subjects of the following sections. In cold climates the intent is to raise the surface temperature. Accordingly the aim should be surfaces with higher absorptivity values in the solar range and lower emissivity in the infrared range. Table 2.4 shows values for different common building materials but also for some glasses developed with more designed values.

To differentiate emissivity and absorptivity is to use different terms for the same property depending on at which wavelengths the property is used. Figure 2.27 shows examples of emissivity / absorptivity at wavelengths from 0.2 to 20 μm.
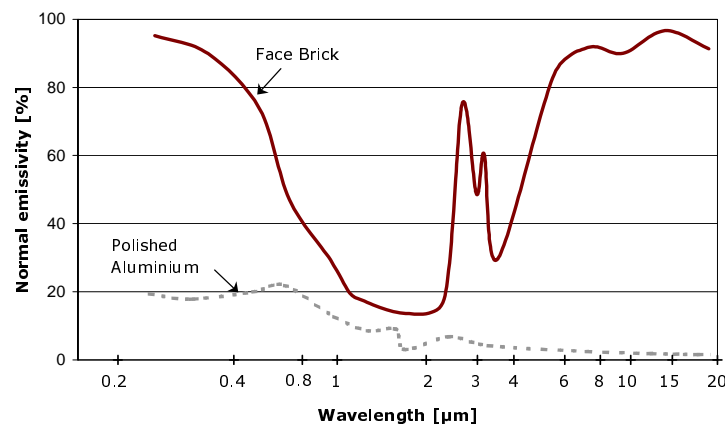
Figure 2.27: Total spectral normal emissivity for face brick and polished aluminium. Values for α_{sol} and ε as seen in Table 2.4 are is found at short and long wavelengths respectively. Based on Zürcher at al. (1982).

2.4.1.1 Absorptivity

The term used to describe how large a part of solar radiation is absorbed at the surface is here called absorptivity, although also other terms are used in the literature e.g. absorptance or the reverse; reflectance or albedo, depending on in which field the author is active. Absorptivity is 1 - albedo. Albedo is an often used term to describe the reflectance of solar radiation, a more precise term than reflectance, which sometimes has been misused as a description for reflectance of *visible* light (Bretz & Akbari, 1997) but in fact also exists for long wavelengths.

Although colours give a good indication for absorptivity, increasing with darkness, this is not the only factor. Berdahl & Bretz (1997) have reported different influences on the absorptivity:

- Measurements of absorptivity in white paint varied from 0.26 to 0.15. For comparison white asphalt singles were measured as well; the values were here 0.71 to 0.79.

- In pigments of red Fe_2O_3 (responsible for the red colour of clay) was a small amount of Fe_3O_4, magnetite, which is black, the impurities made a slight difference in the visible colour of the pigments. When the pigments were heated the magnetite was oxidized to Fe_2O_3 and the absorptivity in the 1.1 to 2.1 μm range decreased from 0.8 to 0.2.

- Metals generally have low absorptivity and the findings of Berdahl & Bretz (1997) of aluminium pigmented roof coatings show that the absorptivity decrease with the amount of exposed aluminium flakes.

- Roughness lowers the reflectance of a surface. If the roughness of a surface is on a larger size scale than wavelengths of light, a photon reflected from a rough surface is likely to hit the surface more than once before it escapes. In an example of white paint on microscope slide and on shingle the absorptivity changed from 0.20 to 0.40. Berdahl (1995) claims that paints have been developed entirely on visual reflectance and absorptivity properties could probably be improved by e.g. changing the pigment size, without affecting the visual impression noticeably.

2.4.1.2 Emissivity

According to Equation (2.21) the surface temperature would increase if the emissivity was low. However, most building materials have high emissivity approximately 0.9-0.95 (see Table 2.1). Metals on the other hand generally have low emissivity; the reflectance of metals drops in the UV and visible region, resulting in high absorptivity, the exception is polished aluminium, which has high reflectance in the whole spectrum of thermal radiation i.e. low absorptivity and emissivity (Chaudhuri et al. 1997). Polished aluminium has an emissivity of approximately 0.05 (Zürcher, 1982) but the value would not last, as aluminium anodise and form a weather-proof oxide layer at the surface. This layer has a high emissivity, which can be seen in Table 2.4.

Nevertheless the use of different metals on surfaces seems to be the most effective way to reduce the emissivity and surface treatments containing metal flakes is therefore a possibility. Hammerschmidt & Sabuga (2000) have measured emissivity of different paints for facades, which were said to have low emissivity. One paint was supposed to acquire low-emissivity through its content of titanium and aluminium micro particles. However, the emissivity was 0.9 not different from conventional paints. Two other paints were both dual component paints with an emissivity of 0.8 and 0.5 respectively. Unfortunately there is no information on how these low emissivities were achieved.

Simpson & McPherson (1997) used paints on roofs to reduce the cooling loads. Their main interest was the absorptivity, which was lower for the silver paint than a

dark paint, but the emissivity was also lower, therefore the silver coloured roof became warmer than a much darker roof. The silver paint contained aluminium powder.

The conclusion of the experience of the authors mentioned above must be, that there are possibilities in using metals powder in low-emissivity on-site paints, but the efficiency depends on the mixture. The polymers used in mixtures might also change the emissivity, but as Berdahl (1995) states; the IR absorption of polymers is not well understood. Instead he has a suggestion for an invisible extra coating containing mica flakes coated with semiconducter oxide. This coating could be applied to substrates of any colour, without changing the colour. However, it remains to be seen if this is possible.

If the surface treatment can be applied under controlled conditions, i.e. in factories, the possibilities are extended. Zürcher et al. (1982) tried to develop a surface treatment for aluminium sheets, used for facades. The idea was to apply an additional layer of chromium, which would result in very low emissivity. However, hard Cr and soft aluminium alloy had different thermal expansion coefficients, and Cr flaked off. A possibility to avoid this is applying a Cu and/or Ni layer between the two layers. The conclusion of the experiment was, that it is possible to manufacture low-emissivity layers on aluminium and alloys hereof, but considerable effort is required to make it useable for large-scale industry, which is necessary if the sheets should be used for building envelopes.

As well as absorptivity is changed by surface roughness, emissivity could be influenced. Hammerschmidt & Sabuga (2000) applied a metal containing paint, in two different ways; by roller and by spatula, and did not find any significant difference in emissivity. However it was the same paint that was found not to have the expected low emissivity. Cockeram et al. (1999) specify, that emissivity is increased if the surface texture has roughness with a height to width ratio > 1:5, as this would mean the protrusions would serve as individual black-bodies. This would be undesirable if the aim is to reduce the emissivity.

2.4.1.3 Combination of high absorptivity and low emissivity

While absorptivity or emissivity has not been a field of noticeable interest in the building industry in general, the glass industry and car manufactures have had far

more interest in the matter and are investigating combinations of high absorptivity and low emissivity for solar collectors and energy saving windows. The industry has developed selective absorper paints involving silicone binders, which have a high IR transmission in the 3-7 μm range, and pigments of PbS, $CuCrO_x$, $FeMnCuO_x$ or CuCrMnSiFe. The a_{sol} / ε ratio of these paints ranged from 2 to 10, only one of the paints were commercially available (Chaudhuri et al. 1997). Instead of paints more advanced coatings with different layers are now used. Transparent metal coatings (layers of ~ 15 nm) at glass are common low-emissivity films, e.g. glass – metal oxide – silver – barrier – metal oxide, the barrier protects the silver layer, which is very vulnerable, the metal oxide is durable against salt, sulphur dioxide and humidity. A further development is multilayer coatings, where two independent silver layers are used, this can decrease the emissivity from 0.13 (single silver layer) to 0.04 (Shaefer et al. 1997).

Demands on glass are much higher than on paint, because glass must be transparent, but glass is manufactured under well-controlled conditions, where high rate sputtering processes or pyrolysis makes it possible to apply layers with thickness of 10 nm (Shaefer et al. 1997). This is not possible in traditional in-situ surface treatments, where the same technique cannot be used. The closest thing is aluminium and other metallic paints and bare metal surfaces, which all have low infrared emissivity but high reflectance in the visible band.

3. SOILING

The term soiling is in this thesis used in a wide sense; it describes the process by which the original surface in time is being covered by a layer of either biological growth or environmental particles. The soiling process is a natural course as time goes by, it can only be reversed by actively removing the layer, but favouring certain surface properties can inhibit the process. This chapter begins with a reflection on whether soiling is an actual problem, that should be handled or just a fact we have to live with and make the best of. Later in this chapter are different kinds of soiling described and how they adhere to the surface.

3.1 Is soiling a failure?

When time causes changes in the character of a building's surface it does not necessarily mean that the surface is depreciated, sometimes soiling provides the building with a desired patina. In that case some would not see soiling as a failure, but what if the soiling causes deterioration? What has become more important: visual appearance or durability?

3.1.1 Physical change

Depending not only on the soiling but mainly the combination of soiling and surface, soiling can cause changes in the shape of building parts or prevent deterioration of surfaces. Whether one or the other is the case will often determine if the soiling is seen as failure or not.

3.1.1.1 Deterioration

That old monuments deteriorate with time is well known, often the deterioration is a combination of wear-and-tear and soiling. During the last 200 years has soiling become an increasing problem to monuments and buildings (Mansch & Bock 1998), Grobe (1996) has pinpointed the start of increased deterioration to about 1870 as a result of the industrialization as shown in Figure 3.1.

The increased burning of fossil fuels has released large amounts of sulphur, which has caused acid rain. The combination of acid rain and marble, a popular building material for ornamentation and monumental buildings, changes marble to gypsum; a gypsum crust is build. This new layer can be regarded as soiling because the colour is often dark. The crust obscures the expression of the ornament or building part.
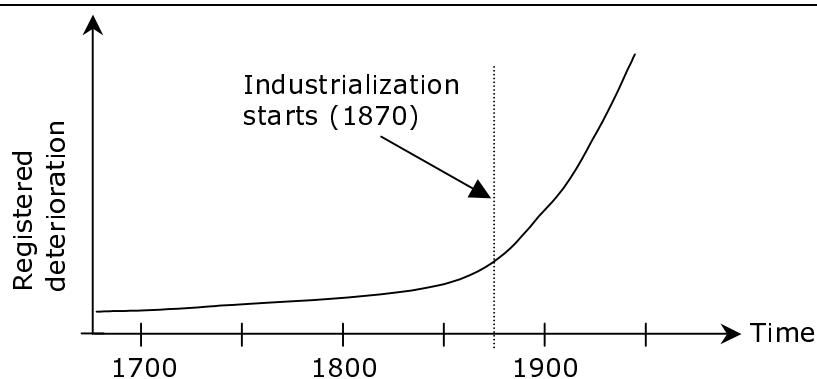
Figure 3.1: Principle of increase of registered deterioration at historic buildings, arbitrary linear units for deterioration (After Grobe, 1996).

Gypsum has low durability, which results in loss of material, leaving more marble exposed to the acid rain and further deterioration. In this case the soiling has formed a chemical combination with the surface and just removing the soiling can no longer restore the original expression of the monument.

Biological growth can be a deteriorating kind of soiling. Whether algae, lichen and moulds influence the durability of materials is questionable (see Section 3.2) but higher plants (moss and above), which have found footing because of soiling, can penetrate surfaces and start deterioration of building parts.

3.1.1.2 Protection

Soiling can have a positive effect on durability. Environmental particles can have an oil-based origin and form a greasy layer on the building envelope, this layer will be water repellent and the material behind the surface is protected against water ingress and possible damage caused by moisture or aggressive chemicals transported by water.

Clean surfaces are exposed to weathering e.g. wind driven particles and thermal stress. A layer, e.g. of biological growth, could protect the surface against abrasion and thermal shocks.

Traditional roofing tiles tend to become tighter during the first year (Frambøl et al. 2003-b), although the soiling can not be seen by the naked eye, it seems to have a positive effect, protecting the roof from water ingress. Frambøl et al. 2003-b, have also concluded that evaporation from tiles increases with increasing growth of algae or lichen. This is very surprising, as traditionally it has been claimed that biological

growth detains the evaporation of moisture, and therefore keeps the material moist (e.g. Schultze et. al. 1997). The theory of Frambøl et al. is that biological growth enhances the surface area and therefore evaporation will increase. However, the findings of Frambøl et al. are based on only a few specimens and are not backed up by measurements of how the evaporation is when algae or lichen is gently removed from the specimens. Another theory could be that biological growth deteriorates the surface, which results in an increased surface area, and consequently a larger evaporation rate. In this case biological growth might protect the material from accumulation of moisture, but biological activity and chemical reactions caused by the growth is reducing the service life of the material. For further discussion of service life see Section 6.1.2.2.

3.1.2 Aesthetics

Durability set aside, the consequences of soiling are still discussable; aesthetical questions of whether soiling is a nuisance, preventing the building or monument from looking like it did on day one, or a benefit giving the building a unique expression.

3.1.2.1 Subjective

Whether one considers soiling as an aesthetic nuisance or a benefit is highly subjective, and often dependent on situation, material and use of the building. Architects sometimes talk about how some materials patinate beautifully, mellowing the building. Materials are chosen for their ability to soil in a way that the building, with time, will not look brand new but age with dignity, the appearance of the surfaces will only slowly change, giving the building a kind of timeless expression. Tile have some of these abilities, naked brick walls and tile roofs are typical examples.

While some people favour materials that in time will soil, others either want to give the building an old expression from the beginning or want to mask future soiling by using materials with soil-like patterns. Figure 3.2 shows an example. However, soiling patterns depend not only on the material but highly on the situation of the building, as shown in Figure 3.2. Areas with shadow are susceptible to algae growth, which will cover parts of the surface with a film. In urban areas soiling caused by environmental particles will cover parts not exposed to rain, creating a very different pattern than the biological growth.

Figure 3.2:   Eternite (fibre cement) roof fabricated with "pre-soiling" patterns. The patterns give the surface more life but are different from the natural soiling pattern. At the northern side of the roof (to the right) algae growth has resulted in a greenish discolouration of the roof.

Old buildings do not have to look new, in fact depending on individual taste, some might prefer that old buildings look old, it can be seen as being more honest and romantic than trying to make a building look new. Aesthetically, soiling could be seen as a benefit.

On the other hand, soiling can mask some of the details on a building, and uneven soiling give undesired patterns that disturb the expression of a building. For a building owner, the expression of the building can be a part of an image; dirty surfaces like facades with discolouration due to soiling may not fit the image, and are therefore undesirable.

From an aesthetical point of view there is no clear answer to the question of whether soiling is a nuisance or a benefit, it is a highly subjective issue, depending on kind of soiling, situation and individual taste.

3.1.2.2 Time dependence

Time is not unimportant when considering whether soiling is a nuisance or a benefit. It is mentioned above, that some people prefer that old buildings look old, and some use materials with "pre-soiled" patterns. But the important thing is, that the building owner can decide how his building would soil. Surfaces that soil very fast may after three years have soiling patterns, which are unacceptable at that time, but could have been accepted, if the building was 15 years older.

Even in cases where soiling is accepted, the soiling layer will continue to grow, and at some point soiling will dominate the expression of the building and become unacceptable. Therefore, after a short or long period of time, soiling will become an aesthetical problem.

3.1.2.3 Failure or maintenance

If soiling appears fast, or is more dominant than expected, it could be regarded as a failure, and actions must be taken to rectify the situation, e.g. by cleaning or using surface treatments that reduce the soiling. However, in some cases cleaning of surfaces is a natural part of the maintenance schedule of the building, along with e.g. painting of woodwork. Although some soiling always will appear, a maintenance problem might evolve into a failure if the soiling is more drastic than expected. The reasons for this could be unexpected surface properties or unforeseen soiling because of changes in the environment e.g. high content of NO_x, pollution or the opposite; reduced content of environmental poisons.

Once again the expectations of the building owner are important to whether soiling is a problem or just another expense on the maintenance budget.

3.1.3 Soil removing

At old monuments and buildings some degree of soiling is expected and accepted, however, renovation of older buildings will often include restoration of the surface to its former appearance. This means cleaning the soiling off. A thorough exposition on cleaning methods is beyond the scope of this thesis, only a general description on cleaning principles is given. Although this section divides the cleaning methods in chemical and mechanical methods, combinations of the two are also possible.

When choosing if and how to remove soil it should always be considered that the process of cleaning a surface might in itself be a threat to the building or the surface, and chemical as well as mechanical methods bear the potential danger of making the surface more susceptible to soiling in the future. Soil removal should only be initiated after careful considerations.

3.1.3.1 Cleaning with chemicals

A chemical cleaning method means dissolving soiling or killing biological growth with chemicals and if necessary afterwards removing of the remains. Depending on

the situation in which the method is being used, there are possible advantages and drawbacks, and no chemical agent is suited for all surfaces or soiling. Possible chemical reactions must be considered from case to case. The used chemicals can be of different strength and the advantages and drawbacks are accordingly.

Possible advantages:

– Less labour intensive than mechanical methods

– Targeted treatment; killing biological growth or dissolving specific particles

– Inhibits new soiling

Possible drawbacks:

– Chemical attack not only on soiling but also on the surface beneath, leaving the surface more open and susceptible to new soiling attacks.

– Controlled use, neighbouring surfaces might be vulnerable to the chemical.

– Discolouration due to formation of salt or soap

– Waste problem; the disposal of the chemicals can be an environmental problem

For removal of biological growth on buildings Frambøl et al. (2003-c) have investigated what chemical agents are used in Denmark, the investigation showed that a wide range of the most used agents cannot be used in accordance with current legislation. The only agent, which is in accordance with legislation, is new in the market and has not been fully tested by the trade yet. The waste problem could therefore often be a limiting factor. However, chemical agents not in accordance with current legislation are widely used, although the manufacturers are aware of the problem and do not recommend the chemicals for the purpose of removing biological growth.

3.1.3.2 Mechanical cleaning methods

Instead of a chemical cleaning, abrasive methods where soil is physically removed can be useful. Typical examples are sand blasting, high-pressure sluicing or brushing of surfaces. Like for the chemical agents there is no method that applies to every situation. The nature of the surface/soiling combination decides whether

rough or gentle methods are suitable. Advantages and drawbacks will also depend on the used force.

Advantages:
- Chemical agents can be avoided. Waste problem and discolouration problems are minimised
- After initial tests the process is easier to understand and control than chemical methods

Drawbacks:
- Damages to the surface, leaving it open and possibly more susceptible to new soiling
- Weaker parts of the surface or ornamentation disappear
- Methods with water under pressure can result in water damage behind the surface
- Parts with difficult accessibility need extra attention

Rough methods are more effective in removing soil than refined methods but the damage to the surface might be extensive, pressure will often have to be adjusted along the way. Some methods do not use pressure, and soiling is removed very gently e.g. by seeping of water or hand brushing, methods of this kind are very time consuming and may not be useful with more resisting soil.

As stated above ultimately soiling becomes a nuisance, but cleaning methods are expensive and the risk of altering the surface towards increased susceptibility to soiling is high. Therefore methods to prevent or inhibit soiling are interesting from a durability as well as aesthetic viewpoint. But to understand why some methods work, it is necessary to know what soiling is and how it adheres to surfaces.

3.2 Biological growth

Soiling of exterior surfaces of buildings can basically be divided in two groups:

- Biological growth
- Environmental dirt

The two groups are very different in origin, soiling pattern and where and how they adhere. Although there are interactions between them, the two groups will be treated separately, beginning with biological growth.

3.2.1 Growth types

Biological growth at surfaces can be caused by a variety of organisms; from bacteria to higher plants. However, bacteria, which are invisible to the human eye and higher plants that are obvious signs of deterioration, are beyond the scope of this thesis and will only be touched upon briefly. With the exception of the blue-green algae, which biologically are bacteria but will be treated as algae in this thesis. The different microorganisms can depend on each other; first colonizers might act as nutrient and form the basis of growth for other organisms. Kotakemori et al. (1995) have conducted experiments with different microorganisms at cement paste. The result was, that killed bacteria were very effective as nutrient for fungi, about twice as effective as killed algae.

3.2.1.1 Algae

The term algae covers about 25,000 species scattered over 2,000 genera, algae can be monocellular organisms related to bacteria others have common feature with fungi and some seem to be primeval form of higher plants. (Frambøl et al. 2003-a)

Algae that soil facades and roofs are aerial algae very often chlorophyta (green algae). Determination of species require culture of the algae in the laboratory but for non-biological purposes, knowing that it is a chlorophyt is often sufficient and the species may not need to be determined. Aerial algae live on nitrogen from the air and photosynthesise with chlorophyll. (Frambøl et al. 2003-a).

Algae growth will often be greenish, from light to dark, sometimes with different shades of red. (Frambøl et al. 2003-a). A wet algae layer is often mucilaginous, and algae undergo large volume changes with water content. As algae undergo cycles of drying and moistening, the induced shrinking and swelling might cause loosening grains of the material, resulting in damage of the surface (Ortega-Calvo et al. 1991). Beside this biogeophysical weathering process a biogeochemical process might also cause deterioration as algae release acidic or chelating metabolic products, etching the surface of the substrate material (Flores et al. 1997).

3.2.1.2 Lichen

Lichen is a symbiosis of a fungal component, the mycobiont and an algae or more rarely cyanobacteria, the photobiont. Together, the mycobiont and the photobiont form the thallus (Lee & Parsons 1999). Sanders (2001) describes lichens as the first example of agriculture: The fungus feed and protect the algae (like in a green house) and at the same time lives of the algae. More specifically the photobiont provides the mycobiont with organic nutrient created by photosynthesis. In return the mycobiont provides the photobiont with minerals, procured via hyphae into the substrate and production of lichen acids (Warscheid & Krumbein 1994). Figure 3.3 shows a schematic presentation of the structure of lichens, based on Adamo & Violante (2000) and Frambøl et al (2003-a).

Lichen living on rocks, saxicolous species, can be divided into three groups depending on how they are attached to the substrate (Adamo & Violante, 2000 and Chen et al. 2000):

- Crustose. Firmly attached to the substrate by the hyphae of the medulla, there is no cortex under the photobiont. Some of these lichens are growing inside the substrate (endolithic) others on the surface (epilithic).

- Foliose. More or less firmly attached to the substrate by rhizines, e.g. bundles of tendentially parallel aligned hyphae. Thallus has flattened lobes.

- Fruticose. Attached to the substrate but often with erect strap-shaped lobes.
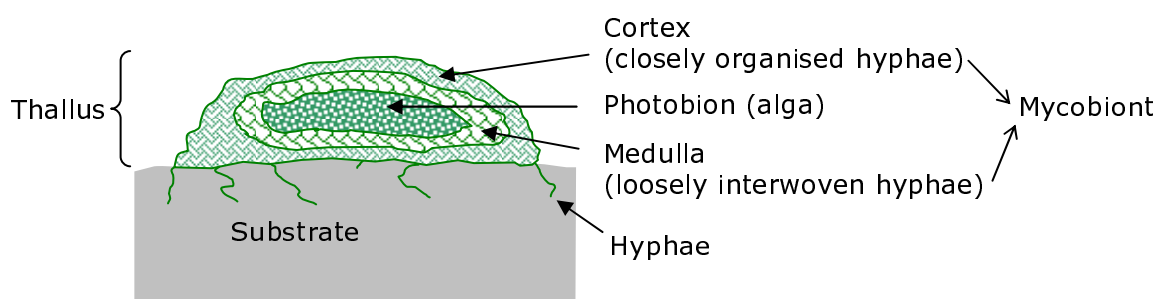
Figure 3.3. Principles in the structure of lichen, based on Adamo & Violante (2000) and Frambøl et al. (2003-a). The mycobiont, especially the dense cortex protects the photobiont (alga) from direct exposure to the environment. A lower cortex is not always present; in crustose lichen the hyphae of the medulla form the attachment to the substrate.

All three groups can occur as soiling on buildings and monuments.

Lichen can be responsible of biodeterioration, as well as bioprotection of surfaces, depending on the substrate, the lichen and the environmental conditions.

Four main mechanisms are responsible for biodeterioration due to lichen growth:

- <u>Hyphae</u> penetrate the substrate. Endolithic lichens with its hyphea, that penetrate the substrate through intergranular voids, cleavage and fissures.

- Moisture induced <u>volume change</u> of the medulla. The medulla can contain up to 300% moisture of the dry weight, which means lichen subjected to wetting and drying can induce tension in the substrate. (Chen et al., 2000). Freezing and thawing of the lichen will have a similar effect.

- <u>Lichen acids</u>. The metabolism of lichen result in so-called lichen acids (although not all of them are acids), these are usually present in the medulla and may account for up to 8% of the dry weight of the lichen. Lichen acids can form complexes with the metal cations in the rock-forming minerals, these substances promote chemical processes, which enables lichen to decompose lithic constituents (Adamo & Violante, 2000). Mineral neoformation of e.g. metal oxalates is another effect (Chen et al., 2000).

- <u>Incorporation of mineral fragments</u> into the thallus. Grains of the substrate that have been loosened by different mechanisms become integrated in the thallus.

In experiments reported by Chen et al. (2000) lichen on limestone were subjected to wetting-drying cycles, limestone fragments (10-50 µm along the longest axis) were found in the thallus. This was possibly the result of a combination of the mechanisms listed above. The process of biodeterioration caused by lichen is schematically shown in Figure 3.4.

Reports on how lichen are responsible for biodeterioration are numerous, but some researchers have written about how lichen protect surfaces e.g. Frambøl et al. 2003-b, Carter & Viles 2003 and Ariño et al. 1995.

Bioprotection provided by lichen growth as described by the researchers listed above can be divided into different groups:

– <u>Protection against thermal stress</u>. In hot summers with few but heavy showers, high surface temperature and the sudden cooling of the surface caused by the rain, might induce thermal stress, enhancing existing fissures or creating new ones. If the substrate is covered with lichen, the hygroscopic medulla, which can retain water, will reduce the thermal stress. (Carter & Viles, 2003)

– <u>Protection against abrasion</u>. A surface covered with lichen is not that exposed to wear and tear, abrasion by e.g. windborne particles will therefore be reduced. (Ariño et al. 1995)

– <u>Formation of metal oxalate</u>. Through chemical reactions with the substrate, lichen acids can form metals oxalate, which is insoluble in water. The result is a visible layer at the surface obscuring the visual appearance, but preventing the surface from further deterioration. (Bonaventura et al. 1999).

These mechanisms are reported by several researchers. As described in Section 3.1.1.2 Frambøl et al. 2003-b have found that lichen growth enhances the evaporation from the surface, the result would be a drier surface. This is contrary to other findings, and is not consistent with the nature of the medulla, whose water retaining capacity is important in protection of the photobiont.

3.2.1.3 Moss

There are about 9.500 species of moss (Raven et al. 1992). A description will therefore be very general and some species might in some points differ from this description. Mosses are small green plants with stems and leaves but no roots; they adhere to surfaces by rhizine (threadlike filament). Mosses absorb water and nutrient solutions through the whole surface (leaves, stems and rhizine), and most mosses need high humidity conditions for survival, although some can endure drought for a longer time and enliven when moisture is supplied again. (Frambøl et al. 2003-a).

Like algae and lichen moss retain water, and the volume change of moss can in the same way create tension in the substrate rock and result in deterioration.
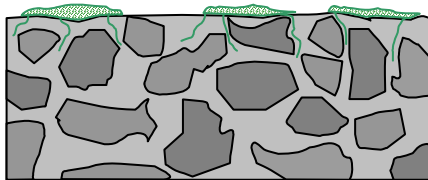
Thalli at the substrate rock. Hyphae of the mycobiont is beginning to penetrate the substrate rock through intergranular voids, cleavage and fissures
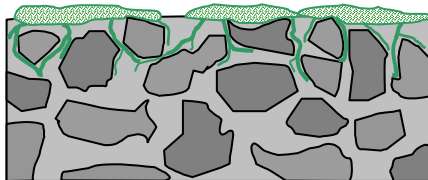
Thalli is growing into the substrate, hyphae penetrates further, encircling single grains.
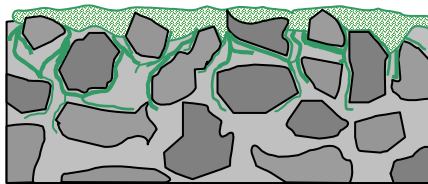
The medulla can contain up to 300% water of its dry weight. When subjected to wetting and drying or frost and thaw, the volume change of the lichen can loosen grains.
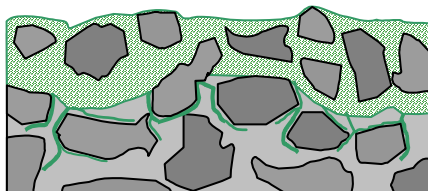
Incorporation of loosened mineral fragments into the thallus.
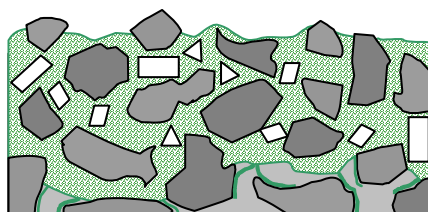
Mineral neoformation of e.g. metal oxalates due to chemical weathering of lichens.

Figure 3.4.   Principles of biodeterioration by lichen, based on Chen et al. (2000). The process of biodeterioration by lichen is highly dependent on the porosity of the substrate and the living conditions of the lichen. The time before visual signs of exfoliation of the surface appear can vary accordingly, sometimes less than 10 years (Chen et al. 2000).

3.2.1.4 Moulds

Moulds are fungi, like the mycobiont in lichen. While algae, lichen and moss use photosynthesis and therefore are dependent on light from which nourishment can be achieved, moulds can live in the dark but need moisture and nourishment from the surroundings to survive. Moulds consist of spores, which are used to spread the fungus, and a mycelium (web of hyphae) (Frambøl et al. 2003-a), by which the moulds adhere to surfaces similar to how lichens adhere. Mould attacks are often black or green, but can also be white. (Frambøl et al. 2003-a)

While algae, lichen and moss as biological growth on exterior surfaces are often described in the literature, moulds are more rarely described. However, recently several cases have been reported at relatively new buildings (e.g. Becker & Putterman, 2002 and Sandin, 2002). In these cases the problem have only been regarded as being aesthetical, but as they occurred at relatively new houses (< 10 years old), it was considered to be unacceptable, and remedies were taken.

3.2.2 Growth conditions

The organisms described above are very diversified species, even among their own genera; the growth conditions vary accordingly. The organisms have specialised in different ways, and an exposition of growing conditions for the different species would be immense and beyond the scope of this thesis. However, the parameters, that are important to the different species for their growth are listed and explained.

3.2.2.1 Nourishment

All living organisms need food to survive. However, the organisms responsible for biological growth at exterior surfaces are often hardy species, which have found ways to extract nourishment from the surroundings in a way that restriction on nourishment is not a realistic way to prevent biological growth. On the other hand, abundance of nourishment might cause excessive growth. An example is the excessive algae growth at surfaces in the close vicinity of pig farms, where the air is very nitrogenous.

Contrary to higher plants, the organisms mentioned above have no roots and use the whole organism to absorb nourishment. Algae, lichen and moss all contain chlorophyll, enabling them to use sunlight and carbon dioxide from the air for

growth, other minerals and nourishment can be obtained form airborne particles, caught in the biofilm, or from the substrate rock.

Fungi do not photosynthesise, but need organic material to survive. Normally sufficient matter can be obtained through soiling of the surfaces by bacteria or other kinds of biological growth or by organic matter in the substrate e.g. in paint. (Sedlbauer, 2001).

3.2.2.2 Moisture

Like nourishment, moisture is essential to life. Microorganisms have adapted themselves to different moisture levels and have developed ways to retain water and thereby reduce the risk of desiccation. At a cellular level desiccation can have a profound effect on the viability of the microorganisms as it can lead to (Lighthart & Mohr, 1994):

- Structural changes in cell membranes

- Osmotic imbalance within the cell

- Change of the concentration of various substances (e.g. metabolic by-products), which can reach levels that are toxic to the cell.

As a result, in a combination with how the species have found ways to protect themselves, different species react differently on drying-wetting cycles, and the moisture pattern at a surface can be decisive for what kind of biological growth will colonize a surface. For example:

- Moulds need a minimum of moisture for a period of time to start growing, and a reduced level to continue growth. At organic surfaces with moisture content corresponding to less than 70-75 % RH there seems to be no risk of mould growth (Sedlbauer, 2001 and Valbjørn 2003). Moulds that are dried out die. A biofilm of moulds can occur at moist areas without direct sunlight.

- Lichens can retain water in the medulla and are generally well protected (see Figure 3.3), when first established, some lichen species can survive for a long time without water, even after total desiccation (Frambøl et al. 2003-a). This means that wetting does not have to be regular, and lichen

can survive at surfaces with fast changing climate, like roofs exposed to sunlight.

– Moss need very high moisture content to establish and continue growth, the leaves can retain water, but depending on species, some moss die after desiccation while others can remain alive for years without water and quickly start growth again when exposed to water (Raven et al. 1992). As a result moss at roofs are mostly seen where it is protected from direct sunlight e.g. at the north facing sides.

– Algae is a very diversified genus, aerial algae are most common as soiling on surfaces, but most algae species live in water, e.g. visible as soiling in fountains (Nugari & Pietrini, 1997).
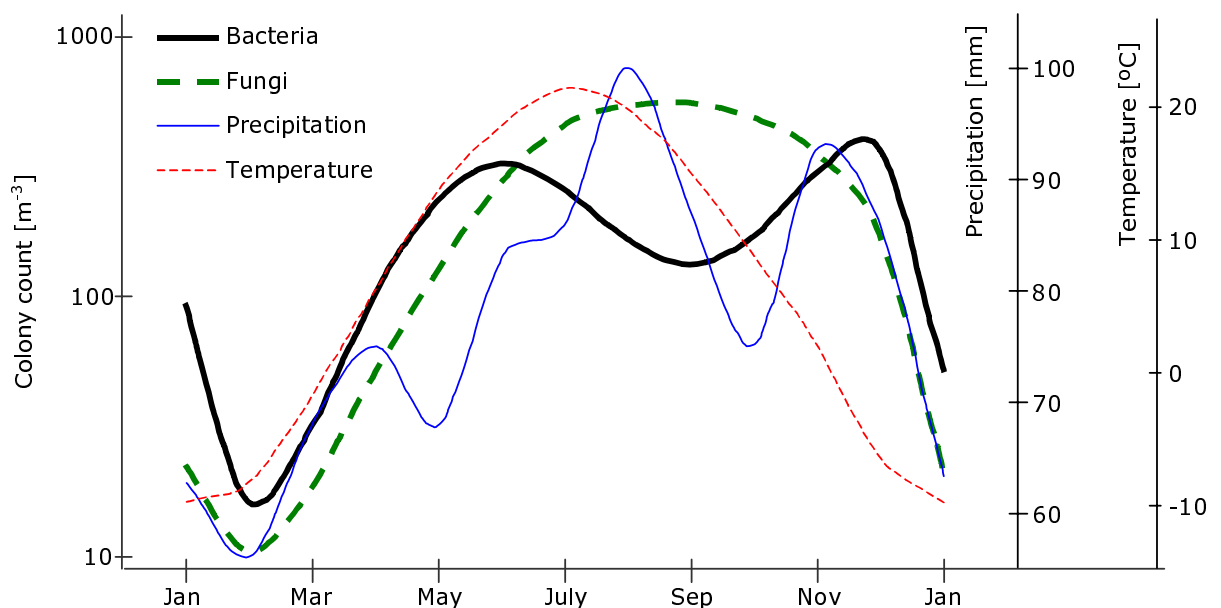
Figure 3.5:   Principle of annual concentration cycle of airborne bacteria and fungi measured in the air on a 120 m high building in Montreal in 1951, based on Lighthart & Mohr, 1994, compared to the annual precipitation and temperatures in the area (Meteonorm, 2000). Temperature seems to be an important factor for growth; increasing temperatures means increasing fungi growth. Bacteria activity decrease when the temperature becomes too high. Activity continues or revives in the cooler fall, where precipitation is high.

3.2.2.3 Temperature

Microorganisms have different temperatures at which they have a maximum growth rate; at too high or too low temperatures growth will stop. Figure 3.5 illustrates how bacteria growth decrease in the summer, while fungi seem to be able to continue to grow despite of the higher temperatures in the summer. The growth should be compared to the climate in the region, showing, that temperature as well as moisture are decisive factors when it comes to biological growth.

As shown in Figure 3.5, biological activity is very low in periods with frost but does not stop. Frost does not kill the microorganisms. Frost causes intracellular water crystal formation, which might cause damage to the membrane of the cells and cause their death, but it is dependent on the water permeability of the membrane and cooling rate. High permeability and slow cooling rate result in high viability (Lighthart & Mohr, 1994), and could explain why some organisms e.g. lichen seem to be able to survive extreme climates.

3.2.2.4 Light

Organisms that photosynthesise need light. From the microorganisms listed above this would include: some bacteria, algae, lichen and moss, but not fungi.

Simplified photosynthesis is a process where carbon dioxide and water under the influence of light is converted to carbonhydrates and oxygen:

$$6\ CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2$$

Energy from sunlight
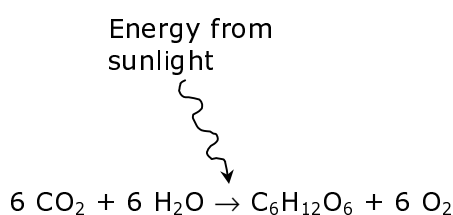
Photosynthesis is more complicated than this and involves several interacting processes in the chlorophyll granule of the microorganisms, where the chlorophyll itself catches the sunlight. However, photosynthesis is beyond the scope of this thesis, and will not be treated any further.

3.2.2.5 Sulphur, nitrogen and pH

Different levels of pH and sulphur and nitrogen deposits favour different species. Some substrates e.g. concrete roofing tiles and mortars, have very high pH at the beginning, favouring some species, but due to carbonatisation pH will decrease,

favouring other species. The levels of pH and sulphur and nitrogen content of the surroundings are highly dependent of anthropogenic activity (see Section 3.3) and the occurrence of biological growth can therefore be influenced by e.g. pollution. Especially lichens are sensitive to these factors, and are therefore often used as markers for pollution rate in areas. The diversity of lichens is often limited in polluted areas (Spencer, 2001, Mitchell & Gu, 2000 and Jalkanen et al. 2000).

While atmospheric pollution with SO_2 has decreased in Western Europe since the 1970s, emissions of NH_3 and NO_x have increased. This means that the biological growth has changed towards microorganisms that can use these compounds as substrates. (Mansch & Bock, 1998).

3.2.2.6 Surface roughness and porosity

As illustrated in Figure 3.4 lichen establish themselves by hyphae penetration of the substrate through cracks an fissures. In substrates with high porosity and rough surfaces this is relatively easy, and laboratory experiments by Guillite & Dreesen (1995) show that the speed of appearance of biological growth correlate with the macroporosity of the materials. However, at the end of the experiment the mean number of species growing on rough surfaces was only slightly higher than that of species growing on smooth surfaces. Whereas some filamentous microorganisms like the lichen illustrated in Figure 3.4 use the rough surface to find footing, other microorganisms have a thick mucilage, which they use as a system of suction-discs to stick to smooth surfaces.

Substrates with high porosity and rough surfaces offer more anchoring points than denser and smoother substrates, but when microorganisms once have established themselves, the climate becomes more important. High porosity might not be an advantage, as it would enhance the evaporation of water (Guillite & Dreesen, 1995).

Glazed tiles are an example of the surface influence: the initial soiling rate of glazed tiles is slower than of ordinary tiles, consequently seem glazed roofing tiles more resistant to biological growth than ordinary tiles. However, not all glazed roofs are free of growth, if the growing conditions are in the right range, algae will find ways to adhere to the smooth surface of the glazing.

	Algae	Lichen	Moss	Mould
Characteristics	Colour: greenish, from light to dark, and sometimes different shades of red. Wet algae layer is often mucilaginous.	Symbiosis of a fungal component, and an alga	Small green plants with stems and leaves but no rots. Absorb water and nutrient solutions through the whole surface	Mould attacks are often black or green, but can also be white
Living conditions	Aerial algae live on nitrogen from the air and photosynthesise with chlorophyll, need light.	Alga provides fungi with organic nutrient created by photosynthesis, fungi provides alga with minerals. Hardy species, can survive long droughts but are sensitive to pollution.	Can survive longer droughts. Need light for photosynthesis.	Sensitive to moisture content. No photosynthesis and no need for light
Biodeterioration	Undergo large volume changes with water content loosening grains of the substrate. Release acidic or chelating metabolic products, etching the surface of the substrate material	Hyphae penetrate the substrate. Loosening grains and neoformation due to release of acidic or chelating metabolic products	Undergo large volume changes with water content, inducing stress in the substrate.	Penetrates substrates with hyphae.
Bioprotection	Mucilaginous layer protects against thermal stress	The thallus protects against thermal stress and abrasion. Lichen acids can form metals oxalate, creating a layer which is insoluble in water	Protects against thermal stress and abrasion.	
Example				

Table 3.1:   A summery of the most common biological classes of biological growth, with living conditions and influence on substrate.

3.3 Environmental dirt

The term environmental dirt is in this thesis used as opposed to biological growth; it describes dirt, which does not consist of living organisms or the remains hereof. Although environmental dirt can be transported by water in e.g. streams, only airborne environmental dirt will be considered in this thesis. Airborne dirt that settles at surfaces and is transported by rain to other areas is included.

A fast indication of whether discoloration is caused by biological growth or environmental particles can be obtained by observing the smudging pattern. Environmental particles are transported by air and to some extent washed away by rain, leaving exposed surfaces cleaner than other parts. Biological growth, on the other hand, is typically seen on exposed surfaces that for some reasons are moist. Through a microscope the difference is often clear, because of the biological characteristics of the growth e.g. hyphae and thallus.

However, this rule of thumb does not always apply; the mucilage of some microorganisms might catch environmental particles, creating a soiling layer, which is a combination of the two dirt types.

Figure 3.6: Soiling patterns indicate the origin of the dirt. Left: biological growth at exposed moist areas. Right: in polluted areas the rain will wash off some of the particles in unprotected areas. The rain will not clean areas under protective items like sills or coverings. This results in darker areas under protective items.

The composition of the dirt layer depends on the environment. Soil and dust can be dominant in rural areas whereas soot and oil dominate in urban areas. Important factors for the formation and composition of a dirt layer are:

- Particle origin

- Particle size

- Weather conditions and deposition

The factors interact; the particle size depends on the origin, and smaller particles are carried further by wind than larger and heavier particles. The aim is to describe:

- What are environmental particles, and where do they come from?

- How do they get to the surfaces?

- How do they stick to surfaces?

The last question is essential to this work, as it is the only parameter that can possibly be changed by material engineering. At the same time it also applies to biological growth and will therefore be treated in a separate section (Section 3.4).

3.3.1 Sources

Environmental particles can be generated in different ways and the origin determines the composition and size of the particles. Generally large and small particles are generated and compounded differently.

3.3.1.1 Mechanically generated

Large particles (diameter > 1 µm) are often mechanically generated, e.g. sand and ashes by erosion, from traffic tyres and brake lining, or in marine areas NaCl (Bagda, 2001). Because of their size, mechanically generated particles have a tendency to sediment near the source (see Section 3.3.2), as a result there are differences in the particles collected in rural areas compared to particles from urban areas.

3.3.1.2 Gas phase

Combustion of fossil fuels or other CO_2 emissions generate particles, which start as a gas phase but convert into small particles by the following process (Fauser, 1999):

1. Volatile compounds are generated by e.g. CO_2 emission.

2. At decreasing temperatures volatile compounds condense and the gasses convert to less volatile compounds.

3. These very small particles <0.1 µm coagulate and form larger particles (0.1-1 µm).

The result of this process can be seen in the distribution of particles in different areas: Near heavily trafficked roads and in urban areas, the faction of small particles is very high, and it decreases with the distance to the emission sources (Bagda, 2001).

Not only traditional pollution sources are responsible for the formation of particles. In Denver, brown cloud is an episodic wintertime occurrence of low visual air quality. Investigations by Sloane et al. (1991) have shown, that one of the reasons for this phenomenon is probably an excess of ammonia in the rural areas near Denver. The particles formed in that area are afterwards transported by the wind to the city. Spindler (2001) describes how blue haze sometimes can be observed over large forests, probably due to particle formation caused by natural CO_2 emission. The former notorious London fog might be an example of the same phenomenon caused by individual heating by burning of coal. The result can be seen as soiling of buildings.

3.3.1.3 Composition of particles

The composition of particles depends on their sources and varies accordingly. However Fauser (1999) has given a general description of particle composition and mass distribution versus size range. Figure 3.7 is a modified picture of this information. The difficulty in describing particle composition is illustrated in Figure 3.8, based on Noll et al. (1987), which shows that the variation in composition of coarse particles can depend on wind direction and location. In rural areas only limestone and silicate could be found together with pollens. When the wind blew

from the industrial area, the content of fly ash and coal increased. Rubber from tires were significant in the commercial area, which was dominated by transport-related emissions.

Direct comparison between Figure 3.7 and Figure 3.8 is impeded by different classification of the compounds in the two sources, while Figure 3.7 does not consider e.g. rubber tyre, Figure 3.8 does not show the water soluble salts.
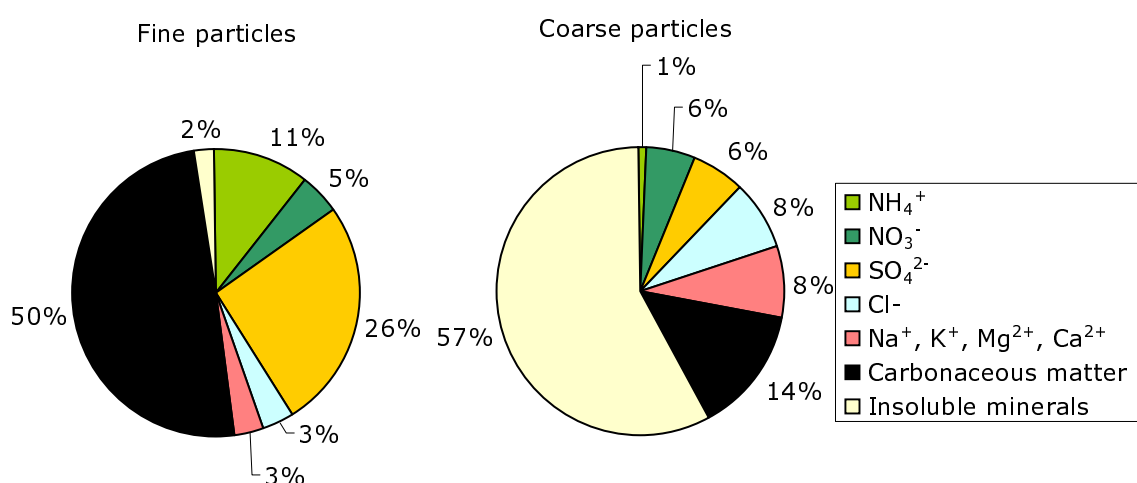
Figure 3.7: General description of particle composition in fine (<2.5 µm) and coarse (2.5-15 µm) particles. Based on Fauser (1999)
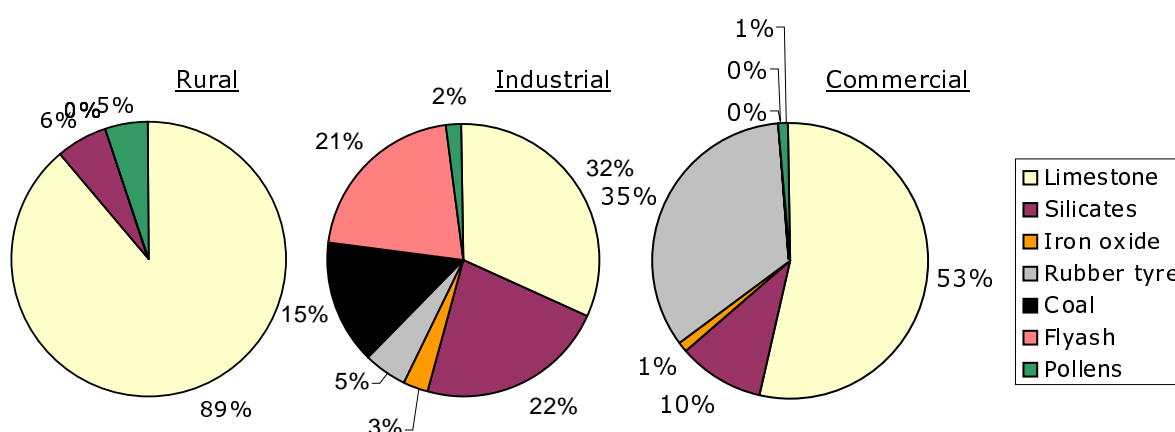
Figure 3.8: Composition of coarse particles (> 6µm) from the Chicago area. The rural particles were collected 37 km southwest of Chicago, the industrial and commercial particles 5.7 km south of the central Chicago, with respect to wind direction from either southern (industrial) or northern (commercial). Diagrams based on information in Noll at al. (1987).

Some general comments might be made on the composition of small particles:

- – In urban areas the content of elementary carbon is increased (Spindler, 2001)

- – Particles with inorganic content like Si, Fe, Al, K or Mg are present, independent of location (Baumstark 2001).

However, the particle composition will vary with source, size, wind direction and velocity in a way that makes it impossible to operate with "standard" particles simulating a "standard" situation.

3.3.2 Transportation and deposition

In the beginning of Section 3.3 it was defined, that only airborne environmental particles, were to be considered, as a result the means of transportation is wind. However, the deposition of the particles is not entirely by the wind: while larger particles might settle close to their origin, smaller particles can be held floating in the air for days before they wash out in rain and deposit. Size distribution and mechanisms of deposition are important when describing how particles reach the surfaces.

3.3.2.1 Size distribution

The size distribution of environmental particles in air shows a close dependency on the sources of the particles. Mechanically generated particles are often coarse (diameter of particles > 1µm), while particles generated from combustion are small (< 1µm).

Particle frequency versus size in air can be depicted in different ways: By volume, mass, surface area or number. By number and surface area the fine particles are by far the most common, while by mass and volume, the distribution is trimodal, with a clear distinction between fine (bimodal) and coarse particles, see Figure 3.9. As illustrated the distribution coincide with the sources and therefore the composition of the particles.

Figure 3.9:   Schematic depiction of particle frequency (by mass or volume) versus particle diameter in the atmosphere. Based on Hansen et al. (1988), Fauser (1999) & Spindler et al. (2001).

In regard to soiling, the particle size becomes important, as the adherence to surfaces is highly dependent on size, see Section 3.4.1, and the colour of the particles depends on their origin and therefore is related to the size.

3.3.2.2 Deposition

Gravity is the most important factor for sedimentation. While large particles (>10 µm) only can stay floating in air for a relatively short period (hours) before they sediment, smaller particles (0.1-2 µm) can stay floating for days or weeks, and be transported over 1000 km. Particles smaller than 0.01 µm, are not stable in the atmosphere, they will either react with oxygen or coagulate to larger particles (Bagda, 2001). See Figure 3.10.

3.4 Adhesion

To understand soiling, not only the dirt but also the forces that make the dirt adhere to the surface must be known. How biological growth adheres to surfaces depends on the species and is described in Section 3.2.1 under the different types of growth. In this section focus will be on how particles are attracted to or repulsed from surfaces. In principle the same forces apply to biological matter, although microorganisms have additional means to stick to surfaces, which might be stronger than forces described in this section.
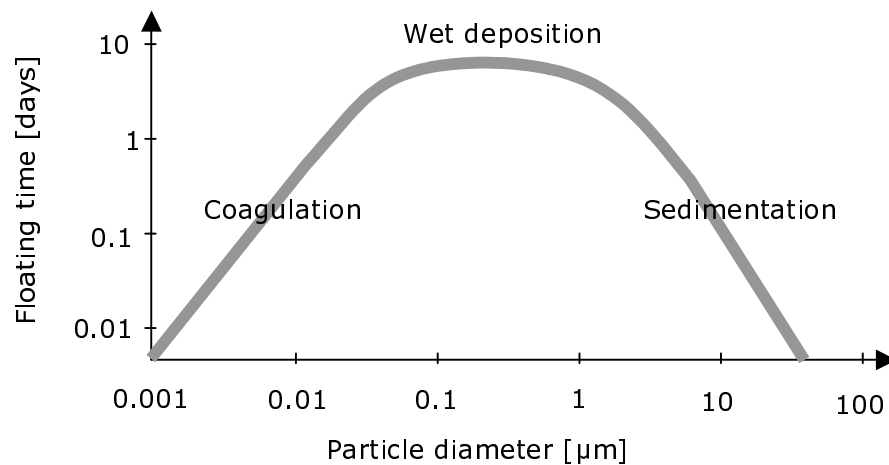
Figure 3.10: Schematic depiction of floating times depending on the particle size. Actual floating times vary and depend on e.g. wind velocity. Deposition depends on particle size; large particles can stay floating only for a short period before they sediment, on the other hand very small particles are not stabile and will coagulate. After Bagda (2001).

Different forces of adhesion work at the interface of two solids or a solid and a liquid. The significance of the forces depends on the scale at which the adhesion is considered; some forces have a very little range and become insignificant when larger particles are considered and other forces take over. However these small forces might be decisive when new properties of a surface are to be obtained.

The term adhesion covers different processes (Myers, 1991):

- Mechanical adhesion involves mechanical interlocking of microscopic roughness. It occurs over a significant part of the contact area.

- Chemical adhesion involves formation of chemical bonds across an interface.

- Thermodynamic adhesion is described by the reversible work needed to separate two surfaces to overcome the molecular interactions across the interface.

Mechanical adhesion takes place at a larger scale than the two others, it is therefore natural to divide the description of the forces relevant to adhesion in a microscopic level (µm) and molecular level (nm). Other reasons for making a distinction are:

- Mass becomes significant when particles are larger than 1 μm, which influences floating times, see Figure 3.10.

- The particle size distribution makes a distinction between coarse and fine particles natural.

- Soiling patterns differ with particle size; particles > 1 μm settle at more or less horizontal surfaces, while smaller particles cause a uniform soiling independent of the physical character of the surface (Bagda, 2001).

- With light microscopes objects larger than approximately 1 μm can be identified.

Before particles or molecules adhere to surface, they have to be placed there either by settlement or by adsorption, the focus of this section is therefore how particles or molecules get to the surface and how they stay there.

3.4.1 Microscopic level

Coarse particles > 1 μm are not only larger than floating dust particles but also heavier, which is decisive for floating times and sedimentation. The size however is important when considering the removal of soiling caused by large particles.

3.4.1.1 Gravitation

All particles are influenced by gravity; the force driving the particles to settle is given by the mass times the acceleration of gravity. Heavy particles therefore settle faster than light particles. As the direction of gravity is downwards, large particles settle at horizontal surfaces or at projections on rough surfaces. As a result rough surfaces generally soil faster than smooth surfaces (Bagda, 2001)

Figure 3.11: The dominating force on large particles is gravity; the downward force causes settling of particles. At vertical rough surfaces particles will settle at projections.

3.4.1.2 Lotus effect

Although large particles settle easier at rough surfaces, if surface roughness has the right size, it can facilitate the cleaning of the surface and might compensate for the enhanced soiling. In fact self-cleaning properties can be obtained. This is the idea of the Lotus Effect (Barthlott & Neinhuis, 1997).

Barthlott & Neinhuis made their investigation on different leaves. The main results were:

- Leaves without epicuticular wax crystals (e.g. wax crystals at the uttermost surface) had high wettability (contact angle < 110°) and a smooth surface

- Leaves with epicuticular wax crystals were water repellent (contact angle > 150°) and the crystals formed a regular microrelief of about 1-5 µm in height.

- When contaminated with different types of particles (size of 1-25 µm) rain or fog could remove the particles from the leaves. Independent of particle composition.

- Small particles (0.5-3.5 µm) could not be removed to the same extent, but gentle rain would remove the small particles as well.

Based on these observations they invented the term Lotus Effect, which now is patented (European Patent Office 1998-a) and used for surface treatments e.g. in paint and on roofing tiles. The latter is the subject of the experiments described in Chapter 5 of this thesis. The principle as it is described in the patent is illustrated at Figure 3.12.

The self-cleaning properties are a combination of enhanced hydrophobicity, due to the protrusion on the already hydrophobic surface (see Section 2.3.2.2) and very little contact between particle and surface. In the patent the protrusions are described as having a spacing of 5-200 µm, preferably 10 – 100 µm, and height of 5-100 µm, preferably 10-50 µm. Moving water will catch particles that will adhere to the water instead of the surface and the water will remove the contamination.
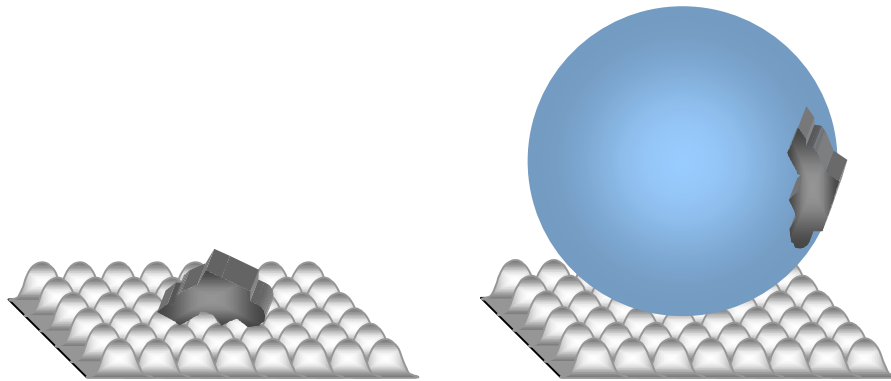
Figure 3.12: Schematic principle of the lotus effect, based on the description in the patent (European Patent Office 1998-a). Left: a particle has very little contact to the surface as it only touches the protrusions in small points. Right: When water is placed at the hydrophobic surface it forms an almost perfect droplet and as droplets run off, particles will adhere to the water not the surface. The surface is self-cleaning. In this drawing the protrusions are about 25 μm high with a similar spacing, the particle 100 μm and the droplet 0.2 mm in diameter (very small).

The scale in the patented lotus effect is different from some of the descriptions in Barthlott & Neinhuis (1997), where the micro relief of wax crystals, as observed by others, are reported to have heights of 1-5 μm. However, some of the pictures in Barthlott & Neinhuis (1997) show considerably higher protrusions (≈ 25 μm), which corresponds to the size used in the patent. In the description of the idea in the Patent (European Patent Office 1998-a) it is stated that some plants have an ultra structure with elements smaller than 2 μm, but these are unlikely to be artificially manufactured and would be extremely vulnerable and the model therefore is not suitable for surface treatments. At the protrusions shown in Barthlott & Neinhuis (1997) smaller elements are visible, these could be the wax crystals with heights of 1-5 μm, but are not mentioned specifically in the text.

The conclusion must be that the "natural" lotus effect would include a double system: Protrusions with ≈25 μm heights and spacing and at these crystals with 1-5 μm heights and spacing. This could be why Cerman (2002) specifies that particles lay on the micro and nano structure of the leaves. The "artificial" lotus effect as used at building surfaces on the other hand is a single system, only with the relatively large protrusions of ≈ 25 μm in height and spacing.
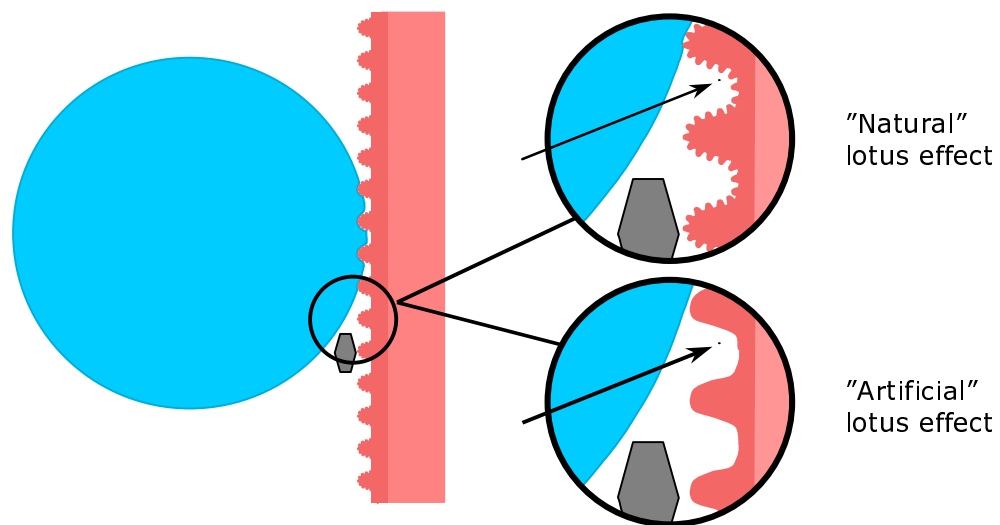
Figure 3.13: Relatively small droplets (≈ 0.8 mm diameter) run off surfaces with different lotus effects. Top enlargement: "Natural" lotus effect with a double structure with small protrusions (1-5 μm) on larger protrusions (≈ 25 μm) like on leaves. Bottom enlargement: "Artificial" lotus effect with a single structure, only 25 μm protrusions, like on building surfaces with a lotus effect treatment. Two particles are shown at both enlargements, part of a relatively large particle (≈ 75 μm) and a small particle ≈ 2 μm (marked with arrows), which is common in atmospheric air.

The lack of small protrusions could be a problem when soiling is caused by smaller particles. However, in the patent (European Patent Office 1998-a) it is stated that raindrops, that hit the surface, are - because of their kinetic energy - pressed between the protrusions and will tear the particle loose and remove it as the droplet runs off. This would indicate that only surfaces exposed to driving rain could benefit from the self-cleaning properties of the lotus effect.

Figure 3.13 show how droplets run off surfaces with lotus effect, natural and artificial. In the figure the dimensions are important: Larger particles can be removed by the water in both cases, while smaller particles (< 5μm) will be difficult to remove. Water will only occur between protrusions when forced in that direction, because when water runs off, the hydrophobicity of the surface will ensure that air is trapped between the protrusions. Otherwise the enhancement of the hydrophobicity caused by surface roughness would not be possible. However, Barthlott & Neinhuis (1997) have observed that even small particles can be removed by raindrops from leaves with a surface similar to the top enlargement in Figure 3.13, how this is possible is not clear from this picture.

There might be other factors involved in the cleaning of leaves: When the plants or leaves used for the experiment were artificially rinsed, the kinetic energy would have allowed the leaves to move. Maybe this pushed the particles to the top of the protrusions, allowing the water to catch the particles. In nature the wind would be an additional way to move the leaves. The experiment showed, that very small particles would not be removed when only fog droplets (1-20 µm diameter) were used. The fog droplets would be too small to run off individually. The protrusions which had the same size would prevent this. Only when more droplets came together, an accumulated droplet would be large enough to run off. This droplet would probably create considerably less movement than rain, and only the principle as described at the top enlargement of Figure 3.13 would be effective. As a result small particles would be trapped between the protrusions of an artificial lotus effect.

The effectiveness of the artificial lotus effect on roofing tiles will be discussed further in Chapter 6 Discussions.

3.4.2 Molecular level

Although some of the elements described in the previous section were small, adhesion was treated as a connection between a particle and a solid surface. However, surfaces and particles consist of molecules and adhesion between the single molecules become more important as the size of the adhering particle decreases.

Except for polymers, most clean surfaces (including minerals, metals and ceramics) will have quite high surface free energy and will try to reduce this by adsorbing materials. These adsorption processes involve non-specific forces like van der Waals forces, ionic or electrostatic forces and more specific forces, which are involved in chemical bonding. The non-specific bonding, called *physisorption*, is magnitudes smaller than the specific bonding, called *chemisorption* (Myers 1991).

3.4.2.1 Physisorption

Physical adsorption or physisorption describes a weak interaction between a solid surface and an adsorbate (molecule) involving no chemical bonds, e.g. no shared electrons. Depending on the distance between the molecules this interaction might

be attractive (van der Waals forces at medium ranges) or repulsive (Born repulsion at close range) (Chorkendorff, 2002).

Simplified the process can be described in two steps:

1. As a molecule approaches a solid surface it will set up a dipole caused by quantum fluctuations. In a polarizable solid this will induce an image dipole of opposite sign, and as a result the molecule will be attracted to the surface.

2. As the molecule comes closer to the surface, the electrons of the molecule will interact with the electrons of the surface, the force will be repulsive.

As a total the potential energy of attraction in physisorption can be seen in Figure 3.14.

3.4.2.2 Chemisorption

Chemisorption is a result of chemical bonding between a surface and the adsorbate. It involves specific interactions between a solid surface and a molecule and it can only takes place if the molecule structure of the adsorbate is changed. Opposed to physisorption this means:

– The process might not be reversible

– The process can only result in the adsorption of a monomolecular layer

– For changing the molecule structure an activation energy is necessary

The forces involved in chemisorption are larger than those in physisorption. However, because of the activation energy, chemisorption would only occur under rather powerful conditions if physisorption was not involved; as can be seen from Figure 3.14 the activation energy for chemisorption is lowered by physisorption. Figure 3.14 is only a simplified schematic illustration. The specific shape of the lines depend on the system involved. (Myers, 1991).
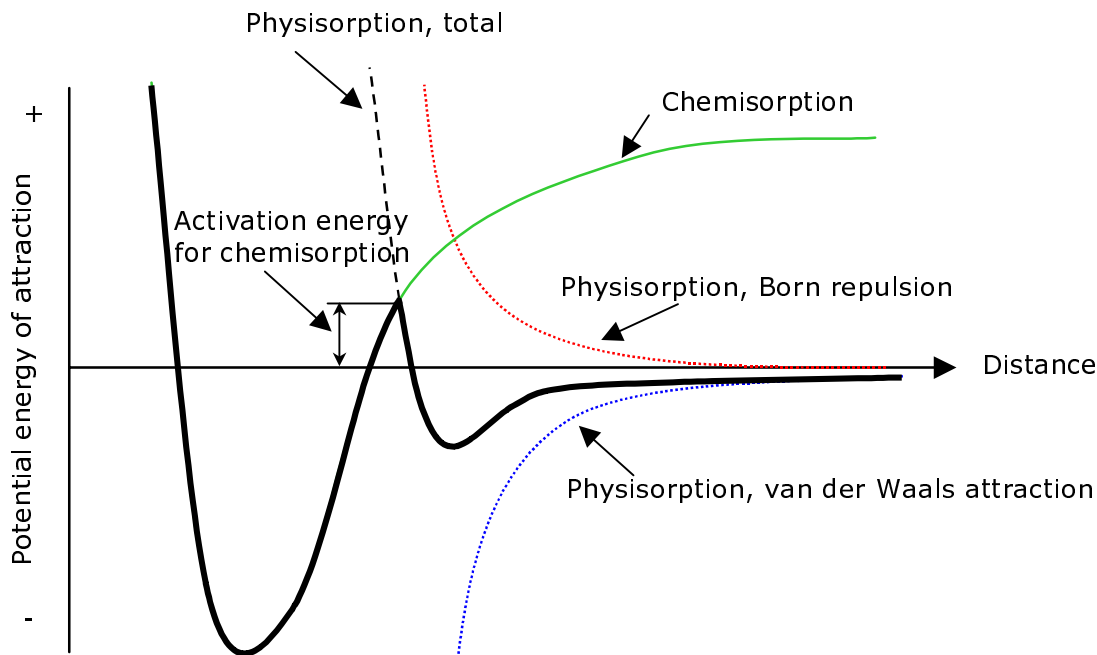
Figure 3.14: Simplified schematic diagram of potential energy of attraction in close vicinity (magnitude of 1-2 nm) of the surface. The fulldrawn black line is the result of chemisorption and physisorption. Based on Chorkendorff, 2002 and Myers, 1991.

3.4.2.3 Fluorocarbons, silicones etc.

Most "natural" exterior surfaces of building materials are polar and have a high surface energy, and will therefore attract molecules from the air or rain. However, the processes can be inhibited in different ways e.g. by lowering the surface energy and making the surface non-polar, a process, which is possible by applying a hydrophobic treatment. The treatment will adhere to the "natural" surface as described in the former sections, but the now coated, non-polar surface with low surface energy will react differently when exposed to contamination either in air or in aqueous solutions as can be seen in Figure 3.15: Molecules in an aqueous solution approach a non-polar hydrophobic surface, physisorption will be limited by the non-polar surface but still be attracted, as the degree of adsorption increases, the molecules will be oriented in a way, that the hydrophilic part will directed towards the aqueous solution, limiting the adsorption to be a monolayer formation (Myers, 1991).
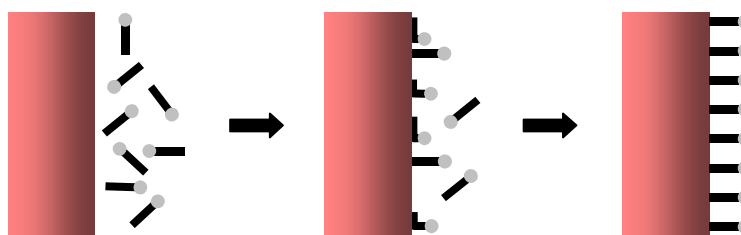
Figure 3.15: Schematic adsorption of molecules from an aqueous solution on a non-polar hydrophobic surface. As the adsorption increases the molecules are oriented with their hydrophilic group (grey circle) directed towards the aqueous solution, as a result only a monolayer of molecules will be adsorbed. After Myers (1991).

	Characteristics	Surface tension mN/m
Water		73
Silane	Small molecule size	22-25
Siloxane	Larger molecules than silane	20-22
Teflon	With fluorine	15-16

Table 3.2: Surface tension or surface free energy for different agents used for hydrophobic treatment, after hydrolysis and condensation. Water shown for comparison. (Adamson 1990; Gerdes, 2001; Drummond & Derek 1996)

Silicone-based polymers like silane or siloxane are the most used hydrophobic treatments at porous building materials. They fulfil the requirement of having a low surface energy. But there are other alternatives, mainly with fluorine that have even lower surface energies. Table 3.2 shows a comparison between different polymers used for hydrophobic treatments.

Teflon is listed in Table 3.2 because it has the lowest reported surface free energy for solid homogeneous organic materials. In fact fluorocarbon seems to have the best possibilities for making "nonstick" surfaces, however, the van der Waals interactions between materials across air or water are always positive, and surfaces can therefore not be truly "nonstick" but only low-adhesive. (Drummond & Derek, 1996).
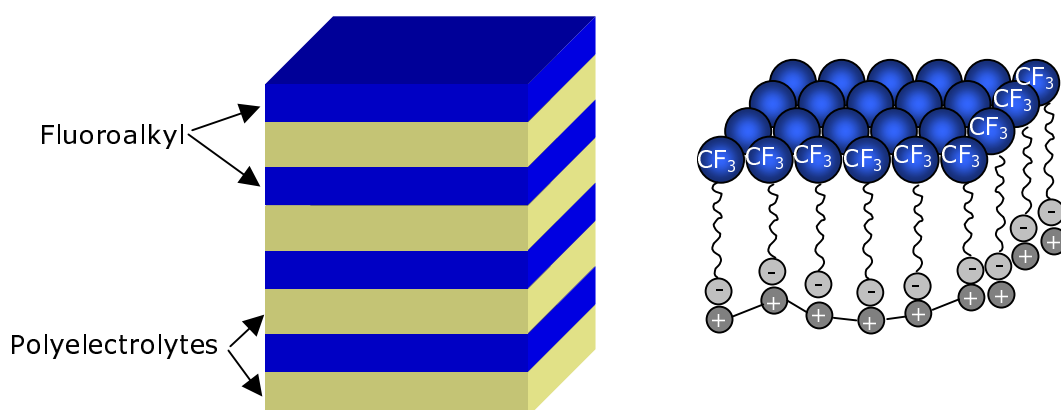
Figure 3.16: Principle depiction of a polymer complex of fluorinated amphiphiles and polyelectrolytes. Left: Lamellar complex structure alternating layers of fluoroalkyl and polyelectrolytes. Right: Molecular arrangement at the complex interface to air, which is dominated by an enrichment of CF_3 groups.

While Teflon has the lowest reported surface free energy for solids, even lower values can be obtained in monolayers. Thünemann (2000) has reported how fluorinated amphiphiles (molecules that consist of both a hydrophobic and a hydrophilic part) in combination with polyelectrolytes can form complexes, which can be prepared as nano-structured coatings with surface energies of 6-18 mN/m.

The complexes create a multilaminar structure with an enrichment of CF_3 groups at the surface, ensuring the low surface energy.

With atomic force microscopy (AFM) it has been possible to visualise the surface, although the surface seemed smooth at a micrometer scale, a structure of nanometer size was discovered: The structure consisted of elevations and depressions with a spacing of 100-300 nm between the elevations, which had a very uniform height of 3.4 nm. This is similar to the description of the "natural" lotus effect as described in Section 3.4.1.2, although the spacing is somewhat smaller in the complex film.

Unfortunately islands of a laminar structure might cause the elevations in a "head to head" arrangement at the surface. The edges of the islands are energetically very unfavourable. When exposed to a polar solvent like water, the surface will reorganise fast resulting in a higher surface tension (34 mN/m), and the advantages of the treatment are lost. Although waterborne nano-dispersions of

such a complex have been developed, it will probably need further development before it can be useful in the building trade.

3.4.2.4 Ways of adhesion

Figure 3.17 is a summary of the different kinds of adhesion described in this chapter. Although the scale at which the different forms of adhesion take place differs considerably, the mechanisms can be depicted in this simplified form.

This is similar to the "Hierarchy of spontaneous Adsorbed Layers" referred to by Speaker (1993), who sees soiling as a process with three different layers on top of each other. The attachment to each other differ in strength, consequently the energy needed to remove the layers varies accordingly. The description is given in Table 3.3.

A   B   C
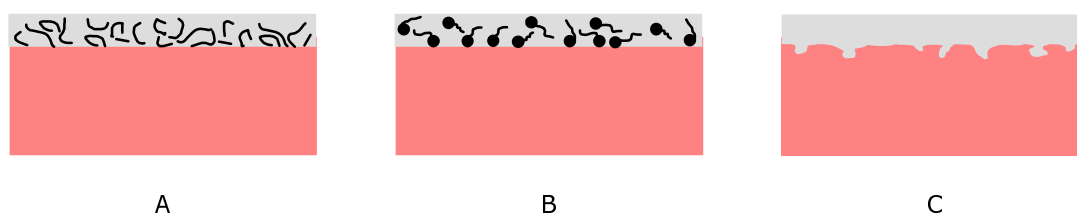
Figure 3.17: Schematic classification of different forms of adhesion:
A) Chemisorption (specific interactions at molecular level).
B) Physisorption, molecular level. C) Mechanically adhesion by interlocking of the two phases at irregularities in the interface, at a microscopic scale, also used by microorganisms. After Myers (1991).

Layer	Adhesion	Removal
A - layer	Strongly adsorbed to the atomically clean surface	Only removable by destroying the interface
B - layer	Strong attachment to the A - layer	Removable by energy-intensive chemical and mechanical measures
C - layer	Relatively loose attachment to the B - layer	Removable with minimal energy input

Table 3.3: Hierarchy of spontaneous adsorbed layers. Soiling can be described as three layer on top of each other, removal becomes more difficult closer to the substrate.

4. CONSEQUENCES OF CHANGING SURFACE PROPERTIES

In the two previous chapters the theoretical principles of different surface properties involving moisture, heat and soiling were discussed. In this chapter the theoretical aspects will be applied to a larger scale and combined. More practical consequences of changing surface properties will be addressed.

As the surface is the outermost layer of a building envelope, its primary function is:

- To be the interface between the environment and the bulk material of the construction. As a result, the surface is crucial to the aesthetical appearance of a building

- Protection of the bulk material and thereby reduce maintenance.

Although pure surface performance like visual appearance will be touched upon, the main issue is how the performance of the construction *behind* the surface is affected by surface properties.

From the viewpoint of many practitioners performance boils down to economical costs, which can be split in *maintenance* and *operational* costs. When dealing with building envelopes, the corresponding terms from the viewpoint of more scientific oriented practitioners (engineers) could be deterioration and heat loss, or in a broader sense *durability* and *energy consumption*, which is why this chapter is divided into sections with these headings.

4.1 Durability

Durability of a material or component describes the resistance against deterioration. Consequently, prior to an evaluation of durability, the deterioration processes must be determined and failure defined. Deterioration of the exterior of building envelopes can be divided into three categories with decreasing severity (Young et al. 2003):

1. Structural effect: The stability and strength of the building envelope is endangered

2. <u>Functional</u> effect: The function of the building envelope is impaired e.g. protection against water ingress

3. <u>Aesthetical</u> effect: The visual appearance of the building is negatively affected

It is very rare that deterioration at the surface has a structural effect, as deterioration generally starts at one of the other categories with the possibility to move up if deterioration continues. But as deterioration at surfaces tends to be visible, actions will be taken before the processes are allowed to become too severe.

4.1.1 Moisture in porous materials

By using hydrophobic treatments, low emissivity or high absorptivity coatings, the possible change in properties can be summarised into the following:

- The wetting behaviour changes: Rain runs off fast with little contact to the surface and brief contact times. The result will be drier surfaces.

- The capillary transport changes: Water will not be sucked into the material, but be repelled. As a result the bulk material will by drier.

- The emissivity or absorptivity changes: The heat loss from a surface diminishes when the thermal radiation is reduced (low emissivity). More heat is gained if the absorptivity is increased. This means the surface and the material will be warmer and drier as more moisture will dry out through diffusion.

The effects focus on moisture transport and moisture content, which have a profound influence on the durability of materials.

4.1.1.1 Freeze-thaw resistance

The processes in frost damage are still not fully understood, but simplified the main processes of frost damage in porous materials can be described as below (Geving & Thue, 2002).:

- When water freezes and changes from a liquid to a solid state, the volume increases 9 %.

- – Ice attracts water and relatively strong forces transport water from small pores to ice crystals, which consequently grow.

- – If wet material is cooled below the freezing point, the water needs space to escape or the material will disrupt. However, not all water will freeze at that point; in fine pores the pressure will be too high and the water is too strong bonded to the pores for the water to freeze. The freezing point is lowered.

Another theory to why frost damage occurs than the forming of ice lenses, is the theory of hydraulic pressure: When materials are subjected to frost the water in he coarse pores closes to the surface will start to freeze. The water in the material in front of the advancing ice front will be pressed in the same direction as the ice front moves, towards larger voids in the material. This results in a hydraulic pressure in the pores. The pressure will depend on how fast the cooling takes place and how far the water must be pressed, which also depend on the permeability of the material. If the hydraulic pressure is to high the material will disrupt (Hansen, 1995).

In the ice lense theory as well as the hydraulic pressure theory the extent of frost damage will depends highly on the amount of trapped water plus the amount and shape of the pores. I.e. the risk of frost damage is a combination of porosity and pore size distribution.

Figure 4.1: Scaling of bricks due to frost damage. Some of the bricks in this detached wall are not frost resistant; 0.5 cm thick layers scale off the brick.

4.1.1.2 Pore size and porosity

The porosity of a material is given by the percentage of air volume of the total volume in a dry material. Because many material properties (e.g. strength, thermal inductivity etc.) depend on the porosity this is often used as a description of a material. However, the shape and size of pores are very important when describing how the material reacts when exposed to water. Irregular pores can result in risk of frost damage, because freezing water cannot escape, On the other hand, fine pores lowers the freezing point. Pore size distribution should be evenly to avoid entrapment of water.

A simple way to evaluate whether water has a tendency to get trapped in a material is to compare the water saturation obtained by vacuum with a critical degree of saturation, which has been established by experiments. E.g. this degree is for tile brick found to be 0.70 − 0.90 (Hansen, 1995).

However, no precise method has been reported from which it can be decided whether a material is frost resistant or not. Therefore accelerated standard test methods have been invented. The main idea in these tests is, that the material is exposed to a number of cycles of artificial rain followed by freezing. The cycles are all of the same duration, which will induce stress in the same area in each cycle. If there is a loss in material after the prescribed number of cycles the material is not frost resistant. However, these tests are often discussed (Wittmann, 1996). Sometimes materials pass the test, but when exposed to natural conditions they fail, and vice versa.

4.1.1.3 Water content

Frost damage occurs only if the moisture content exceeds a certain minimum (dependent of pore size and distribution). If water is prevented from entering a porous material, frost damage cannot occur. By applying a hydrophobic treatment, capillary suction is prevented (see Chapter 2), and water ingress from the outside therefore diminished, and consequently frost damage as well.

If, however, the hydrophobic treatment is incomplete and water can penetrate the treated layer e.g. through cracks, the lack of capillary suction means moisture only can be transported by diffusion, which is a much slower mechanism. The water vapour permeability depends on the water content as described in Section 2.2.2,

the treated layer, which is relatively dry will therefore have a lower water vapour permeability, slowing the process even further. Sandin (1999) has showed that for brick with a water repellent zone of 5 mm, the drying process takes 50 times longer when it has to be by diffusion through the layer compared to untreated brick where moisture evaporates directly from the surface.

As a result the material can have increased moisture content for a longer time and therefore higher risk of frost damage. Sandin (2003) has reported that it seems that once water has penetrated the treatment through a crack, this is more likely to happen again in the future. In his example the first penetration happened after 6 years, hereafter it happened several times a year. The reason could be, that contaminants have been transported into the crack, changing the contact angle and therefore loosing its hydrophobicity.
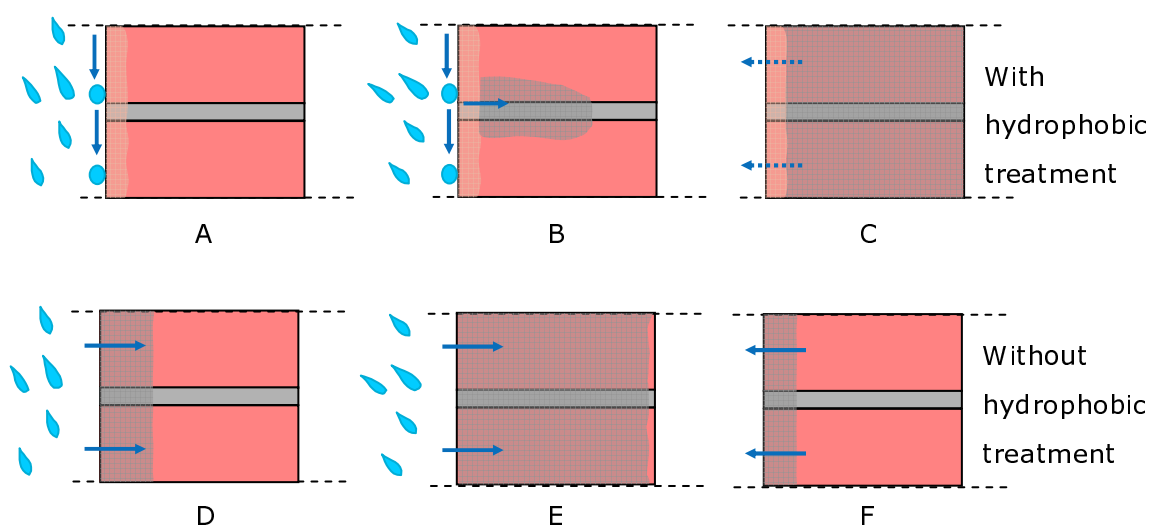
Figure 4.2: Principle in water ingress and drying of brick wall with and without hydrophobic treatment. A: In materials with hydrophobic treatments water is repelled from the surface and will not wet the material unlike the untreated sample. B: If cracks occur or have not been treated, driving rain might force water through the treated layer. C: The hydrophobic treatment slows down the drying of the material, causing high moisture content for a long time, while drying from the untreated material is facilitated through capillary transport. There is a risk the hydrophobic treatment might scale off. D-F: For comparison the moisture transport if the wall had not been treated.

Faadeev & Eroshenko (1997) have a slightly different explanation, they observed the same thing in laboratory testing of porous silica hydrophobized with short alkylsilanes. They described this phenomenon as wetting hysteresis; the contact angle is decreasing for each penetration, a partial hydrophilization of the treated zone takes place.

4.1.2 Decomposition

Weathering is a commonly used term to describe the decomposition of materials just exposed to the outdoor climate. However, the outdoor climate represent a number of different forces and effects over which we have only little control. Forces induced by freeze-thaw cycles are just one example, which can result in material scaling of the host material. More complicated processes take place when the surface is exposed to e.g. particles and chemicals from the environment, which involve mechanical and chemical changes at the surface and ultimately in the bulk material. The result is loss of material.

Excluding biological induced deterioration, the most important factors in weathering are: thermal induced stress including freeze-thaw interactions, formation of gypsum layers and other salt crystallisations. As the more mechanical mechanism of frost damage has already been discussed in the former section, the chemically induced deteriorations will be the subject of this section.

4.1.2.1 Gypsum layers

Due to better filters and a change in heating systems the content of SO_2 in atmospheric air has generally decreased since the 1980'es (i.e. in Copenhagen from 23 µg/m3 in 1988 to 3.8 µg/m3 in 2002, Kemp & Palmgren, 2003). Nevertheless is the SO_2 induced gypsum formation on building materials still a common form of deterioration of building stones.

The chemical backgrounds for the formation of gypsum layers depend on the chemical composition of the building stone. A few simplified examples are shown in Table 4.1.

Origin	Active substance	Reaction
Combustion	Sulphate	$SO_2 + H_2O \rightarrow H_2SO_4$
Limestone	Calcite	$CaCO_3 + H_2SO_4 + H_2O \rightarrow \mathbf{CaSO_4 \cdot 2H_2O} + CO_2$
Sandstone, tile	Calcium silicate	$CaSiO_3 + H_2SO_4 + ½O_2 \rightarrow \mathbf{CaSO_4 \cdot 2H_2O} + SiO_2$
Concrete	Calcium hydroxide	$Ca(OH)_2 + H_2SO_4 \rightarrow \mathbf{CaSO_4 \cdot 2H_2O}$

Table 4.1: Examples of formation of gypsum layer. When water reacts with SO_2, sulphate acid is formed, this reacts with Ca in different building materials, resulting in a gypsum layer $CaSO_4 \cdot 2H_2O$. (Cultrone et al. 2000, Török, 2003 and Herholdt et al. 1985)

When SO_2 is in contact with water (rain) sulphuric acid is formed. When the acidic rain comes in contact with calcium-containing materials, gypsum can be formed. This process can take place at the surface, where the access is easy and a gypsum crust can be formed. The thickness and density of the crust depends on the content of SO_2 in the air, the host material and exposure to rain. Török, (2003) has reported different types of gypsum crusts at limestone in Budapest.

- Thick, hard, white crusts at surfaces exposed to wind and rain. The crusts seem to protect the material behind the crust, as the crust seems to be impermeable and has a higher compressive strength than the material below. A thin white crust with much lower strength was also reported in areas with the same exposure but at more dense limestones.

- Thick black framboidal crusts occurring as isolated patches at sheltered areas with high deposition. Although gypsum is the most abundant mineral it also contains a high level of organic carbon probably due to incorporation of particulate pollutants (Smith et al. 2003). The black crust is more permeable than the white crust.

- Laminar black crusts in sheltered areas, thinner than the frambodial crust and permeable.

Weather conditions and high levels of air pollution might enhance the problem in Budapest, but gypsum crusts that fit into these descriptions has also been reported elsewhere e.g. Beck et al. (2003), Nord & Holenyi, (1999) and Turkington et al. (2003) and this classification is therefore useful in the description of the phenomenon.

There is a distinct difference in whether the surface is exposed or sheltered; generally gypsum crusts are more frequently observed at sheltered surfaces. The explanation could be, that gypsum is soluble in water, and at exposed surfaces parts of the crust will continuously be removed. Another reason could be, that pollutant particles act as catalysts for gypsum formation (Török, 2003 and Cultrone et al. 2000) and at sheltered areas these particles remain, as no rain will remove them.

Although gypsum crusts may have different properties, they generally seem to be more impermeable and have a higher strength than the material just below the crust. The crust could therefore be seen as a protective layer. Gypsum can passivate the surface of single calcite crystals i.e. products of a chemical reaction physically block further physical activity at the surface. However, it is not known if it applies to larger scales (Antill & Viles, 2003). Török (2003) thinks it is possible that the thickening of the most impermeable crusts take place from the underside of the crust, where solutions might arrive through micro cracks in the crust or irregularities in the substrate. If this is true a probable passivation would not be effective, as there would still be access to new material.

Before a dense crust is formed or if the crust has defects, water can be transported inside the material from where it will dry out again. These wetting-drying cycles result in dissolution and recrystallisation and consequently to deterioration of the stone. How deep this zone goes depends highly on the porosity of the stone.

Török (2003) has compared the strength and the water uptake of the crusts, the host rock and a fresh unaltered stone block. The result was, that the strength of the host rock had decreased, the crust itself might be stronger than the fresh stone, but as the foundation of the crust becomes weaker the net result is a rigid crust. The water uptake in the host rock was also altered to the worse; when the crust was removed, the water uptake was accelerated.

As a consequence of the described gypsum related deterioration the altered material can be divided into three zones as shown in Figure 4.3.

Few millimetres

Some centimetres

Patina
Crystallisation of gypsum
Surface hardened zone

Intermediate zone
Partial dissolution and loss of
material
Weakened stone

Bulk material
Intact stone
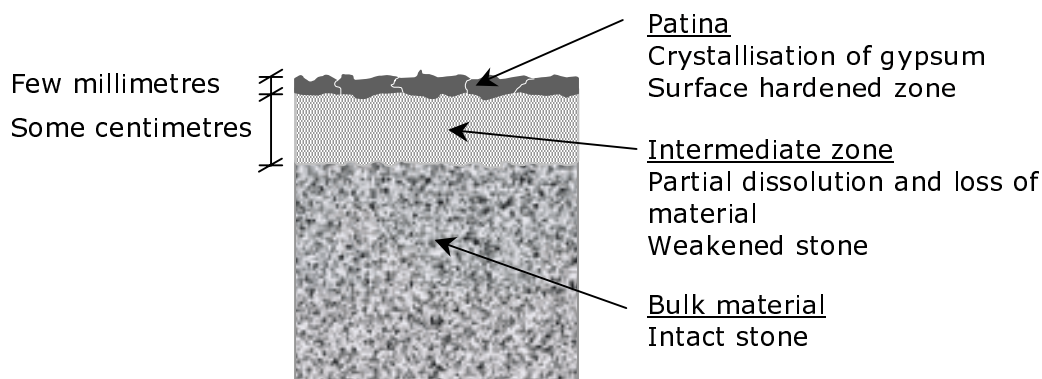
Figure 4.3: Porous material with gypsum crust. While the bulk material is unchanged because water is not transported that far, an intermediate zone is weakened because of partial dissolution. At the outside a gypsum crust is formed. Thickness and porosity of the crust depend on the host material, access to sulphate and exposure to rain. (Based on Beck et al. 2003.)

To sum up: the main problem in the formation of the gypsum layer is:

– Aesthetical, the gypsum layer obscures the image of the surface.

– The material in the intermediate zone is weakened

– The crust is rigid and might fall off, removing not only the crust but also a thin layer of the host material, held together by the gypsum.

The removal of gypsum crusts and thereby full exposure of the weakened intermediate layer could result in an accelerated deterioration process (see Section 4.1.4). Instead ways to reduce the risk of formation of a gypsum layer at cleaned or new surfaces should be explored. Limiting the possibilities to actions at the surface of the porous material these could be:

– Avoid the transport of sulphuric acid into the material.

– Avoid deposition of polluted particles at the surface as promote the formation of a gypsum layer.

Hydrophobic treatments are a possibility; capillary suction would be prevented and raindrops will easier be able to remove larger particles as they have a smaller contact area with the surface and therefore run of faster.

4.1.2.2 Salt crystallisation

While the main source (SO_2) for the formation of gypsum layers is external (the atmospheric air) the source for other salt formations is often internal, except in marine areas where the NaCl is abundant in the surroundings. However, the effects are similar and can in a simplified form be described in three steps:

- Porous materials containing salts are exposed to water, dissolving the salt.

- Water containing salt is transported to an area where the water evaporates, the salt crystallises.

- If the salt crystallises at the surface it will be noticeable as salt efflorescence. If the crystallisation takes place inside the material it might cause deterioration, as the material above the crystallisation will ultimately fall off.

Salt formation of this kind has two of the three problems with gypsum layers, it does not form a dense crust, but in terms of aesthetics and strength of the porous material the problems are similar.

Whether a surface treatment can reduce the problem or not depends on the reason for wetting of the material. A few examples:

- Exposure to driving rain will result in cycles of wetting and drying, which will keep the process going. Preventing the wetting by hydrophobic treatment could be effective.

- Reinforced concrete constructions in marine zones or near roads where NaCl is used for defrosting. Wetting and drying cycles will transport salt into the construction increasing the Cl$^-$ content. At some point the Cl$^-$ content becomes critical, and in the presence of water corrosion of reinforcement can occur despite the high pH of the concrete (the reinforcement is no longer passivated). An effective hydrophobic treatment will prevent water from entering the concrete and thereby avoid Cl$^-$ ingress.

- Rising damp from the underground is a continuous process. The only surface involvement is that the moisture evaporates from the surface. A

hydrophobic treatment would not help. On the contrary, it would slow down the process, which could cause an increase in rising height, which in some cases would move the problem of salt efflorescence from the cellar to the ground floor. See Figure 6.8.

4.1.3 Biological susceptibility

While changing the surface properties might influence the durability of the material in relation to non-living environmental influence, the same effect can be achieved toward biological growth. Biodeterioration, bioprotection and the processes involved are discussed in Chapter 3, and although the effects of biological growth are not entirely negative, Messal (2000) claims that roughly 20% of all renovation cases in Germany are caused by biological growth. Focus in this section will therefore be limitation of biological growth.

4.1.3.1 Roughness

One way to limit biological growth is to hinder the organisms in establishing themselves. As described in Section 3.2.2.6 the roughness of the surface has an influence on how fast biological growth is established, as microorganisms more easily find footing at rough than smooth surfaces. If biological growth is acceptable when the construction becomes old (see Section 3.1.2.2) using smooth surfaces (polished, glazed etc.) could be a solution. However, it can be very difficult to determine why biological growth has been inhibited when a surface is smoothened; glazing changes the surface properties in more than just smoothening, polishing will also limit deposition of particles, which could have been the starting point for biological growth.

4.1.3.2 Heat and moisture

As described in Section 3.2.2.1, nourishment will normally be abundant at exterior surfaces and only some species are sensitive to light. The most limiting factor for biological growth is therefore a combination of moisture content and the temperature. Although most microorganisms prefer high moisture levels, liquid water is not necessary. Consequently biological growth might occur without condensation at the surface.

To save energy the U-value of building envelopes has decreased since the 1970's. As a result the heat flow through the envelope has decreased, changing the temperature and moisture content in the outermost material layer. An example:

Moisture and heat transport through a traditional brick wall as shown in Figure 4.4 has been simulated with MATCH (Pedersen, 1991), using the Danish test reference year. Two simulations were made one with an insulation layer of 50 mm mineral wool and one with 200 mm mineral wool. The results of the simulation are shown at Figure 4.4. The surface temperature is only little affected by the better insulation; in a winter week the temperature of the well-insulated wall is in average 0.3°C colder than the thinner wall. The relative humidity is higher at the well-insulated wall, condensation occurs over a longer period. The moisture content in kg/m^3 changes accordingly; in the same winter week, the average amount of water is roughly double as high in the thick as in the thin wall. However, driving rain is not considered with MATCH, this will probably effect the moisture content. For further discussion see Section 4.2.2.2.
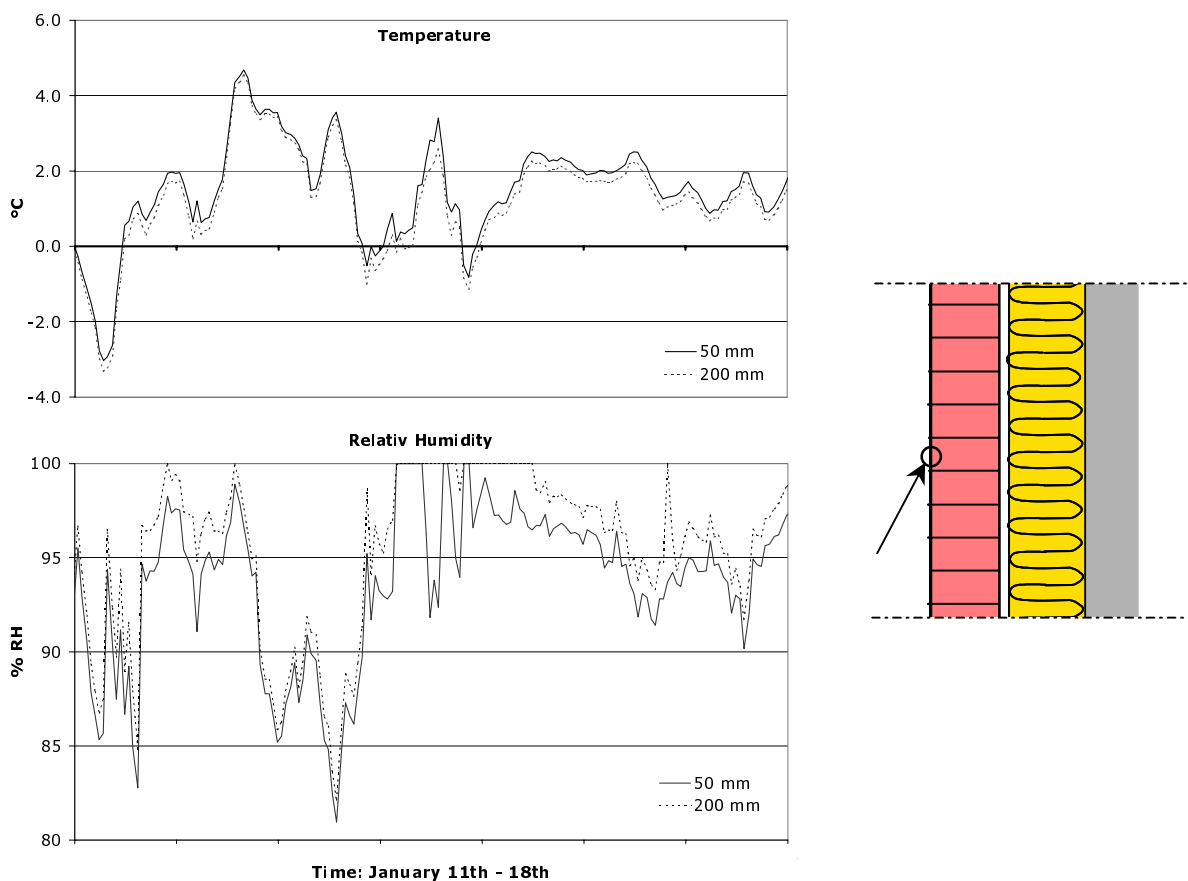
Figure 4.4: Simulation of surface temperature and moisture content in the uttermost 3mm of a traditional exterior north faced wall. Two simulations were made with MATCH: with an insulation layer of 50 mm and with 200 mm. Simulation results for temperature and RH in a winter week (January 11th-18th) in the uttermost 3 mm of brick are shown. The surface of the well-insulated wall was colder and moister.
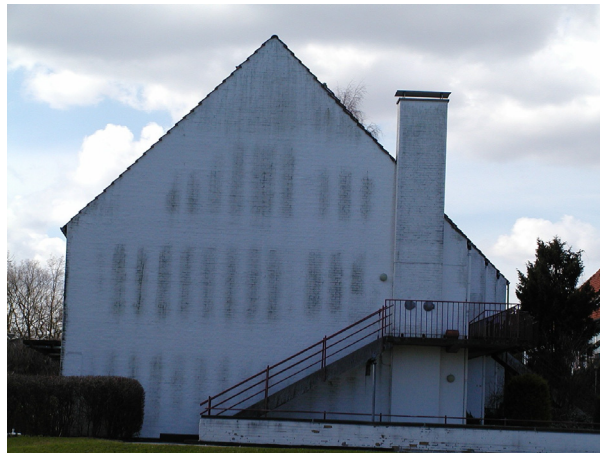
Figure 4.5:   Biological growth is impaired at thermal bridges, here at an east-facing gable.

Becker (2003) has reported how rendered facades in different parts of Europe have developed patterned stains as a result of biological growth (algae and moulds). Künzel et al. (2001) have made a similar observation and seem to think the problem is increasing. In the reported cases the rendering was placed at external insulation. Investigations showed that where the facade was not stained, there was a thermal bridge.

The result of the simulation shown in Figure 4.4 is also an explanation for why biological growth often appears in patterns. Areas with little insulation are thermal bridges, and as the moisture content is considerably lower in these areas, the living conditions are impaired, and growth will become less abundant. Figure 4.5 show an example of how thermal bridges can become very visible.

Künzel et al. (2001) have stated, that the difference between algae growth and no growth can be only a tenth of a degree. In that respect raising the surface temperature even a little becomes important.

Preventing biological growth by reducing the insulation is not an acceptable solution, other methods must be found. Important factors are:

–   Due to thermal radiation surfaces can become colder than the ambient temperature, and as a result, condensation occurs. The phenomenon is more likely to happen if there is only little heat capacity in the outer

layer, e.g. rendering at exterior insulation. Increasing the mass of the outer layer will reduce the risk of subcooling.

– At painted surfaces darker colours could be preferred or paints with low thermal emissivity chosen, this would mean warmer surfaces during the day, which could inhibit biological growth, see Section 6.2.1.1, and in case of the low emissivity paint, also warmer surfaces at night with a reduced risk of subcooling. (See Section 2.4)

– If the outer surface layer is wetted, it is important how fast the moisture will spread into the material. Although vapour permeability is a part of diffusivity, Becker (2003) has through simulations shown how the moisture content of the uttermost layer hardly is affected by the vapour permeability of the layer, but the moisture diffusivity has a high influence. With decreased moisture diffusivity the rate of moisture transport into the material is decreased, i.e. more moisture is stored in the close vicinity of the surface. The consequence is better growing conditions for microorganisms.

Strictly surface related are the considerations about dark colours, low emissivity and decreased moisture diffusivity. These properties can be obtained but can only be preserved, if soiling phenomena like biological growth or environmental dirt do not cover the surfaces.

Hydrophobic treatments have the advantage that water is repelled and not transported into the material. Driving rain will therefore be removed fast, reducing the growth conditions. On the other hand, condensation at surfaces might not result in water run off, especially at surfaces with no or only little slope. Instead of being transported into a porous material, the water will stay at the surface, enhancing the possibility of growth. Figure 4.6 shows how dew stays at roofing tiles with a treatment that optically had a contact angle > 90° longer than at non-treated tiles.

The question is if the effect of water at the surface is higher than the higher general water content and therefore longer drying periods in the non-treated material. At Figure 4.6 the ordinary tiles have also been wet during the night. The effect can only be seen as the temperature rises, in the summer approximately one hour.

Figure 4.6: Dew at low sloped roofing tiles, left: ordinary tiles. Right: tiles with surface treatment. The dew is not transported from the treated surface into the material; the surface stays wet, while the surface at the ordinary tiles is drying fast. The used surface treatment did not prevent water uptake and was therefore not hydrophobic (see Section 6.1.3.1). However, in some situations, like this, water formed droplets beads, as if the contact angle was > 90°.

The influence of hydrophobic treatments on biological growth is ambiguous. Repelling water is a good thing, but beside the effects described above, some hydrophobic treatments are nutritious to microorganisms, which will enhance the risk of growth considerably. Hydrophobic treatments should not be used uncritically; slope, substrate properties like porosity and pore size must be considered before a hydrophobic treatment is used to limit biological growth.

4.1.3.3 Biocide

Instead of focusing on what keeps microorganisms alive, neutralizing the microorganisms by the use of biocides is a possibility.

Frambøl et al. (2003-c) have studied which chemical agents are used in Denmark for cleaning and preventing of biological growth on masonry, clay tile and concrete roofs. A summary of the different groups of chemicals used for cleaning and their effect on microorganisms is given in Table 4.1.

Active compound in chemical agent	Effect
Quaternary ammonium compounds	Positive charged cat ions adsorb at the negative charged surface of the cells, causing damage to the membrane
Hypochloride	Chloride is very toxic to most bacteria and fungi
Organic fatty acids and soaps	Some of the acids inhibit or kill bacteria and fungi, some work through their alkaline reaction combined with their capability to form fatty layers at surfaces and remove this together with bacteria.
Inorganic and organic acids	Most microorganisms are inhibited or killed by very low pH
Inorganic alkaline compounds	Most microorganisms are inhibited or killed by very high pH

Table 4.2: List of chemical agents used for cleaning of biological growth and how they act on the microorganisms. (Based on Frambøl et al. 2003-c.)

In addition to these chemicals different metals may also act as toxic agents; lead, copper and zinc all reduce biological growth. But the metals are only effective in areas wetted by water that has been in contact with the metal. Side effects like discoloration (copper) and accumulation of heavy metal (lead) may appear. After cleaning the surfaces new biological attacks can be inhibited by using preventive methods like hydrophobic treatments, sealing or painting. Especially hydrophobic treatments are used. (Frambøl et al. 2003-c). The main reason for using paints is normally not to prevent biological growth, but some paints contain biocides, which can inhibit growth.

Unfortunately the use of biocides for cleaning purposes or as prevention has a number of drawbacks:

  – To be effective the biocide most be water-soluble, this means it will slowly be washed out by the rain, and a treatment must be repeated from time to time.

  – For environmental reasons the method is undesirable, not only the microorganisms at the surfaces will be killed other organisms might as well, especially when the biocides are washed out.

−   The use of chemicals should be limited and is therefore restricted. In Denmark only one product, which is used to clean surfaces from biological growth, is actually approved for this use (Frambøl et al. 2003-c).

However, sometimes biocides might be the only realistic way to remove and inhibit biological growth (Becker & Putterman, 2002). In some cases biocides can be used for a limited time. Sedlbayer & Krus, (2001) describe how biological growth appears at a new building, because the built-in moisture is transported through the wall. Simulations show that after one year, the moisture content in most areas will have decreased, and the growth would therefore stop. If this had been known from the beginning, a biocide, which only had to be effective for one year could have been applied. This would have minimised the costs and the effect on the environment.

4.1.4 Visual appearance

The aesthetic aspect of soiling has been discussed in Chapter 3. When soiling becomes a problem is highly a subjective judgement. Even signs of deterioration can be acceptable, if it fits the image the building owner wants. Before deciding whether soiling should be avoided, removed or accepted, a definition of failure must be established.

4.1.4.1 Service life

Service life of a building is in ISO 15686-1 (2000) defined as: *"Period of time after installation during which a building or its parts meets or exceeds the performance requirements"* and failure described as *"Loss of the ability of a building or its parts to perform a specific function"*.

When estimating service life for surfaces, specific functions must be defined before it can be decided if a surface has failed. A number of functions could be considered e.g.:

−   The surface must protect the underlying material

−   The surface colour must be in a given range

−   The surface must be intact

Figure 4.7 show examples of different failures.

Figure 4.7:   Different surface failures. Left: the surface paint is not intact and the underlying material is no longer protected. Right: algae growth at a white aluminium facade. Although the facade is still protected, the surface has failed because the building looks dirty and is in contrast to the image the building owner wants.

ISO 15686-1 (2000) introduces a method for estimating service life, this method involves a number of factors that influence the service life, these factors must be multiplied, not all apply to surfaces, but the idea is useful and basically service life can be estimated when:

- The function of the surface is defined

- Experience with the surface or suitable tests on durability are available

- Level of maintenance is established

- An educated guess concerning the future outdoor climate has been made

Surfaces normally changes appearance long before they loose their functionality, therefore service life will decreases if aesthetics becomes a function on equal terms with functionality. Normally long service life would be favoured by building owners and with this definition the impact of soiling on service life becomes more noticeable. Service life estimation will be further discussed in Section 6.1.2.2.

It is generally accepted that paint has to be renewed now and then and indoor cleaning is natural. In the same way soil removing from exterior building surfaces could be seen as a natural part of maintenance. If the cleaning is done often

enough gentle methods will be sufficient. At buildings where patina is wanted, regularly cleaning is difficult, but in many cases it could prevent the destruction that soiling eventually leads to. If the destruction is not just aesthetical but physical by deterioration of material, a process has started, which is irreversible and might only become even more distinct when rough methods must be used to remove an unacceptable soiling layer.

4.1.4.2 Remedial actions and resoiling

There are numerous ways to clean a surface if soiling has become a problem and must be removed; from abrasive techniques like sandblasting to laser cleaning and water spraying. The cleaning method must always be adjusted to the surface and the layer to be removed, and even in a given case, the possibilities are numerous. E.g. Marie-Victoire & Texier (1999) describe ten different techniques tested to clean ancient concrete with a black crust.

As described in Chapter 3 cleaning methods can be divided in chemical and mechanical methods, each of them have their advantages and drawbacks. Some of them touch upon the problem of resoiling, which can become a serious problem as the soiling rate tends to level off with time (Schwar, 1998) see Figure 4.8. I.e. soiling rate is high at freshly cleaned surfaces compared to the soiling rate just before the cleaning, and cleaning would therefore seem to accelerate soiling. In addition, tests comparing new sandstone to cleaned sandstone have showed that some chemical cleaning methods do accelerate the process (Young & Urquhart, 1998).
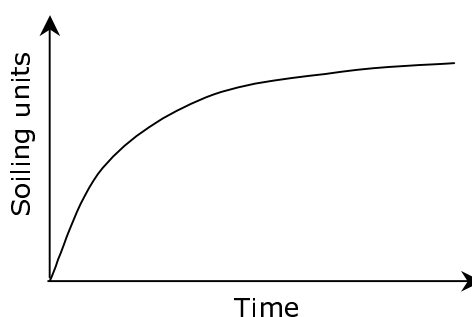
Figure 4.8: Schematic depiction of how soiling rate changes with time. The specific shape of the curve depends on the substrate and the environment. Based on Schwar, (1998).

Some acids used for cleaning contain phosphates, which act as nourishment for biological growth, once the acidity has come down this can enhanced resoiling. Young & Urquhart (1998) have described how test results show increased resoiling by algae growth on sandstones only few months after cleaning with an H_3PO_4 containing acid. The effect depended on the composition of the sandstone; some minerals retain more phosphate than others, the result was, that while the increase in growth declined after about 1½ year in some sandstones, it continued for at least 3½ years (the whole test period) in others. The main difference in the sandstones with long time resoiling was, that they were iron-rich. This is very unfortunately as phosphate-containing acids have been recommended for use at iron-rich sandstones, because phosphate is supposed to reduce iron mobilisation.

Furthermore chemical cleaning may increase the risk of salt efflorescence, as salts can be left in the materials as residues from chemical cleaning. Again, the seriousness of the problem depends on the chemical agent and the porosity and composition of the material to be cleaned Young et al. (2003).

For mechanical or abrasive methods different pressures and different materials can be used for cleaning. Resoiling can also in this case accelerate considerably, even if the used technique is adjusted to the situation as mentioned in Section 3.1.3, and the surface looks clean immediately after the process. E.g. when a gypsum crust is removed, the weakened intermediate zone (see Figure 4.3) is exposed. Aggressive methods will also remove the intermediate zone, disfiguring the surface and with a substantial material loss.

Summarising the problems described above, the cleaning-related problems with resoiling and consequently deterioration can be caused by different mechanisms (Young et al. 2003):

- Salt efflorescence and decay caused by chemical residues

- Enlarged porosity and increase in cracks at the surface caused by abrasion

- Enhanced biological growth caused by chemical residues

- Increased surface area and consequently increased susceptibility to soiling because cleaning has removed weaker parts

    −   Any protection provided by the patina is removed.

Young et al. (2003) have tried to predict the influence of cleaning on surface decay measured on how much surface area would be covered (see Figure 4.9). The surface area varies with the quality of the material and the range of the prediction varies as well, but the tendency is clear: cleaning enhances resoiling.

Many of the cleaning-related problems are irreversible, and restoring the surface would mean replacing deteriorated material or patching with e.g. mortar. This will eventually be expensive, and as Young et al. (2003) point out, the costs for cleaning when repairs are included will exceed the financial benefits of cleaning - such as increased property value.

The sad predictions of Young et al. (2003) points out how important it is to prevent soiling, or at least use very gentle methods for cleaning. If removal of soiling is a part of the maintenance plan and performed regularly, very gentle methods can be used and the negative effect be minimised. In older buildings this might be too late, but new buildings may still be saved.
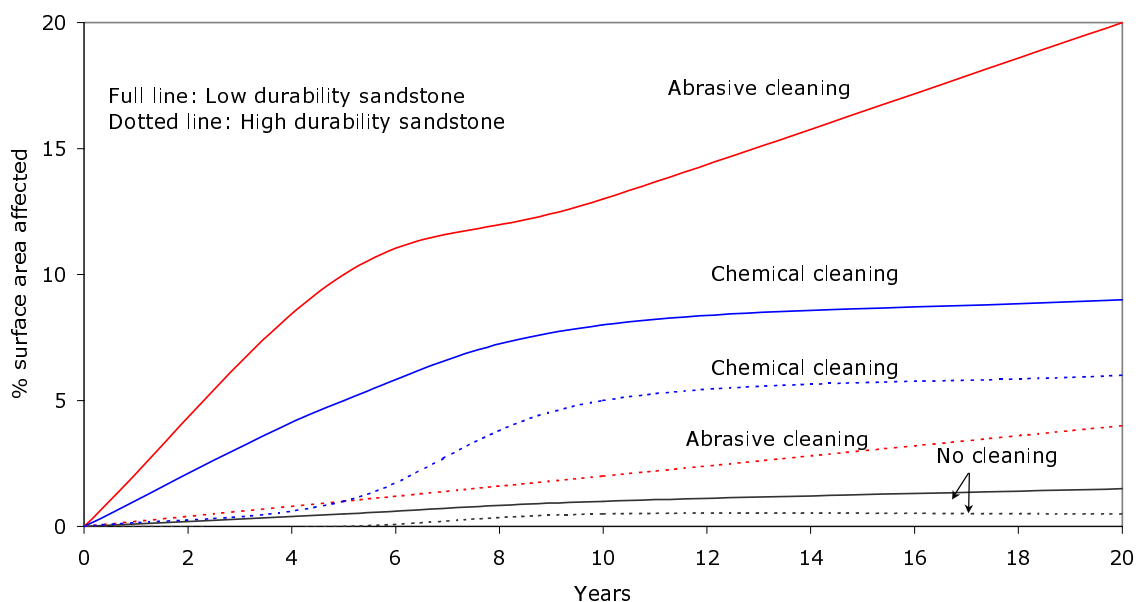
Figure 4.9:   Prediction of stone decay in different sandstones in principle, measured in % affected surface area, depending on cleaning methods. Based on Young et al. (2003)

Figure 4.10: Examples of unacceptable soiling. Left: mould growth at a two year old house. Right: Algae growth at aluminium facade, three years after cleaning with brush and water. Both buildings had to be cleaned, despite the risk of higher susceptibility to soiling.

To ban all cleaning methods is not an option, sometimes the aesthetical influence is too large and remedial actions must be taken. Figure 4.10 show two examples of unacceptable soiling, both by biological growth. One is a new prestige building in Stockholm, about two years old, placed in walking distance from the old town of Stockholm with a view over the archipelago. The other example is at an office building in Denmark located close to a forest. When the house was about 25 years old it was cleaned for the first time. Three years later this picture was taken, now there is extensive algae growth at parts of the facade. The building now looks worse than just before the first cleaning, and a second cleaning was initiated. The picture is a segment of the right-hand picture in Figure 4.7.

4.2 Energy consumption

While durability determines the costs for maintenance, energy costs can be seen as a part of the operational costs for the whole building. As mentioned in Section 2.4 changing surface properties can change the thermal performance. While only the possibilities were discussed earlier, the possible effects will be the topic of this section.

Most of the possibilities in changing absorptivity and emissivity mentioned in Section 2.4 were either theoretical considerations or referring to some not

commercially available treatments. Therefore, the effects discussed in this section are also mostly based on theoretical deductions and simulations will be used to evaluate them.

4.2.1 Possible energy savings

The surface properties that can decrease energy consumption for heating are:

– Hydrophobic properties. Wet materials have higher thermal conductivity than dry materials. Accordingly the temperature at the hydrophobic surface will be lower in the winter (Häupl et al. 2000).

– High absorptivity. If the absorptivity in the solar range is high, the surface temperature increase during the day.

– Low emissivity. When the emissivity is low, the surface will radiate less thermal energy, consequently the surface temperature will be higher.

Häupl et al. (2000) made simulations with the computer program DIM 3.1 on different walls; they varied the orientation, the thermal conductivity, the emissivity and the coating (simulated by a non-capillary active rendering) The six different walls were either monolithic brick walls with internal and external rendering or similar walls with internal insulation. Their findings with these specific walls can be summarized into:

– Coating decreases the moisture content, but there is no difference in how the wall is oriented.

– Comparing the exterior surface temperature over a year in central Europe of four different walls; coated and uncoated walls with $\varepsilon = 0$ and $\varepsilon = 0.9$, showed temperature differences of up to 3°C with the coated wall with $\varepsilon = 0$ as generally being the warmest

– U-values decrease 10-15 % when the wall is coated, the effect is larger for walls with low U values

– U-values decrease ~ 7 % if ε is changed from 0.9 to 0 and the wall is uncoated. The effect is independent of thermal conductivity of the walls.

– The energy saving in changing the emissivity would be more than 10 % in a roof.

While the results listed above are entirely theoretical, Zürcher et al. (1982) have actually built two identical cabins where the only difference is in their exterior skin (facade and roof); one had anodised aluminium (ε = 0.92), the other chromium coated aluminium (ε = 0.07), absorptivity was identical and the indoor climate controlled. Unfortunately there is no further information on the construction or the U-value of the cabins. Compared to the simulations of Häupl et al. (2000), this would mean that the walls were coated. The surface temperatures were measured for two days in February. The results were:

- Subcooling. At the roof with ε = 0.92, the temperature at night dropped below the ambient temperature, the maximum difference was 9°C. At the low emissivity roof, there was no subcooling. At the south facade the subcooling was up to 2.5°C

- Heat loads. The heat loss was diminished by 25% by using the low emissivity cabin. The heat loss through the roof was 62 % of that in the cabin with high emissivity, while the loss through the south facade only was 55 %. The latter part might cause cooling problems in the summer.

Zürcher et al. (1982) have extrapolated their findings to calculations of how the energy consumption in the heating period of different houses would decrease and have incorporated the absorptivity as well. Depending on the house type, they found that changing the absorptivity from 0.36 to 0.65 would improve the total heat balance by 2 - 5 %. Changing absorptivity and emissivity would mean 13 – 21 % savings.

These numbers are surprisingly high and information on the houses and the test cabins is insufficient to evaluate how the savings can be that high when the savings in the presumably simpler cabins were at the reported level in February. The savings are also considerably higher than what the findings of Häupl et al. (2000) suggests, although Häupl et al. see their findings as maximum effects, e.g. ε = 0 is unrealistic. Leonhardt & Sinnesbichler (2000) have measured heat flow though walls with ordinary and low emissivity paints with visually the same colour, they found that on a cold winter day the heat flow was reduced 4 - 11 % depending on the paint. The walls had an U-value of 1.40 W/m^{2}K resembling walls of older houses. American findings of how low absorptivity at roofs in warm climates

reduces the cooling energy (Berdahl & Bretz, 1997) show savings of 10-43 % in Florida, 22 % in Mississippi and 40-50 % in California.

Although some of the numbers seem to be too optimistic, the effect of changing surface properties seems to be promising in both cold and warm climates. But especially if the U-values of the constructions are relatively high.

4.2.2 Simulation

To determine the effects of changing absorptivity or emissivity a combination hereof, simulations on typical building components will be presented in this section. The effect on temperature, moisture content and heat flux will be determined for a typical Danish wall and an almost flat roof. By comparing the results, the most effective factors can be determined.

Four simulations will be performed for each building component; two parameters (α_{sol}, and ε) each parameter has two different settings a "natural" and a theoretical.

The simulations are performed with the computer program MATCH (Pedersen, 1991), with the Danish test reference year TRY as outdoor climate and indoor conditions as 21°C indoor temperature and moisture production of 3 g/m^3 from October to April, 22°C and 2.5 g/m^3 in May and September and finally 23°C and 2 g/m^3 in June to August. The simulations include latent heat.

4.2.2.1 Roofs

The roof construction chosen for simulation fulfil the requirements of the current Danish building code (Boligministeriet, 1995) and consist of: an almost flat (slope of 3°) unventilated roof with a total of 250 mm of mineral wool as insulation layer, and with bitumen based roofing. As the roofing is waterproof no simulation were made how the moisture content is changed. Figure 4.11 show the construction and the four variations.

Moisture content in the uttermost layer of the construction is irrelevant as the roofing is waterproof. Changing the absorptivity of the roofing has very little effect, as the absorptivity already is high, however for the sake of completeness also this parameter was varied in the simulations. Selected typical results on temperature and heat flux in the simulations are shown in Figure 4.12 and Figure 4.13.
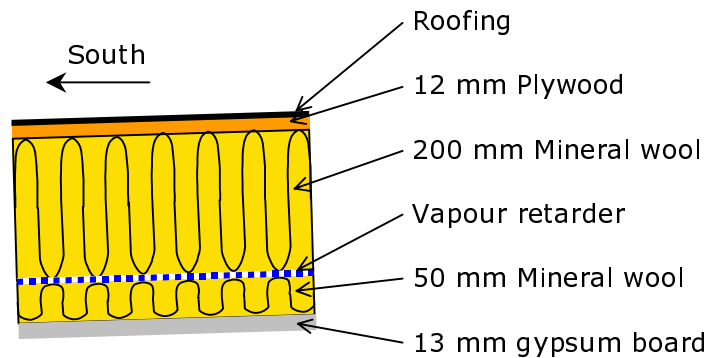
Simulation	Characteristic	ε	α
Roof O	Ordinary roof	0.90	0.93
Roof ε	Low emissivity	0.01	0.93
Roof α	High absorptivity	0.90	0.99
Roof εα	Low emissivity and high absorptivity	0.01	0.99

Figure 4.11: Sketch of roof used for simulation with description of four different simulations.

Generally the results can be summarized in the following way:

- Surface temperature. By changing the emissivity to a very low value the surface temperatures on sunny summer days increased from approximately 40°C to approximately 48°C, at night the temperature was increased by approximately 2 °C. In the winter the changes were smaller (maximum differences day or night were 2°C). Because of the higher temperature the difference between surface temperature and ambient temperature in clear nights becomes smaller, and as a consequence the number of nights with subcooling decreases. The outdoor temperature used in the simulation is shown in Figure 4.12 for comparison.

- Heat flux. The heat flux describes the energy loss or gain through the outer layer of the roof, positive values means heat flux to the outside. Changing the emissivity has only little effect in the winter where the heat flux decreases less than 5%. In the summer change of emissivity shifts the heat flux curve downwards making the influence more noticeable. However, the net result is negative heat flux, i.e. increased heat gain for the building.
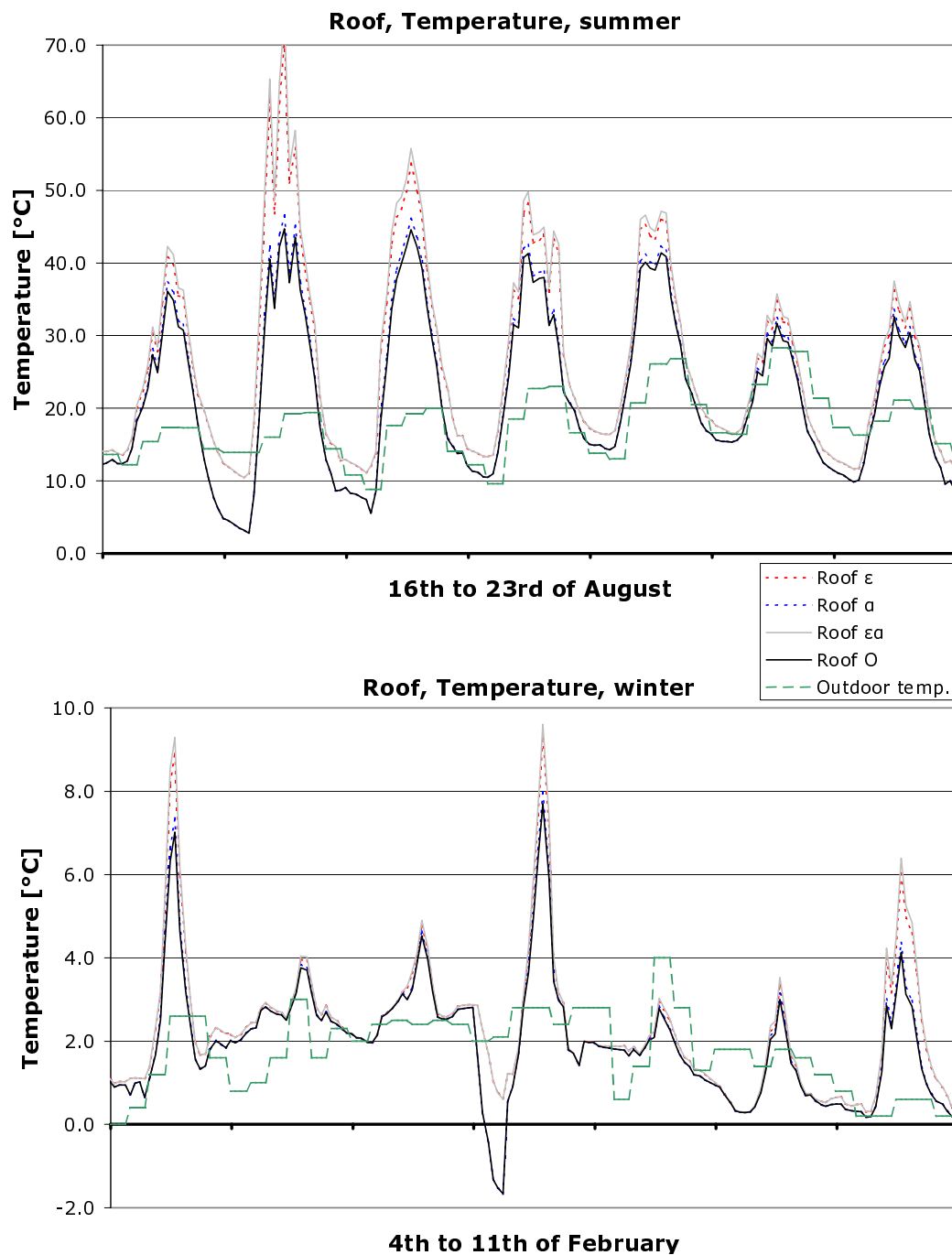
Figure 4.12: Simulation of exterior surface temperature at a roof when emissivity and absorptivity is changed. Typical summer week (16th to 23th of August) and winter week (4th to 11th of February) are showed.

Roof, Heat flux summer

16th to 23th of August

Roof, Heat flux, winter

4th to 11th of February
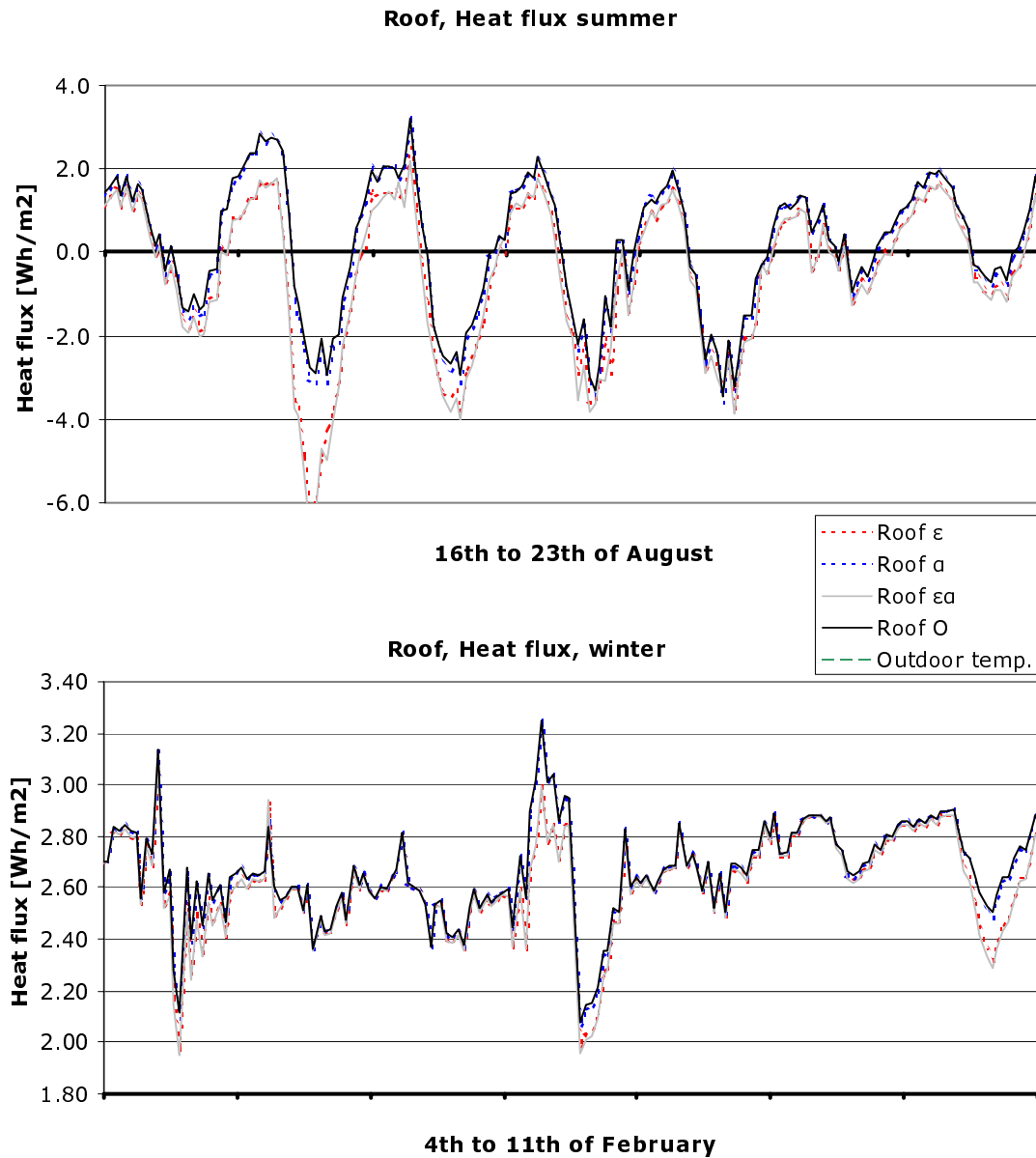
Figure 4.13: Simulation of heat flux through a roof when emissivity and absorptivity is changed. Typical summer week (16[th] to 23[th] of August) and winter week (4[th] to 11[th] of February) are showed.

All in all, the positive effect of changing emissivity and absorptivity at a relatively well-insulated roof is very limited. With this construction it is unrealistic to expect energy savings as high as reported by Häuple et al. (2000) and Zürcher et al. (1982). In fact it is more likely, that some of the drawbacks such as need for cooling and thermal stress in the material might occur.

4.2.2.2 Walls

The wall construction used for simulation is a south facing typical Danish naked brick wall fulfilling the Danish building code, it consists of: brick siding, 125 mm thermal insulation and a load-bearing concrete wall. The construction and how the simulations vary can be seen in Figure 4.14.

The results from the simulations can be summarized as follows:

- Surface temperature. Changing the emissivity increases the surface temperature, on summer days approximately 15°C (week average 5°C) and in the winter approximately 1° during the day, and weekly average 0.5°C

- Heat flux. Changing emissivity and absorptivity have similar effect, neither of them has a noticeable effect in the winter - the effect is less than 2 %. In the summer, however the effect is large, like in the roof the heat gain in the summer is remarkably.

- Moisture content. In the summer the effect of changing emissivity or absorptivity is similar; each reduces the moisture content about 10 %. In the winter low emissivity reduces the moisture content about 50 %

Simulation	Characteristic	ε	α
Wall O	Ordinary wall, not hydrophobic	0.93	0.54
Wall ε	Low emissivity, not hydrophobic	0.01	0.54
Wall α	High absorptivity, not hydrophobic	0.93	0.99
Wall εα	Low emissivity and high absorptivity, not hydrophobic	0.01	0.99
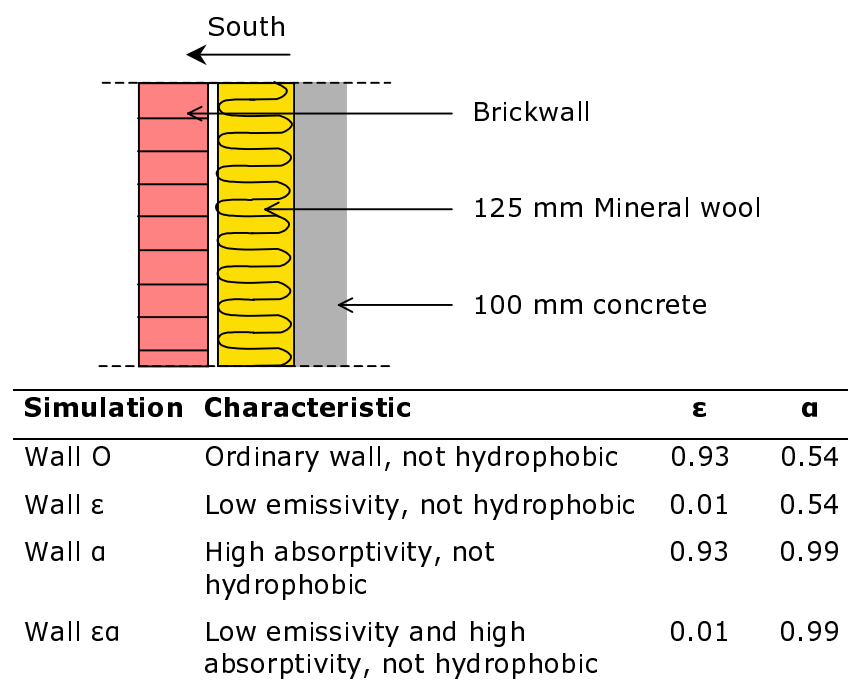
Figure 4.14: Sketch of wall used for simulation with description of four different simulations.

Surface temperature

Heat flux
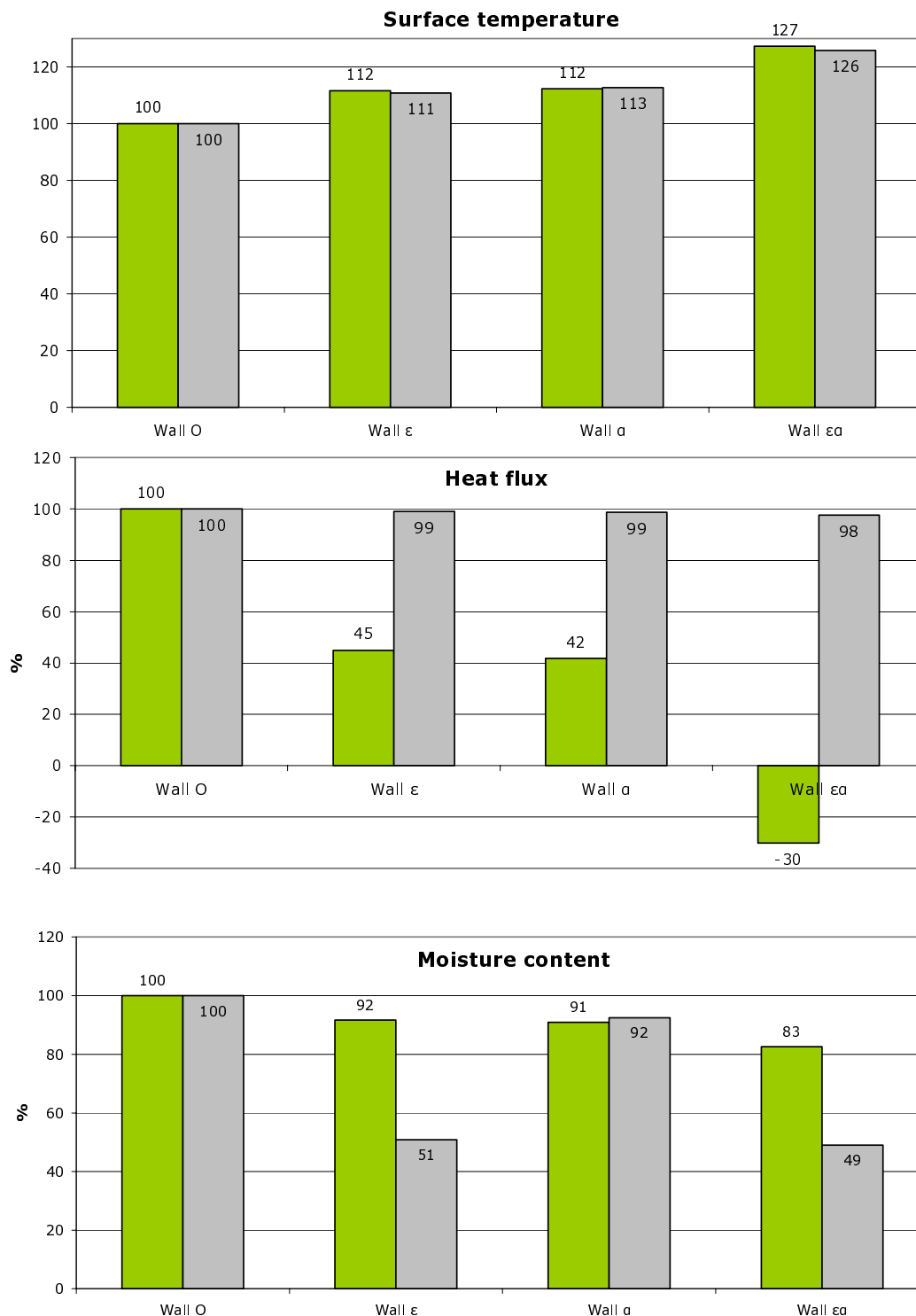
Moisture content

Figure 4.15: Simulation of surface temperature, heat flux and moisture content in a wall when emissivity and absorptivity is changed. The depictions show the differences compared to a "natural" wall (Wall O) with no manipulation of surface properties. Values for two typical weeks, summer ■ (16^{th} to 23^{ed} of August) and winter ■ (4^{th} to 11^{th} of February) are shown. Driving rain is not included in the model; moisture content should therefore be seen as if the surface was hydrophobic.

The version of the program used in this analysis does not include driving rain. The simulations are therefore comparable to protected surfaces on which the sun can shine, very similar to hydrophobic surfaces. This can be simulated by making the uttermost 10 mm of the surface capillary inactive. Svendsen et al. (2000) have tested to incorporate driving rain in calculations on moisture content of walls. The findings were not validated, but the tendency was, that driving rain was a determining factor for the moisture content, different U-values could not change this. However, lower U-values decreased the surface temperature. The simulations here of moisture content could therefore be seen as changes if the surfaces were hydrophobic. Heat flux and surface temperature have the same tendency as if the program did include driving rain.

The results of the simulations are rather discouraging. Like in the roof, there is no real energy saving in the winter. Except when the emissivity is low, then changing the surface properties seem to have a positive effect in the winter. This effect could be important as it can affect the risk of freeze-thaw damage. Another positive effect is the enhanced surface temperature, which might prevent biological growth.

4.2.3 Drawbacks

The main focus until now has been the possible positive effects of changing surface properties. Unfortunately there are also some drawbacks, which shall be briefly mentioned here:

- Low emissivity coatings and/or high absorptivity can in the summer result in high surface temperatures. Because of thermal dilatation this might cause thermal stress, and ultimately deterioration of some materials.

- The most noticeable effect in changing surface properties was in the summer where the daytime heat flux towards the interior of the building could increase. In the summer this is not desirable, because this means extra heat gain for the building. The net effect might therefore be enhanced energy costs if the heat is removed by cooling systems.

- Hydrophobic treatments bear the risk of having large moisture differences in the same material very close to each other. This could result in hygric stress, similar to thermal stress, as moisture expansion might occur in one part of the material but not the other. Vasic (1997) has reported how siliconated roofing tiles were scaling due to moisture expansion. The tiles

were immersed in a water-based silicone solution immediately after firing to prevent two-sided efflorescence. The scaling started several months after the tiles were installed on roofs.

Despite the possible drawbacks and the discouraging simulations, the possible advantages in changing surface properties may outweigh the risks. Consequently, further investigations were planed on commercially available materials with changed surface properties. The plan was to investigate hydrophobic treatments as well as treatments which have changed the thermal properties. Roofing tiles with and without hydrophobic treatment were commercially available but unfortunately low emission paints were not. Maybe the latter is symptomatic as several paints, which were said to have these special properties, have been reported not to work, e.g. Stopp. et al. (2001).

5. EXPERIMENTS

Experimental work illustrates the difference in understanding *how* or *why* a phenomenon works, as discussed in Chapter 1. Experiments can therefore have two purposes:

- Phenomenological description (illustrating *how*)
- Test of a hypothesis (theories of *why*)

While a phenomenological description can include a high degree of complexity, simplicity is necessary when testing a hypothesis to make sure other phenomena do not become more important than the one in question.

Instead of trying to give a full phenomenological description the experiments in this work are more designed to test specific parts of a general hypothesis stating that it is possible to change the hygrothermal performance of a building envelope by changing the surface properties.

Throughout this chapter graphs showing comparisons between materials with and without a treatment, the results of the treated material is drawn in blue, the untreated in red.

5.1 Test material and site

As soiling can change acquired surface properties experiments should include test of self-cleaning properties. Unfortunately there is no standard accelerated testing of resistance to soiling (Eiselé et al. 1999). Probably due to difficulties in defining "standard" particles and "standard" soiling situations as stated in Section 3.3.1.3. Therefore these tests would have to be in real time and with natural exposure to nature.

Besides testing for self-cleaning properties, tests of hydrophobic properties and the effect of a coating with low infrared emissivity would have been of interest. Unfortunately no paint with low infrared emissivity was available and the experiments were therefore concentrated on self-cleaning and hydrophobic properties.

5.1.1 Material

When designing the experiment the first step was to choose appropriate test material, one with a self-cleaning and hydrophobic effect and one without, the main considerations were:

– To minimize the differences between the two test materials they had to be *similar* in any respect except for the treatment.

– The treatment had to be *well defined* to reduce differences due to application technique.

After considering different kinds of paints the idea of testing paints was abandoned because the composition of paints is very complex; there would not be one painting with self-cleaning and/or hydrophobic properties and the same painting without. The chemical composition of the paints would differ considerably and self-cleaning properties could be affected not only by protrusion at the surface but also by e.g. softener, extender and pigment volume. An extra obstacle would be gathering complete information of the chemical composition on commercially available paints; this would probably not have been possible.

5.1.1.1 Roofing Tiles

In spring 2001 roofing tiles with so-called Lotus Effect became commercially available. Ordinary roofing tiles from the same factory, with the same dimensions and almost the same colour were also available. According to the manufacture the tiles with and without Lotus Effect were similar, the only difference was, that the latter had received an extra treatment, which would give them their self-cleaning properties (Heidtmann, 2001). The treatment was supposedly applied under well-controlled conditions, ensuring a consistent level of quality. These two types of roofing tiles fulfilled the requirements listed above and were used for further investigations.

5.1.1.2 Surface treatment

According to the patent application (European Patent Office, 1998-b) roofing tiles with Lotus Effect were supposed to be self-cleaning and hydrophobic because they are dipped in a dispersion of inert powder particles in a siloxane solution.

There is no guarantee that the treatment stated in the patent application is the actual treatment used at the tiles in the experiments, therefore tests were performed on the surface composition, as described in Section 5.4.2.

5.1.2 Location and orientation

After choosing roofing tiles the actual placing of the set-up had to be decided:

- Soiling is very dependent of the <u>environment</u>; some urban areas have a large amount of particles in the air, which result in a fast discolouration of surfaces, and in some rural areas biological growth occur after short time. Areas with high particle content are rare in Denmark, most particles are due to traffic. Therefore an area close to heavy traffic would be preferable when validating how smudge from environmental pollution is repelled by a surface. The area with field experiments at BYG-DTU is situated 150 m from one of the most busy motor ways in Denmark, but at the same time surrounded by trees, which could enhance the chance of biological growth on the surface. The area was therefore considered to be very suitable as test site.

- Soiling varies with the <u>slope and orientation</u> of the surface; horizontal surfaces are more likely to soil than vertical surfaces, and the compass orientation is also important, as weather and light conditions change. Especially biological growth is known to be most common on north facing surfaces.

- The <u>colour</u> of the surface could have an effect on smudging; especially biological growth might be sensitive to the temperature of the surface. Roofing tiles with Lotus Effect were at that time only available in one colour - lotus-red – that was very similar to the ordinary red tiles, thermal differences in the tiles because of colour differences were expected to be small, but has been tested in Section 5.5. But an experiment of how major colour differences influence the soiling by comparing different pairs of tiles e.g. red and black, with and without lotus effect had to be omitted.

5.1.3 Set-up

As a result of the considerations listed above a set-up as shown as shown in Figure 5.1 was made at the test site at BYG-DTU.

Figure 5.1: The set-up at DTU. Tiles with Lotus Effect are placed at the eastern side of each roof. In this and the following pictures from the set-up are the tile types divided by a dashed line with an arrow facing north.

Four different set-ups as described above with different orientations:

1. Set-up with a 12° slope, facing south
2. Set-up with a 12° slope, facing north
3. Set-up with a 45° slope, facing south
4. Set-up with a 45° slope, facing north

The low slope of 12° was chosen as a minimum, because this was the lowest slope the manufacturer recommended in roofs with this tiling. A roof with a low slope <18° would require an underlay to be tight, but this was omitted in this case as water tightness was not required. A 45° slope was chosen as a "normal" slope of a pitched roof with tiles.

The backside of the tiles were subjected to the outdoor climate as the set-up did not include underlay, insulation or heating.

The set-up was inspired by a Danish standard for test of frost resistance of roofing tiles in which 3 rows of tiles with at least 3 tiles per row is tested (Danish Standard, 2000). In this case the number of tiles was 5 per row, this gave the opportunity to remove some of the tiles for destructive testing during the experiment.

The tiles were left at the test site for nearly 2½ years, visual inspections and different tests were conducted during this time.

5.2 Soiling

The set-ups described above were visually inspected during the test period. After one year a greenish layer became visible at some of the tiles, starting at the edges of the tiles, see Figure 5.2. The layer became more visible after longer exposure and spread from the edges. After more than two years some of the tiles were partly covered with a very conspicuous green layer.

As the layer became more visible it was possible to identify the layer as biological growth of algae, which was done by a biologist. Not all tiles were soiled in the same degree, there were differences depending on position and surface treatment.

5.2.1 Slope and orientation

Slope and orientation is expected to influence how a surface soil in different ways:

- The lower the slope, the faster environmental particles soil the surface.

- Direct sunlight has substantial influence on biological growth; sunlight inhibits biological growth at building surfaces, probably because of the higher surface temperature.

Figure 5.2: After 1 year a greenish layer became visible at the edges of north facing ordinary tiles (morning picture).

North facing tiles are only exposed to direct sunlight for short periods, and as illustrated at Figure 5.2 the light comes from an angle which means that there will always be shadow at some part of the tiles.

North facing tiles with steep slopes are even less exposed to direct sunlight than at low slopes, and soiling could therefore be less at low slopes, however, this contradicts the gravitational influence. From these simple considerations it is not possible to predict at which slope the most soiling (environmental dirt and biological growth in combination) is to be expected. However, soiling due to biological growth is more likely to appear during the relatively short test period of approximately 2½ years, than environmental dirt.

The hypothesis for this particular experiment is:

> *Soiling will be more abundant at north facing surfaces than south facing surfaces, and most noticeable at steep sloped roofs*

The result of more than two years exposure showed, that algae growth became first visible at the edges of north facing tiles with a steep slope, but soon also became visible at north facing tiles with low slope, this delay seem to continue throughout the test period. The soiling of south facing tiles was negligible at both slopes. The hypothesis was corroborated.

5.2.2 Lotus Effect contra ordinary tiles

As explained in Section 3.4.1.2 the lotus effect is a self-cleaning mechanism that in nature makes it possible for plants to stay clean, therefore the hypothesis for this experiment is:

> *Roofing tiles with Lotus Effect are self-cleaning; soiling will be washed off.*

If the tiles with Lotus Effect stayed clean, this could be due to the environment or the self-cleaning effect, therefore both tile types were necessary.

Biological growth was first seen at ordinary tiles but soon after it also became visible at tiles with Lotus Effect. During the period there seemed generally to be a delay of a few months in biological growth at tiles with Lotus Effect.

Figure 5.3: Soiling of north faced surfaces after 28 month. To the left in each picture are tiles with Lotus Effect, to the right ordinary tiles (separated through a dashed line). In the picture of low sloped roof (left-hand picture) the soiling forms a distinct stripe, while the overall impression is, that tiles with Lotus Effect soil, but at a somewhat slower rate than ordinary tiles.

The visible impression after more than two years was that at the north facing steep roof, the ordinary tiles were more soiled than the tiles with Lotus Effect. At the north facing low sloped roof the soiling on the tiles with Lotus Effect formed a pattern, which was not that distinct on the ordinary tiles, see Figure 5.3.

Visual inspections and interpretation of ordinary photographs will often be used in practise but are somewhat subjective. More objective measurements of colours are typically conducted with a colour meter, that describes the colours in a point by the three parameters L* (ligthness), a* (redness-greenness) and b* (yellowness-blueness) (Fassina et al. 1999). However, measurements of this kind only give information on the average colour in a spot of a certain size, which might be sufficient when analysing the colour of new paint, but does not give any information on how large a part of the surface has this colour or if the soiling is uniformly or clustered.

To test if another colour measurement could be more useful in describing soiling, experiments with light emitting diode technology (LED) were conducted. The advantage of the LED method is, that it provides information on the extent of the soiling and e.g. tendency to form clusters.

The principles in using multispectral LED measurements are as follows (Videometer, 2003):

– The sample to be analysed is placed in the device, e.g. the method can at the moment not be used in the field.

– A picture is taken with 9 different lightings, this results in 9 digital grey scale pictures each taken at a light with different wavelength.

– In this particular case the picture taken with wavelength = 630 µm was chosen as being the best to separate algae growth from background, an example is shown in Figure 5.4. A threshold value is determined and the pixels, in the grey scale picture, below the threshold resemble soiling.

– The number of pixels below the threshold value is a measurement for the extent of the soiling.

– By counting objects (e.g. clusters of pixels) and the size of the objects, information is gained on how the soiling is distributed, homogeneously or clustered.

The aim of the experiment was to test the method, not as much the results. Therefore only 16 samples were analysed, see Figure 5.5. New and old tiles were chosen to compare the difference. The soiled area is therefore the number of pixels below the threshold in the old sample minus the number of pixels below the threshold in the new sample.
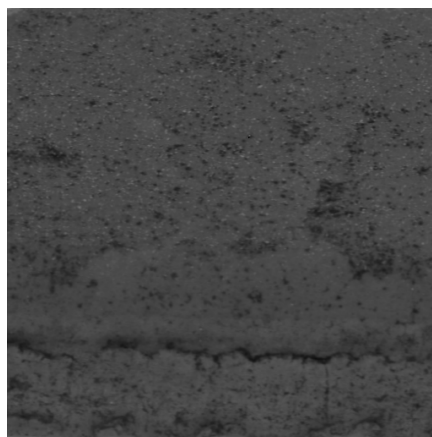
Figure 5.4: Example of LED picture taken with wavelength 630 µm. The picture show sample 1 (see Figure 5.5) of an old tile with Lotus Effect. The investigation was performed at Videometer A/S.

Top edge

Flat area

Rounded
area

Bottom edge
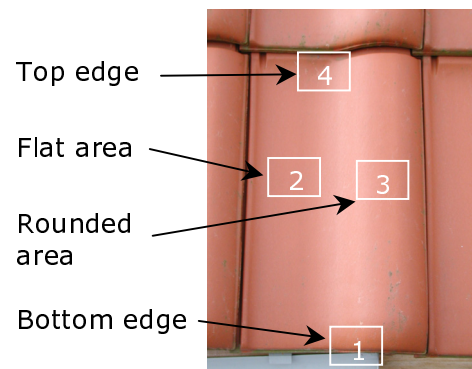
Four tiles:

N- New tile, ordinary

N+ New tile with lotus effect

O- Old tile, ordinary

O+ Old tile with lotus effect

Figure 5.5:   Areas chosen for soiling analysis on four different tiles.
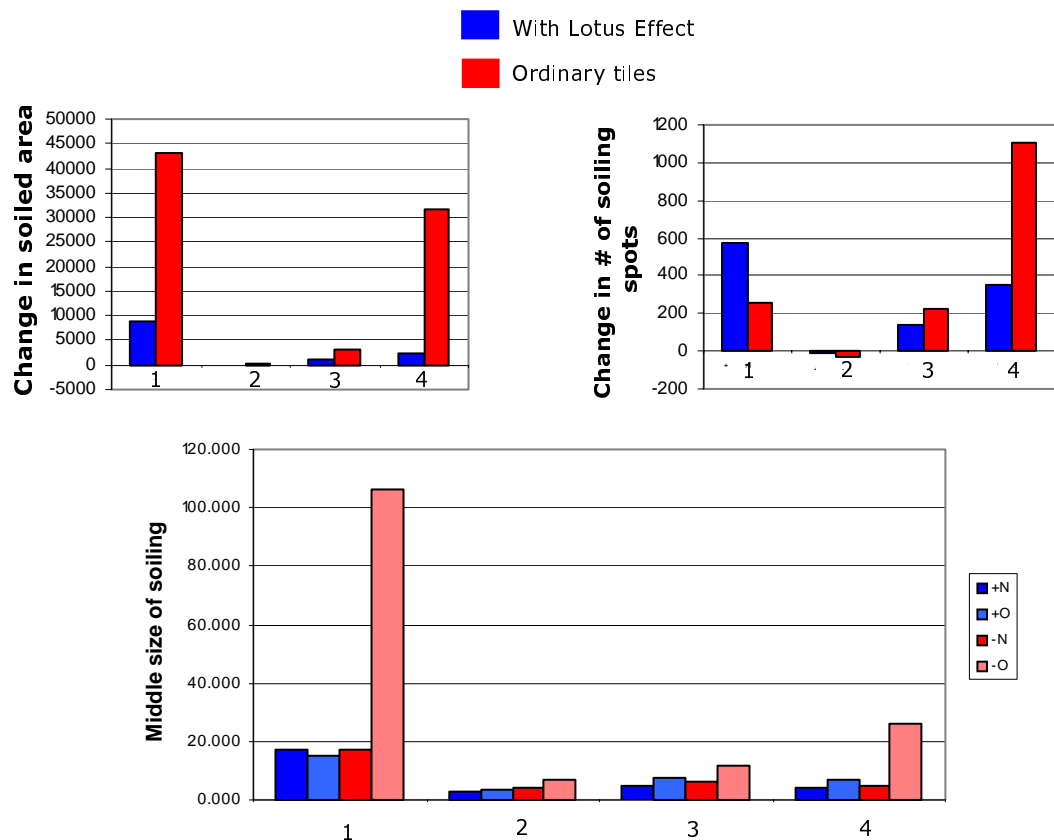
Figure 5.6:   Results of soiling measurements with LED technique.

The result of the analysis is showed in Figure 5.6. Although some of the results seem odd (e.g. negative change in sample #2) the results can be summarized as:

- The ordinary tiles are more soiled than the tiles with Lotus Effect

- The most soiled areas are at the edges, mostly at the bottom

  − The number of soiling spots increases in the most soiled areas. At the bottom edge the increase is relatively small probably due to the very large size of the spots. The algae seem to grow together

These results are based on only one observation in each tile and can therefore not be used to evaluate soiling behaviour, but they indicate, that the used method might be useful. If the results are analysed anyway, the difference between the two tile types seems to be larger than pure visual inspections indicated. When the tiles were removed for testing, the overall impression was, that the ordinary tiles were only slightly more soiled than the Lotus tiles. Nevertheless, a month later the difference at the remaining tiles were much more noticeable. The measurements revealed soiling that was not visible to the naked eye at that time.

5.3 Wetting

The tiles with Lotus Effect are supposed to have a combination of self-cleaning properties and a hydrophobic treatment. The set-up described in Section 5.1.3 could therefore also be used to investigate the wetting properties of the different tiles as a phenomenon. Investigations in Section 5.4 is an attempt to enlighten *why* these differences occur.

5.3.1 Water run-off

The hypothesis for this experiment was:

> *At tiles with a hydrophobic surface there is no capillary suction, rain will be repelled and run off as droplets and have little contact time with the tiles. When exposed to rain this means that more water will run off tiles with a hydrophobic treatment than off ordinary tiles.*

To test this hypothesis the set-up described in Section 5.1.3 was supplemented by gutters placed under each of the eight set-ups. The gutters, which all had the same length were carefully placed under the three tiles in the middle of each set-up to avoid boundary effects. The amount of water that ran off the test tiles was registered by weighing the plastic containers in which the water was collected from the gutters. How often the containers were weighed depended on the weather; often in periods with heavy rain, and more seldom in drier periods. Figure 5.7 is a photograph of the set-up.

Figure 5.7   The set-up used for soiling and wetting tests. For the soiling and water run-off tests three rows with 5 tiles with and 5 tiles without Lotus Effect were placed in different slopes (12° and 45°) and two orientations (north and south). Gutters were placed under the central tiles in each set-up, and the water was collected in plastic containers, here hidden by metallic sunscreens. Tiles for weighing were placed at the same frames and can be seen in the back as two rows of 4 individually tiles.

The results of the measurements can be seen at where the difference in water run-off from the different surfaces is calculated as:

$$\Delta m = \frac{m_{lotus} - m_{ordinary}}{m_{ordinary}} \cdot 100\%$$
(5.1)

Where m = mass off water that have run off the surface with the given subscript, subscript lotus and ordinary means surface with or without Lotus Effect respectively.

Table 5.1 shows that generally the difference in run-offs is negative (the difference was only once positive), i.e. more water runs off the ordinary tiles than the ones with Lotus Effect. Slope and orientation have only small influence (difference increase slightly with slope and the difference is smaller at the north faced roofs than the south faced), however, the weather conditions were of importance; in heavy rain the differences were small (about 2 %), but after a long period with almost dry weather and only occasionally light showers the differences were considerably higher (about 10 %).

	North low	North steep	South low	South steep
Average (%)	-3.26	-4.56	-4.03	-4.18
Minimum (%)	-10.37	-13.94	-10.34	-12.88
Maximum (%)	-0.55	-1.18	0.07	-1.02
Standard deviation	2.06	3.11	2.23	2.93

Table 5.1: Differences in water run-off in percent. A negative difference means that more water runs off the ordinary tiles than the treated tiles.

The result does not corroborate the hypothesis, in stead it shows the opposite tendency: Less water runs off tiles with Lotus Effect.

5.3.2 Water up-take

Hydrophobic treatments should prevent water uptake, but when less rain runs off tiles with Lotus Effect than ordinary tiles it raises the question of where does the rain go. The next experiment was designed to test the following hypothesis:

When exposed to rain, tiles with a hydrophobic treatment will take up less water than ordinary tiles.

The tiles in the set-up described in Section 5.1.3 were not to be touched, as they were left exposed to natural conditions for soiling. Therefore a water up-take test had to be performed at some other tiles. The set-up was extended with four individually mounted tiles of each type in each direction and slope, a total of 2x4x4=32 tiles. The extended set-up is shown in Figure 5.7, where the individually mounted tiles are seen in the back.

For nearly 5 month (from July to end November 2002) the tiles were weighed almost daily to register water up-take and drying when the tiles are exposed to natural weather conditions. Figure 5.8 shows the result of the weighing. The experiment was repeated one week in February and again one week in July the following year to determine whether frost or aging made any difference.

There were only small differences in the water uptake from the different positions. Figure 5.8 shows therefore the water uptake as an average of all ordinary tiles and all tiles with Lotus Effect respectively. The weight of the dry tiles are in average: Lotus tiles: 2.800 kg and ordinary tiles 2.980 kg. This means that during the summer, heavy rain results in 5-6% weight increase in tiles with Lotus Effect and 0.5-1% increase in ordinary tiles.
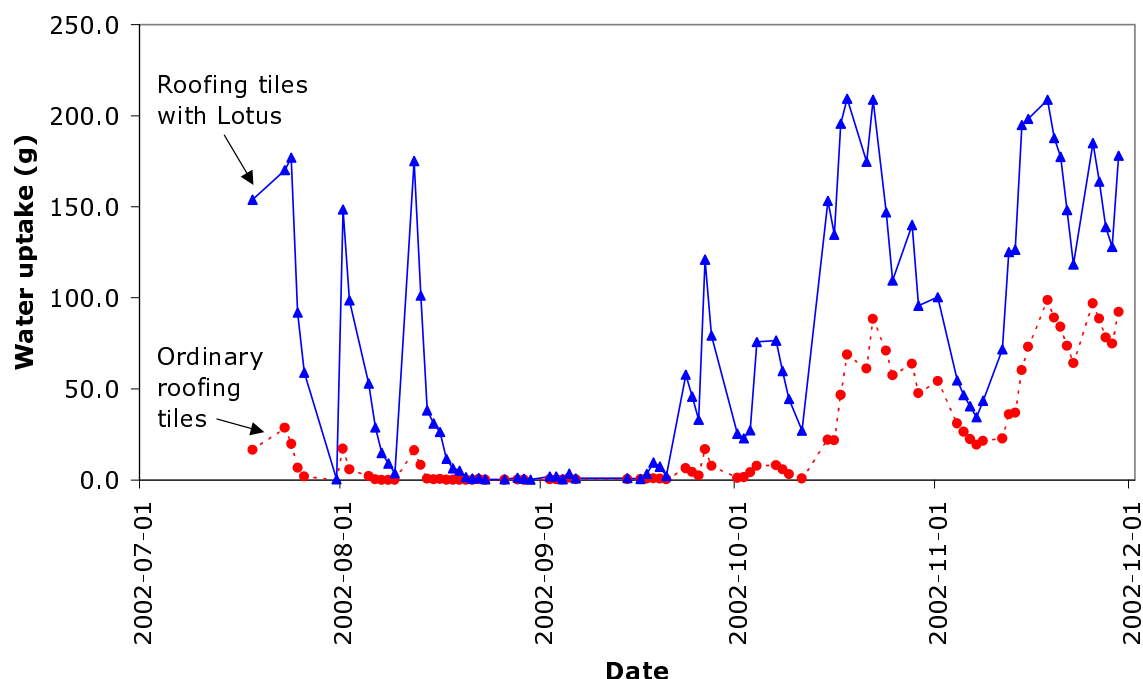
Figure 5.8: Water uptake in tiles exposed to natural weather, the two lines represent the average of the tiles in four different positions, a total of 16 tiles.

In the late autum where longer periods with rain may occur, and the tiles do not dry out between showers, the difference in the two tile types is smaller but still distinct; tiles with Lotus Effect take up about 7.5 %, and ordinary tiles up to 3.9% of their weight. Frost or aging did not change this.

The experiment does not corroborate the hypothesis. Instead tiles with Lotus Effect take up more water from the rain than ordinary tiles. This corresponds with the findings of the water run-off tests, the water that does not run off the tiles with Lotus Effect is instead absorbed by the tiles.

5.3.3 Freeze-thaw test

Apparently the water uptake in tiles with Lotus Effect is considerably higher than in ordinary tiles. Too high water content in porous materials exposed to natural weather might cause frost damage. The next experiment was performed to test if there is any difference in the frost resistance of the two tile types. The hypothesis for this experiment is:

There is a higher risk of frost damage in tiles with Lotus Effect than in ordinary tiles.

To test the hypothesis four tiles of each type were mounted vertically in one row and subjected to an accelerated frost resistance test consisting of 168 cycles each with duration of 6 hours, the cycle is described in Figure 5.9. The test was performed at Danish Building and Urban Research.

After the test neither of the tile types showed any of the damage types described in the Danish Standard DS/EN 539-2 for test of frost resistance of clay roofing tiles (Danish Standard, 2000); no additional cracks, scaling or other surface damage was visible after the test. However, there was a slight weight loss in tiles with a surface treatment; the tiles lost 8 − 10 g each, while the ordinary had a weight difference of less than 0.5 g.

This test did not show any risk of frost-thaw damage in the tiles with Lotus Effect and could therefore not corroborate the hypothesis.
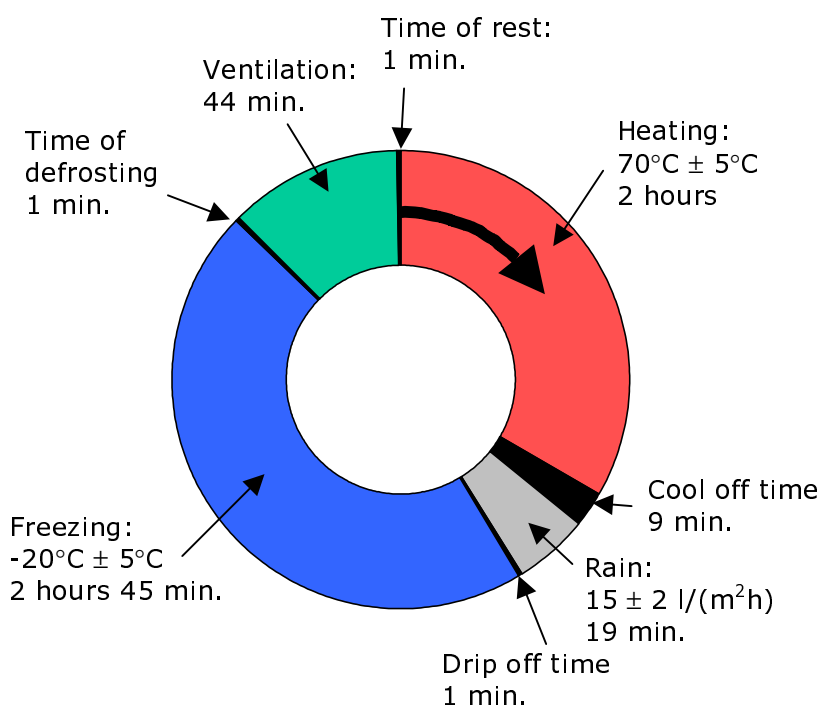
Figure 5.9:   Test of frost resistance. Description of one 6-hour cycle. The tiles were subjected to 168 cycles.

5.4 Material properties

After having tested the tiles on a phenomenological basis deeper examinations became necessary to explain the observed behaviour. The investigations have been divided in: test of the bulk material, and tests of the surface treatment.

5.4.1 Bulk material

If the bulk material in the two tile types is not identical, a comparison of the behaviour of the two tile types is not relevant, as it is not necessarily a result of the surface treatment. Porosity, pore size and chemical composition are the major factors in how the bulk material absorbs moisture. The investigations were therefore concentrated on these factors.

5.4.1.1 Porosity

Six specimens, 5 x 5 cm, cut out of each tile type, were used for the test of differences in porosity. The hypothesis was:

> *The bulk material in the two tile types is similar; therefore there will be no difference in porosity of the two types.*

The specimens were placed in an empty desiccator and the air was evacuated, after three hours water was let into the desiccator, the specimens were left in the water first with low pressure later with atmospheric pressure for a day. The specimens were weighed under water and, after being wiped off with a moist cloth, weighed in air. Afterwards the specimens were dried at 105 °C until constant weight.

The porosity was calculated by the equation:

$$p_{open} = \frac{m_{ssd} - m_{dry}}{m_{ssd} - m_{sw}} \qquad (5.2)$$

Where:

p_{open} = open porosity

m_{ssd} = mass of specimen in saturated dry surface condition

m_{dry} = mass of dried specimen

m_{sw} = mass of specimen, weighed under water
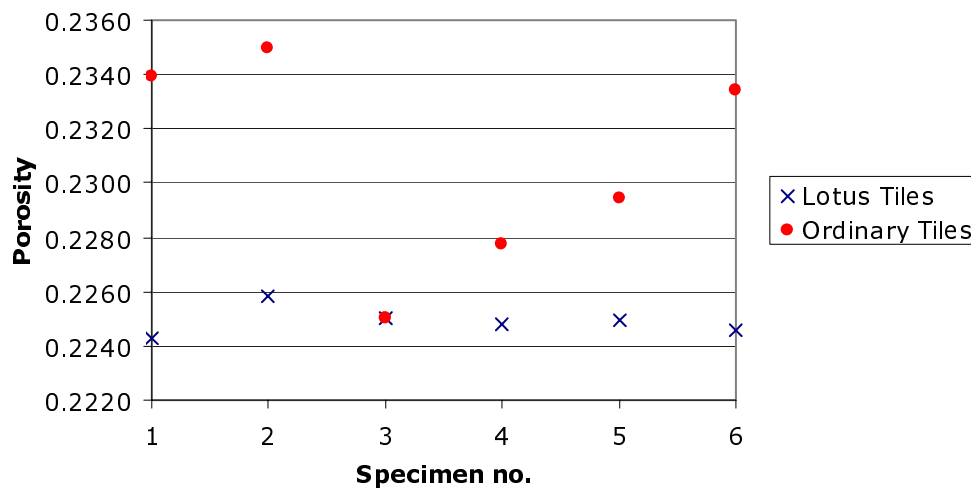
Figure 5.10: Porosity measured in six specimens with Lotus Effect and six ordinary specimens.

	Lotus tiles	Ordinary tiles
Average	0.2249	0.2308
Minimum	0.2243	0.2250
Maximum	0.2258	0.2349
Standard deviation	0.0005	0.0036

Table 5.2:   Statistical information on the measurements shown in Figure 5.10

The result of the measurements are shown in Figure 5.10 and Table 5.2. It shows that there is only a small difference in the average porosity but a larger difference in standard deviation. A statistic analysis shows that on a 5 % confidence level there is no significant difference between the two porosities. The hypothesis of the two bulk materials having the same porosity cannot be rejected.

5.4.1.2 Pore size distribution

Two materials having the same porosity do not ensure the same capillary behaviour; the pore size distribution is significant for this. Three experiments were conducted to test the following hypothesis:

The pore size distribution in the two tile types is similar.

The experiments are:

- Capillary suction from a free water surface

- Capillary moisture transport between two materials in a sealed bag

- Pore size distribution obtained by measurements with pressure plate membrane

Capillary suction

Six specimens of each tile type were sealed on four sides and placed upside down at supports in a tray filled with water to approximately 3 mm above the suction surface. The water uptake in the specimens was measured after 1, 2, 4, 8, 16, 32, 64, 128, 256 and 512 minutes. The results are shown such that the square of the water uptake per suction area (Q) is drawn as a function of time.

The water seems to rise slightly faster in tiles with Lotus Effect than in ordinary tiles, and the total water uptake is also higher. Statistical analyses show that the hypothesis of similar straight lines for the two tile types in the areas 0-100 min. and 100-512 min. can be accepted on a 5% level.
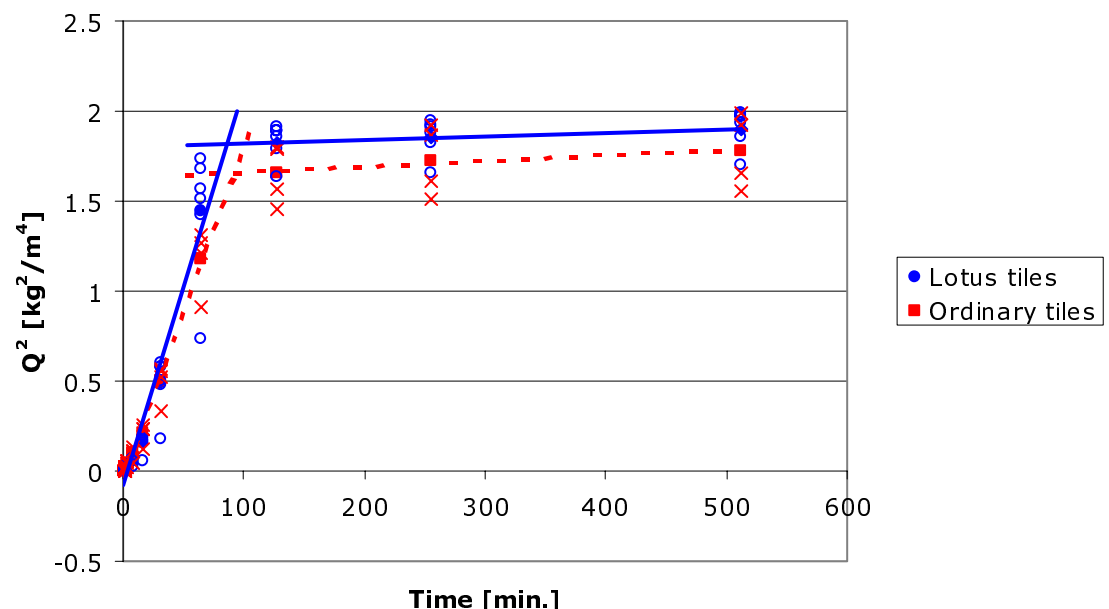
Figure 5.11: Measurements (open symbols) and average (filled symbols) of the square of the water uptake per suction surface as a function of time. The results are a combination of two straight lines. The curve breaks show at what time the waterfront reach the top of the specimens.

Sealed bag

If the pore size distribution in the two materials is similar, and the two materials are placed in a sealed bag, then after some time their moisture equilibrium will be the same, independently of their moisture content in the beginning of the experiment. Only hysteresis effects might blur this, but depending on how the experiment is planned, this effect can be cancelled out. The experiment was conducted at the hygroscopic level and above.

Five specimens (approximately 80 x 80 mm) of each tile type were placed in a climate chamber with 85 % RH until equilibrium. Hereafter all 10 specimens were weighed and placed in a sealed bag and stored at constant temperature. After three weeks, when the specimens were expected to have reached their equilibrium again the specimens were weighed. If there had been a change in moisture content between the two types of tile, the pore size distribution was different.

The first experiment showed, that all specimen lost weight, but the treated tiles lost more than the others. As the total weight loss only could be explained by a leak in the bag, the experiment was repeated. This time there was no pattern in weight loss and gain, which all were very small.

As the hygroscopic level did not show any differences the experiment was changed to involve capillary moisture transport. To make sure that there could be maximum contact between the specimens in the next experiment the backside of the specimens were grinded and cut in half. One half of each original specimen were placed in water until capillary saturation, the other half was dried at 103°C until no further weight loss. Ten pairs were formed: five with wet Lotus specimens and dry ordinary specimens and five with the opposite. To improve the contact between the specimens 2 ml of water was placed at the wet backside before the two specimens were united back to back. The pair was hold together by a rubber band and placed in a bag that was sealed. After three weeks the specimen were weighed separately.

To evaluate a probable effect of hysteresis the experiment was repeated. Again one half of the original specimen was placed in water the other in the oven. This time the pairs were formed by the two halves of the original specimen, i.e. the same material.
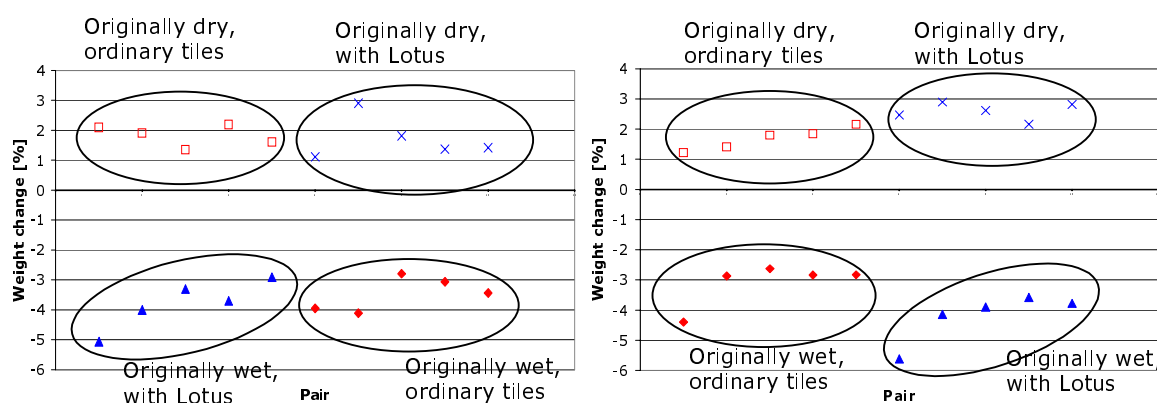
Figure 5.12: Capillary moisture transport between wet and dry specimens in a sealed bag. Left: pairs with materials from different tile types. Right: pairs with the same material.

The results can be seen in Figure 5.13. There is no difference in behaviour whether the pairs are formed by materials from two different tile types, or from the same tile. This experiment corroborate the hypothesis of similar pore size distribution. However there are many possible errors in the method; the contact between the two parts of the pairs were often doubtful, water droplets were formed at the inside of the bag in a way that none of the specimen were in direct contact with it. The experiment was easy to conduct and had it revealed differences, it could have been useful. But as it is, the experiment corroborates the hypothesis but is not a very strong indication of anything.

<u>Pressure plate method</u>

A more precise measurement of the pore size distribution was obtained by using pressure plate measurements as described in the nordtest method NT Build 481 (nordtest 1997). Basically the method relies on the pore water pressure to determine the size of a meniscus in a pore as given in Equation (2.1), i.e. by increasing the pressure, water is pressed out of the small pores. By gradually increasing the pressure and measuring the water that was pressed out in each step, the volume of pores in a given size range can be determined. The principle of the method is as follows:

1. Ten vacuum saturated specimens of each tile type were weighed and placed in a pressure vessel as shown in Figure 5.13. To insure a good capillary contact between specimen and plate, the plate was covered with kaolin in

which the specimens were pressed. A cloth was placed between the kaolin and the specimen to prevent the kaolin from adhering to the specimen.

2. A low pressure (0.03 bar) was applied to the vessel and water pressed out of the specimens. When the water flow stopped (no additional water for two days) the specimens were weighed and returned to the vessel.

3. Step 2 was repeated with different pressures (0.05, 0.1, 0.3, 0.5, 1.0, 3.0, 5.0, 10, and 30 bar), the number of specimens was reduced to four of each type in the last measurement.

The results of this experiment are shown at Figure 5.14. Although the values measured in tile with Lotus Effect vary more than values of tiles without Lotus Effect, the tendency is that ordinary tiles have larger pores than treated tiles. The two curves cross each other, explaining why the two materials seem to have the same porosity but different pore size distribution.

The hypothesis is not corroborated.
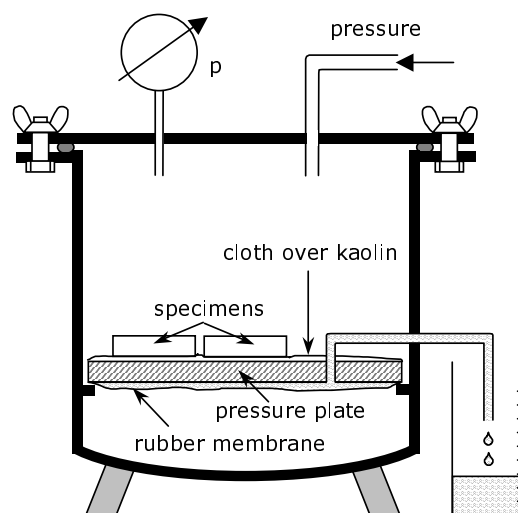
Figure 5.13   Pressure vessel. Pressure is applied to the vessel and water from pores larger than the corresponding size is pressed out of the specimens. Because of the capillary contact, ensured by the kaolin, the water is collected and led out of the vessel. Equilibrium is achieved when the moisture outflow is less than 0.05 cm^3 in 48 hours. Afterwards the specimens were weighed, returned to the vessel and the experiment continued at a higher pressure. (Figure inspired by Krus & Kießl 1998)

Pore size distribution
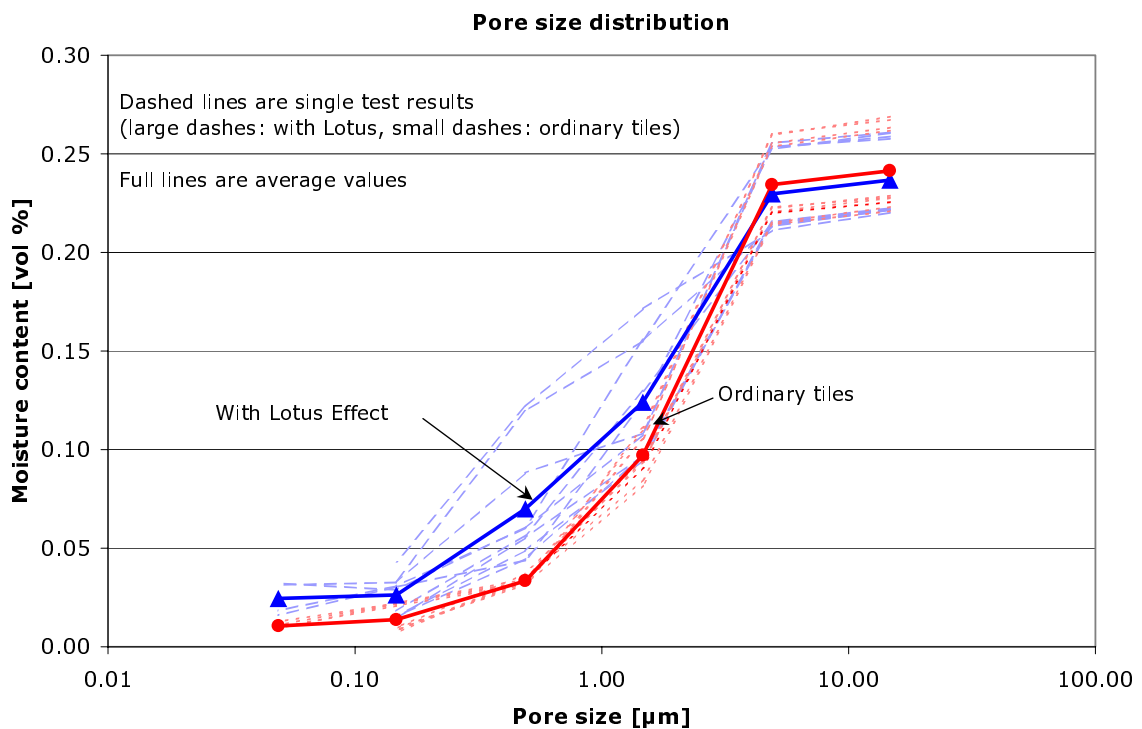
Figure 5.14: Pore size distribution obtained by pressure plate measurements. The curves are not identical; tiles with Lotus Effect vary more than untreated tiles. Generally ordinary tiles have larger pores than tiles with Lotus Effect.

5.4.2 Surface treatment

The theoretical Chapters 2 and 3 deal with the potential influence of a materials surface for the hygrothermal performance of the whole material (surface + bulk material) and the soiling of the surface. To evaluate the possibilities in treating tiles with Lotus Effect as much knowledge as possible of the surface treatment must be obtained. The treatment is described in the patent application EP 0909 747 A1 (European Patent Office, 1998-b) with the following characteristics:

- The treatment consists of a dispersion of powder of an inert material with particles with a size from 5 to 100 µm, preferably from10 to 30 µm, in a siloxane solution.

- The treatment is applied by immersion.

- The powder is of ceramic origin e.g. clay.

- The siloxane is from the heteropolysiloxane group.

Experiments were conducted to analyse if these properties are true and gather further information on the surface treatment e.g. how thick the layer was and if and how it changes over time.

5.4.2.1 XPS

For chemical analysis of a surface the XPS method (**X**-ray induced **P**hotoemission **S**pectroscopy) is well suited because it can be used without preparing the surface in any way and therefore exclude preparation as a source of error, which can be critical in a chemical analysis of an unknown substance. Furthermore, the method is very surface sensitive; the detected photoelectrons come from a depth of up to ca. 5-10 nm (Rehwinkel et. al. 2000).

The hypothesis was:

> *It is possible to detect and determine the chemical composition of the surface treatment on tiles with Lotus Effect by using XPS.*

XPS was used at a surface of an ordinary tile and one with Lotus Effect, the results of the XPS measurement is shown in Figure 5.15. The investigations were performed at the Interdisciplinary Research Centre for Catalysis (ICAT) at DTU. The measurements were conducted at two tile samples, and although the test was conducted twice at different places on the samples at areas in nm size, the experiments should have been conducted at samples from several tiles to be truly representative.
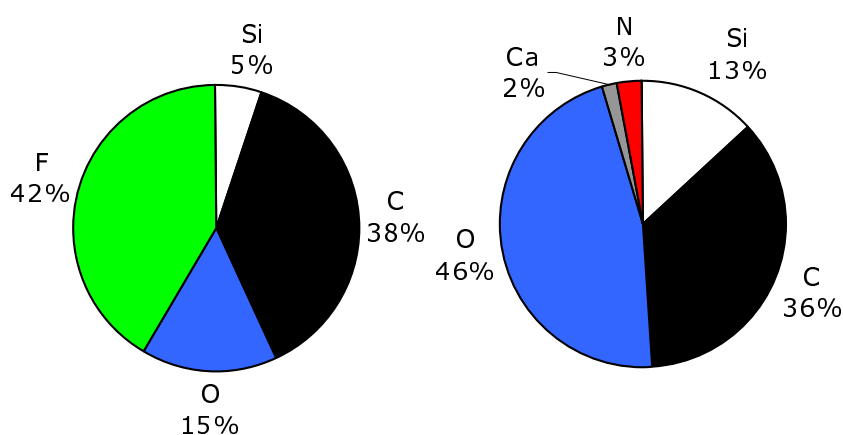
Figure 5.15: Chemical composition of surface determined with XPS. Tile with surface treatment (Lotus Effect) to the left, ordinary tile to the right.

If a surface treatment mainly containing siloxane was used to create the Lotus Effect, one would expect higher silicon content at the surface of the Lotus tile than at the surface of an ordinary tile. Instead of silicone a very high content of fluorine was detected, this indicates that not siloxane but a fluorinated polymer like e.g. Teflon was used to create a hydrophobic surface.

Although the outcome of the XPS analyse was not as expected, the method seemed useful in determining the chemical composition of the surface. The hypothesis is therefore corroborated.

5.4.2.2 SEM analysis

While XPS analysis operates on a nano scale, SEM analysis (Scanning Electron Microscope) operates in µm. Combined with EDX (Energy Dispersive x-ray spectrometer) SEM analysis can also provide the chemical composition of a surface. The drawbacks and advantages of this method compared to XPS are:

- Samples must be prepared for the analysis. To make the surface electrically conducting a thin layer of gold or carbon has to be applied to the surface.

- EDX analysis must be performed at a ground plane surface.

- SEM images show the topography of the surface.

The hypothesis in using SEM analysis, as a supplement to the XPS analysis, was threefold:

- *SEM images will show differences in the topography of the surface of the two tile types.*

- *SEM used at fragments can show the penetration depth of the treatment*

- *SEM combined with EDX can show the chemical composition and how it changes through a sample when performed at a ground plane cross section.*

For SEM analysis samples four different sample types were prepared; the two tile types both as new tiles and as tiles that had been exposed to natural weather for 21 months. The SEM analysis was performed at The Department of Manufacturing Engineering and Management (IPL), DTU.

Topography

In Figure 5.16 the topography of the different samples are shown in different enlargements. There seems to be a difference in the images of the two tile types, but the topography of the surfaces does not change noticeably after 20 month of natural weathering. The surface of ordinary tiles seems to be very smooth, while the Lotus Effect provides the tiles with protrusions in the size of 10 − 30 μm, like described in the patent.

New tiles, Lotus Effect

New tiles, ordinary

Old tiles, Lotus Effect

Old tiles, Ordinary

Bar equals

100 μm   20 μm   5 μm
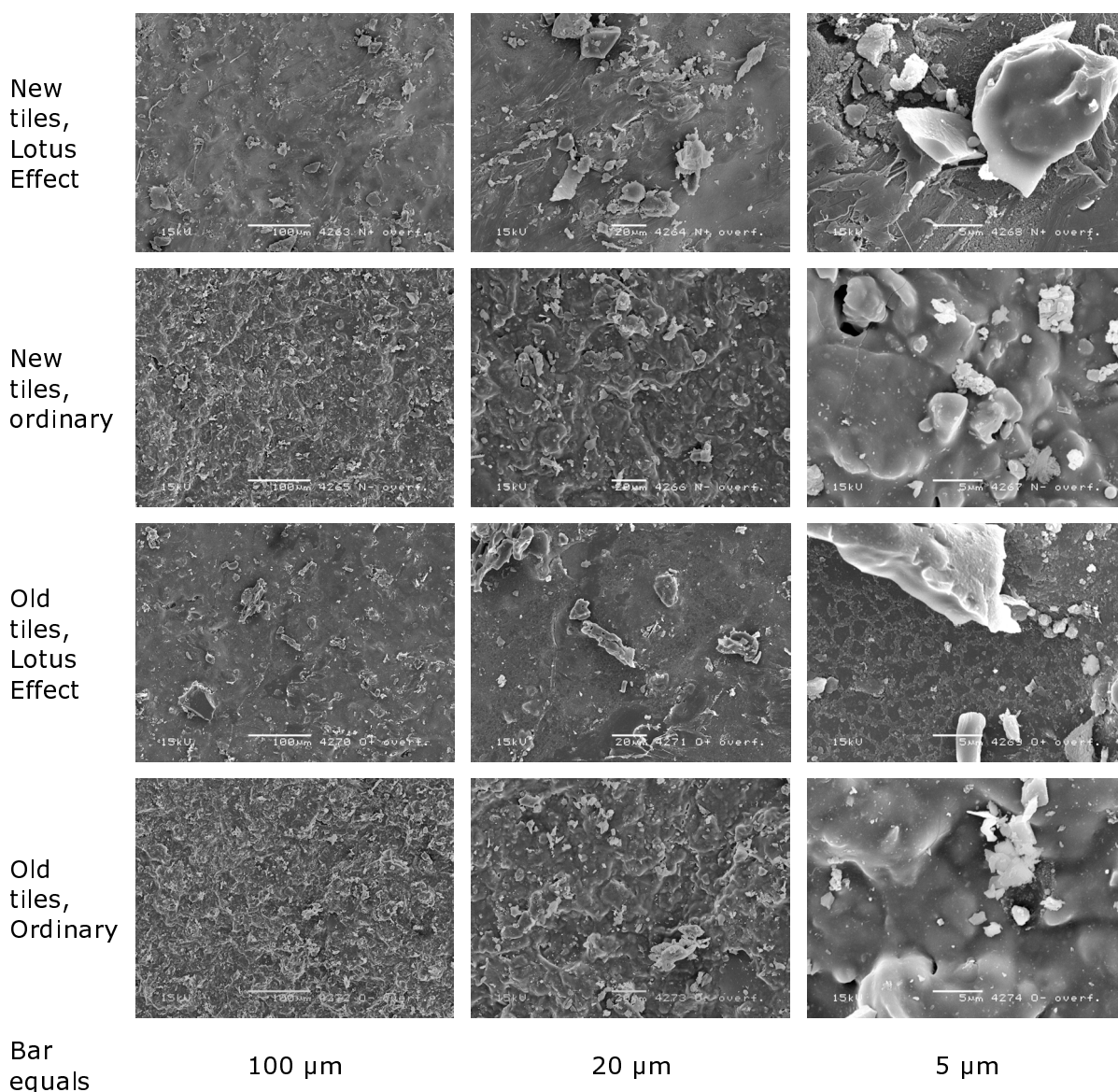
Figure 5.16: SEM images of surfaces of new tiles with and without surface treatment, new tiles and old tiles i.e. exposed to natural weather for 20 month. The surfaces are shown in three different enlargements but not necessarily at the same spot.

Penetration depth

The most common method to determine the penetration depth of a hydrophobic treatment is to spray water at a fracture of the material and observe where the water is repelled; this corresponds to the penetration depth (Besien et al. 2003). However, in tiles with Lotus Effect this simple method was not useful as no difference in water uptake over the cross section was visible to the naked eye, probably because the penetration depth is very small. Alvarez & Fort (2001) have used SEM to describe penetration depths of water-repellent agents on limestone, although some of their SEM images are difficult to interpret, the method seems to be useful. SEM images of cross sections near the upper surface of tiles with Lotus Effect and ordinary tiles are shown in Figure 5.17. If a surface treatment is visible at Figure 5.17, the penetration depth is approximately 10-15 µm.
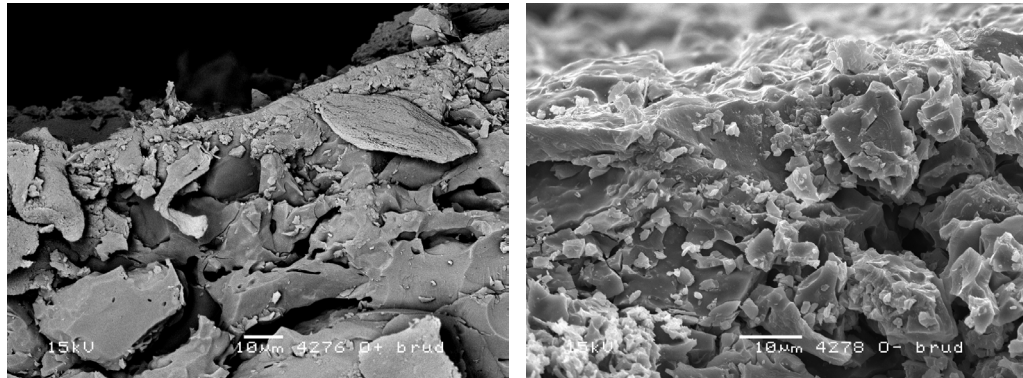
Figure 5.17: SEM images of tile with Lotus Effect (left) and ordinary tile (right). Bars equals 10 µm. Both tiles have been exposed to natural weather for 20 month.
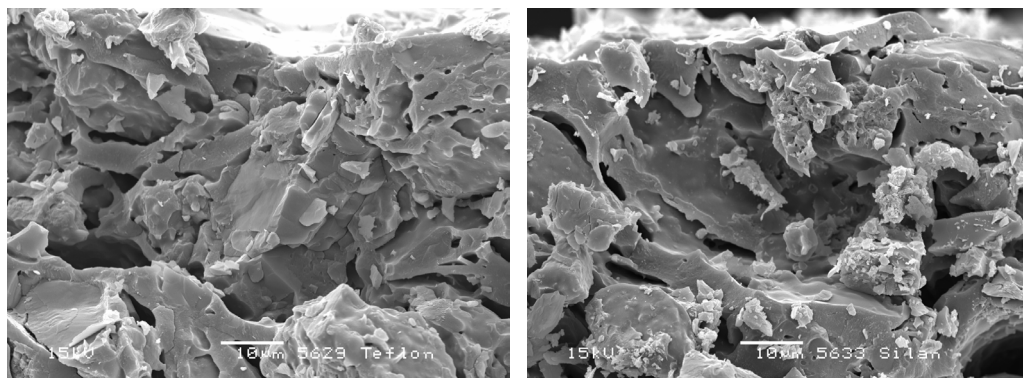
Figure 5.18: SEM pictures of two ordinary tiles with different hydrophobic treatment. Left "Teflon", Right "Dynasylan". None of them differ noticeable from Figure 5.17; SEM is not useful in determining penetration depths of hydrophobic treatments in roofing tiles. Bars equals 10 µm.

However, Figure 5.17 is not very convincing as a proof of a surface treatment. This leads to the conclusion that either there is no surface treatment to be seen, because the layer is very thin, or the method is not suited for this use. To rule out the first possibility two halves of an ordinary tile were treated with different kinds of hydrophobic treatment one labelled "Teflon" and one "Dynasylan", a silane product. Both halves were treated similarly: the hydrophobic agent was applied by brush until the surface stayed wet for longer time. 24 hours later the treatment was repeated. The amount of active agent was difficult to determine because e.g. the Dynasylan was said to be without solvent but had considerable weight loss upon drying. The estimated amount of active agent was 200 g/m^2.

SEM pictures similar to those in Figure 5.17 were taken, these can be seen in Figure 5.18. The images do not differ notably; no surface treatment is visible in any of the pictures. The conclusion must be, that SEM is not useful in determining penetration depths in roofing tiles.

Chemical composition

Although SEM pictures were not suited to determine penetration depths, this does not mean, that there was no hydrophobic treatment. The combination of SEM and EDX might reveal a penetration depth because of the chemical composition. Thus ground plane cross sections of the two tile types were prepared for EDX analysis. To avoid dissolution of e.g. salts during the preparation the samples were prepared in 98% alcohol. SEM images and corresponding chemical analysis are shown in Figure 5.19.

A few more minerals could be found at other places but the shown chemical composition is typical for the two tile types. Although the SEM image of a tile with Lotus Effect was taken at a point, where the surface-near area seems to be denser than the bulk material, the chemical analysis does not show any difference in composition, and there are no traces of fluorine. The results do not correspond with the findings of the XPS analysis. Apparently there is no enrichment of Silicon either. The EDX analysis does not reveal anything about the penetration depth.

The tile samples treated with "Teflon" and "Dynasylan" were polished as preparation for EDX analysis. During this process it became clear, that the preparation itself destroyed any possible surface layer. An EDX analysis was

therefore omitted. Preparation damages however could not explain the SEM pictures of fractured surfaces, as the only preparation in these cases is applying thin layer of gold, the surfaces are otherwise not touched.
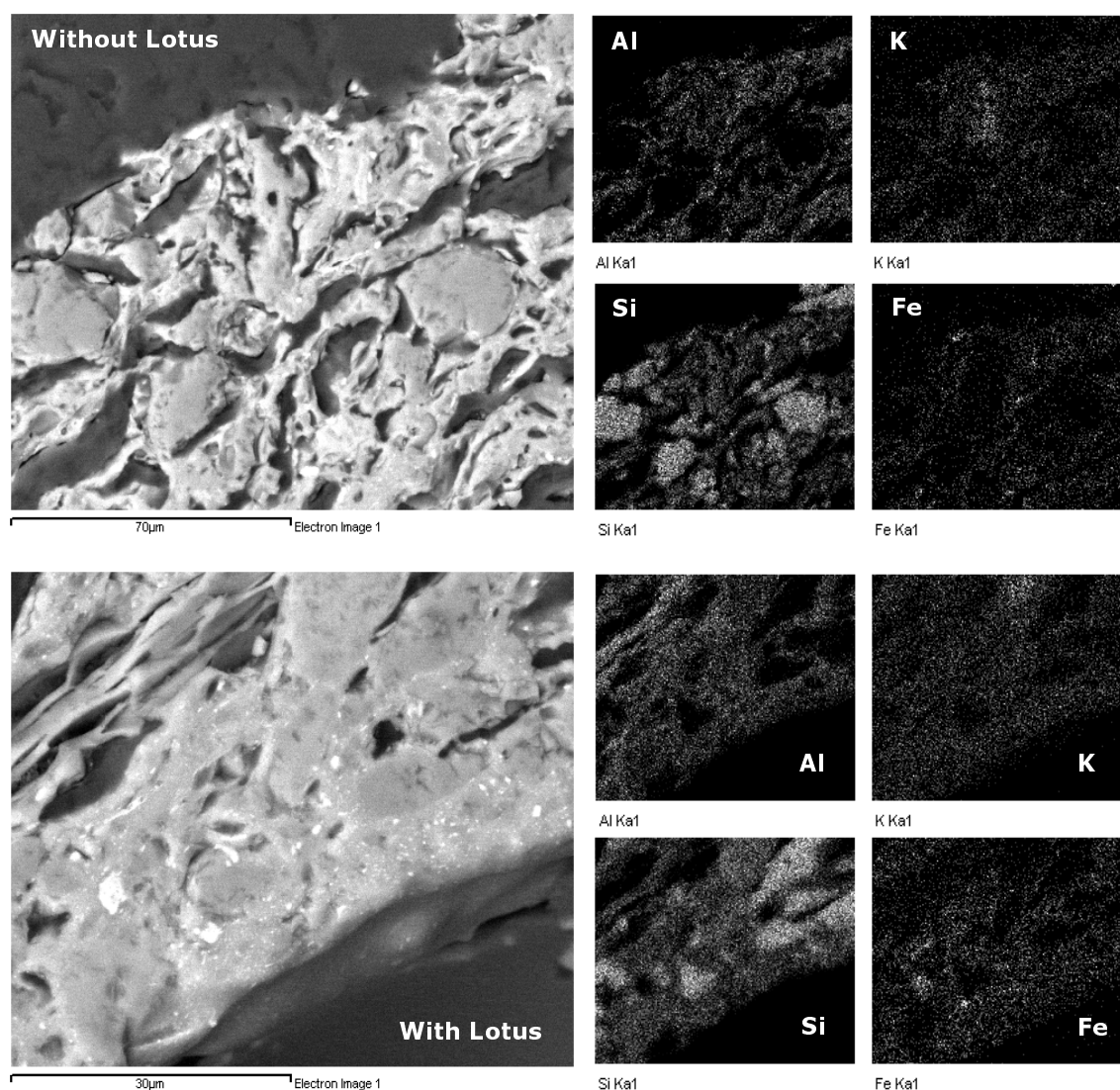
Figure 5.19: SEM image and EDX analysis of a cross section near the surface. Top: ordinary tile, Bottom: tile with Lotus Effect. Notice that the scale is different (top: 70 μm, bottom 30 μm) but it does not change the result: A surface treatment is not recognisable from the chemical composition as determined by EDX. Before this investigation both tiles were subjected to the frost test described in Section 5.3.3.

The hypothesis of how SEM analysis can be useful in this is only partly corroborated:

- SEM images show the topography of the surfaces, there is a notable difference in the two surfaces. Single protrusions with a diameter of approximately 20 µm are visible at the tiles with Lotus Effect in Figure 5.16.

- Determination of penetration depths based on SEM images is difficult. In this case there was no convincing signs of surface treatments even when one with a supposedly detectable thickness was applied.

- A chemical analysis with EDX does not show any differences throughout the material.

5.4.2.3 Water vapour transmission properties

The surface treatment used for creating the Lotus Effect does not seal off the surface. The aim was to make the surface water repellent but to allow water vapour transmission through the surface. As described in Section 2.3.3.3 a water repellent treatment can affect the water vapour transmission properties, as the finer pores might be clocked by the treatment.

The hypothesis to be tested was:

> *The water vapour transmission properties of the roofing tiles are not affected by the surface treatment.*

To test this six specimens of each tile type were tested in a wet cup according to the European Standard EN ISO 12572 (CEN 2001) for determination of water vapour transmission properties. In the test the amount of water that is transported by diffusion through the specimen is measured over time. The temperature is held constant and the relative humidity is constant but different above and below the specimen. The principle of the method is shown in Figure 5.20. The wet cup was chosen because the main interest is how the surface treatment influences the drying out possibilities of the tiles.
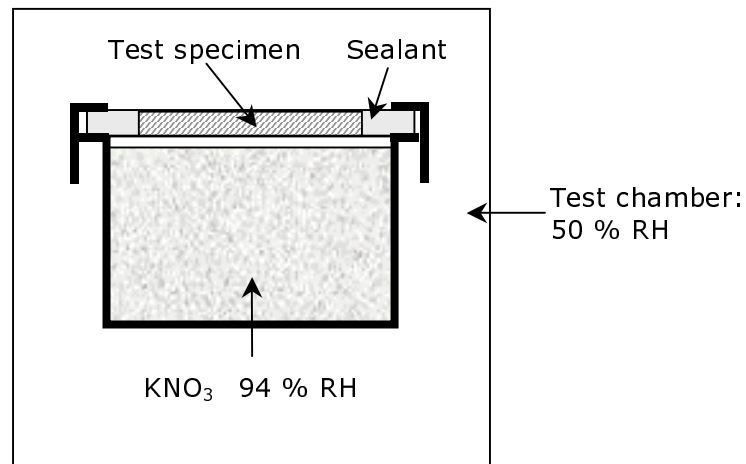
Figure 5.20: Schematic plan of test cup. The relative humidity in the test chamber is 50 %, in the cup RH = 94 % above an aqueous solution of potassium nitrate.
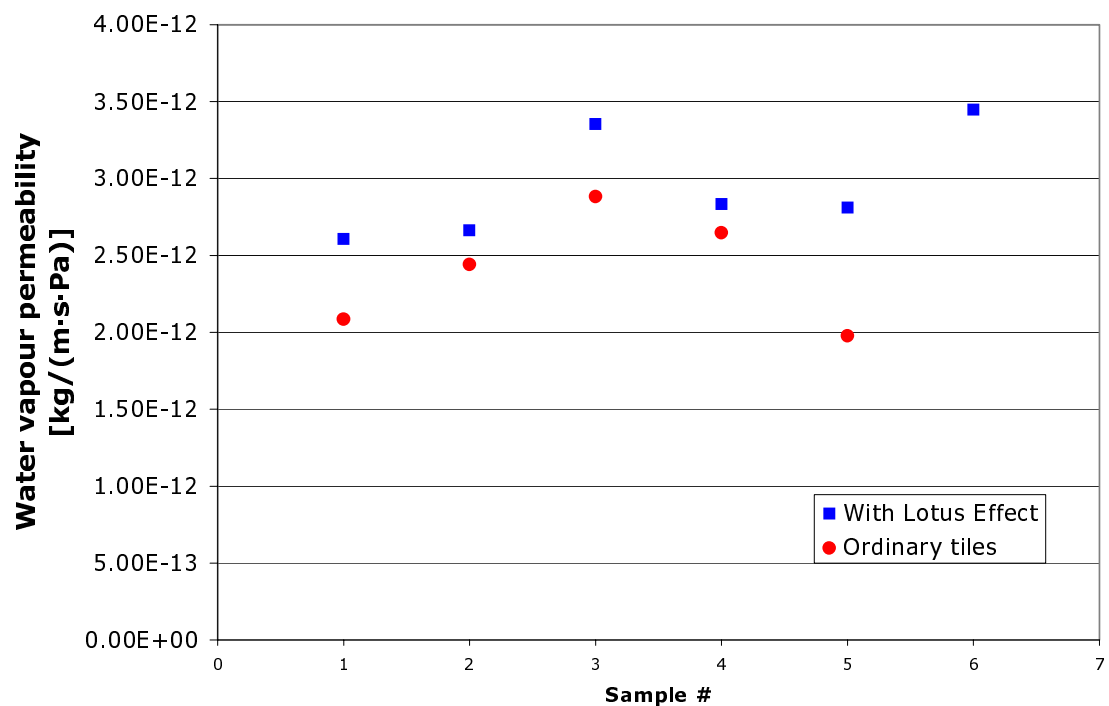
Figure 5.21: Measurements of water vapour permeability with respect to partial vapour pressure.

Due to problems with the sealant, the results must be evaluated very critically, therefore one of the measurements were omitted in the statistical analysis. However, measurements of at least five cups in each series seemed realistic, which is the requirement of the standard. The results can be seen in Figure 5.21 and Table 5.3.

	With Lotus	Ordinary tiles
Average [kg/(m·s·Pa)]	2.95E-12	2.41E-12
Standard deviation	3.27E-13	3.38E-13

Table 5.3:   Water vapour permeability. Average values and standard deviation for the measurements in Figure 5.21.

The statistically analysis showed that at a 5% confidence level, there is a difference between the water vapour permeability in the two types. However, the treated tiles with Lotus Effect are the most permeable. This does not indicate that any treatment clogs up the pores in the tiles with Lots effect. A difference in pore structure seems to be more likely, this will be discussed further in Chapter 6.

As the tests showed a difference in water vapour permeability in the two tile types, this means that under the assumption, that the bulk material is identical, the hypothesis is not corroborated.

5.4.3 Other observations

Working with the two tile types resulted in different observations that were not directly part of any planned test, but observations that could be helpful in understanding *why* the two tile types perform as they do.

One general observation was, that although the patent said, that the tiles would be immersed in the hydrophobic treatment, this could not be true; the back of the tiles was not treated. On the contrary, at the back there were stripes as if a treatment had by mistake run over the surface.

5.4.3.1 Visible hydrophobic properties over time

Hydrophobic properties are linked to contact angles as described in Section 2.3.2.2, and the contact angle on new tiles with Lotus Effect is visible larger than the contact angle on ordinary tiles. However, this visible difference decreases over time as can be seen from Figure 5.22 where only small traces of a large contact angle is visible at the edge of the tile after one year of exposure.

As stated in Section 2.3.3.2 the contact angle and the water uptake do not correspond in practise. Therefore no contact angles have been measured.

Tiles with Lotus Effect   **Ordinary tiles**

After 10
days of
exposure

After 1
year of
exposure
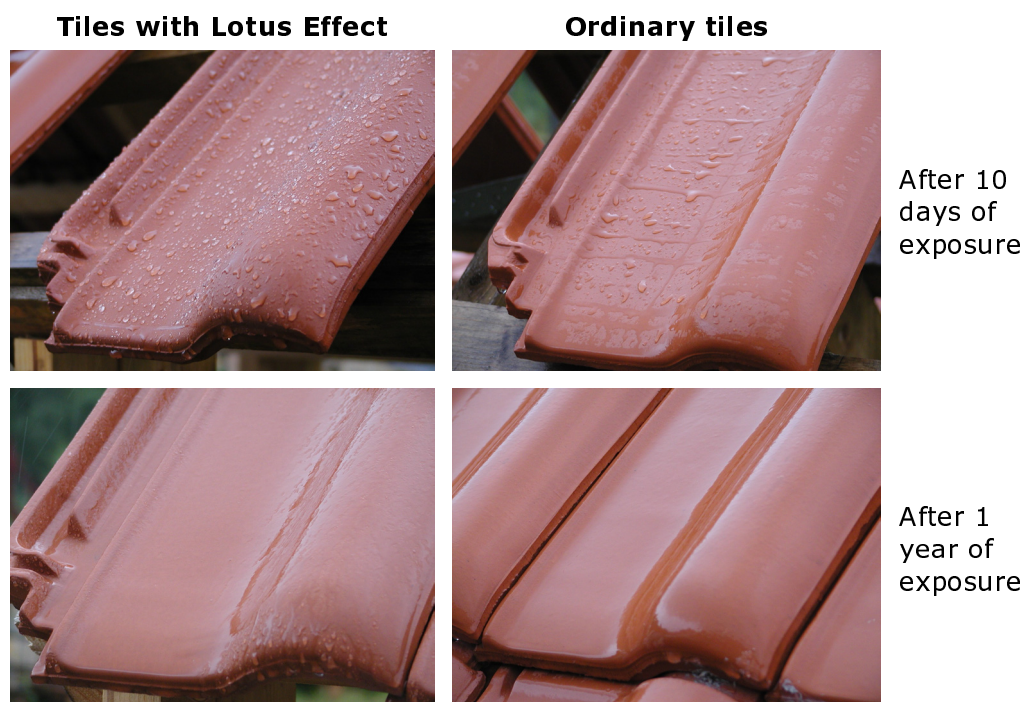
Figure 5.22: Rain form droplets at the surface of new tiles, especially at tiles
with Lotus Effect, but after one year rain form a film at the
surface even at tiles with Lotus Effect. The pictures were taken
right after each other.

Figure 5.23: Dew at tiles. Left: Dew forms droplets at tiles with Lotus Effect.
Right: Dew is only visible as a film on ordinary tiles or has
already dried up.

Although a difference in contact angle of the two tile was hardly noticeable after one year, there was still a difference in how dew was visible at the two tile types, as shown in Figure 5.23. Dew formed droplets at tiles with Lotus Effect but a film at ordinary tiles. The hydrophobic effect might have been diminished during the first year, but has not completely vanished.

5.4.3.2 White cover

Tiles with Lotus Effect which have been exposed to natural weather or artificial aging, as described in 5.3.3, tend to form a white cover at the backside. An example can be seen in Figure 5.24. Ordinary tiles do not form this cover. The chemical composition of the cover could not be determined with EDX analyses, as the area of the cross section near the backside did not show any different chemical composition than the rest of the section.

Experiments were conducted to provoke formation of the cover. It was not clear whether the cover was caused by moisture or heat. Therefore two experiments were conducted after 20 new specimens, ten of each tile type, had been stored at 20°C and 50 % RH until equilibrium:

- Five specimens of each tile type were capillary saturated in water and left to dry at 50 % RH. The specimens were weighed during the drying process, and the backside observed.

Figure 5.24: After exposure to natural weathering the backside of tiles with Lotus Effect have a white covering.

- Five specimens of each tile type were stored in an incubator at 40 °C until equilibrium, and then the temperature was raised to 50 °C until equilibrium. The experiment was repeated with 10 °C steps until 110 °C. The backside was observed during the experiment. The specimens were weighed during the process and cooled off before each weighing.

Only the heated specimens with Lotus Effect showed any signs of white covering at the backside, the phenomenon first occurred at 50 °C at one specimen, later at a few more. But the layer was not very visible. One explanation to why it never became visible at the specimens immersed in water could be, that the layer seems to be water-soluble. A SEM analysis with EDX was performed at a cross section near a white layer. Preparation of the sample were made free of water to avoid wash out of the layer. But the analysis did not show any differences in chemical composition near the white layer.

Yet the experiments with specimens which were either immersed in water or heated brought new findings:

- <u>Immersion in water and drying at 50 % RH</u>: The experiment was conducted ten times with the same specimens, and one time with specimens that had been heated first. Figure 5.25 show the results. Specimens of ordinary tiles generally dried faster than specimens with Lotus Effect. However the drying rate decreased with number of immersions and if the specimens had been heated. There seems to be an aging effect.

- <u>Stepwise heating</u>: The experiment was performed twice with the same specimens but with different starting points (50 % RH and later 85 % RH) and once with specimens that had been immersed in water but were stored at 50 % RH until equilibrium before this experiment started. The result can be seen at Figure 5.26. All five new specimens of tiles with Lotus Effect showed at noticeable weight loss between 70°C and 80°C. This loss was not seen later. However the weight losses were all very small, the difference between the different steps was often in milligrams, and inaccuracies in measurements could explain why some of the curves seem to go up as the temperature is increased.
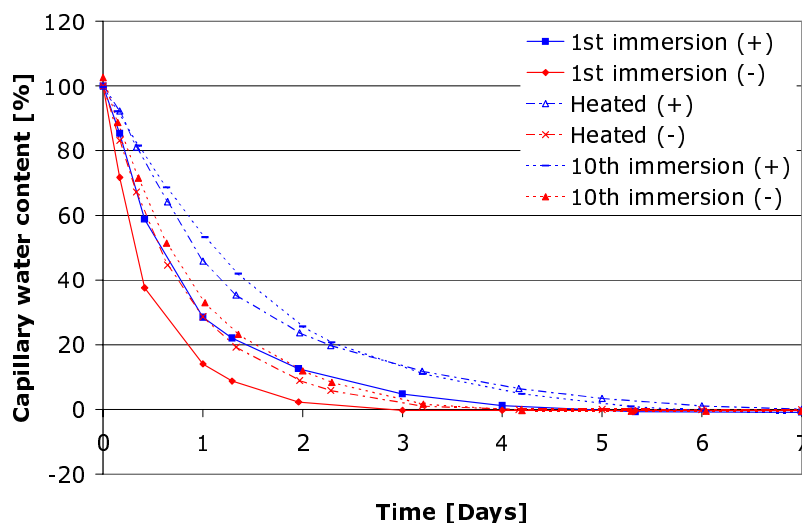
Figure 5.25: Drying after immersion in water, average values of five specimens. The drying rate is generally highest for ordinary tiles but the rate of both types decrease after more immersions or heating. (-): Ordinary tile, (+): With Lotus Effect.
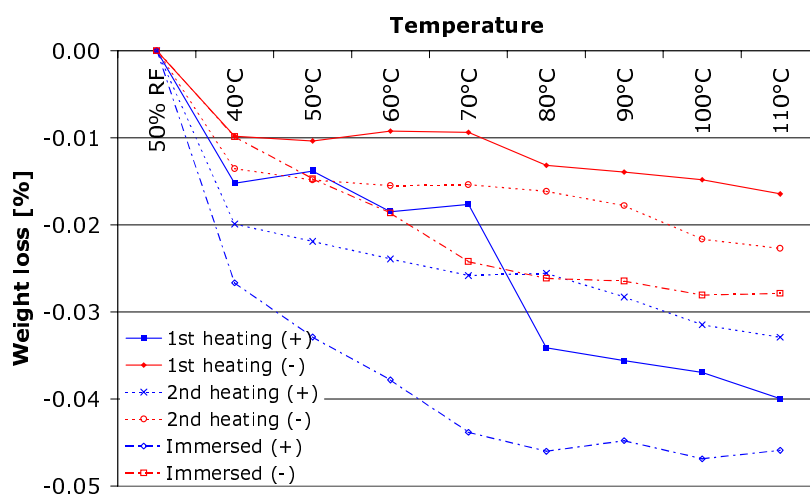
Figure 5.26: Weight loss as specimens are heated, average values of five specimens. The specimens with Lotus Effect generally loose most weight. Immersion promotes weight loss. (-): Ordinary tile, (+): With Lotus Effect.

5.5 Thermal properties

The tiles with Lotus Effect were not said to have any special thermal performances, nevertheless there were noticeable differences in how rimy they became and how snow melted from the two types, see Figure 5.27. Tiles with Lotus Effect seem to

be whiter after nights with rime, and despite their somewhat darker colour snow, did not melt as fast as at the ordinary tiles.

Figure 5.27: Difference in thermal behaviour of tiles with and without Lotus Effect. Left: rimy tiles, the tiles with Lotus Effect (right side) were whiter than the ordinary tiles. Right: melting snow, the snow melts off faster from ordinary tiles (right side).

It was therefore investigated whether the surface treatment was causing differences in surface temperature. One reason could be because of different moisture content in the tiles or because of different absorptivity or emissivity. Although absorptivity and emissivity of a surface is irrelevant when the surface is covered with snow, its influence grows as the snow melts and could therefore have some relevance after all and explain why the snow melts differently at the two surfaces.

5.5.1 Thermography

Measurements of surface temperature in direct sunlight with thermocouple are very unreliable; the value is very dependent on the shape and size of the sensor. Instead infrared thermograpy is a possibility.

In thermography the infrared radiation from surfaces is measured and displayed as colours in a picture. The radiation is proportional to the absolute temperature raised to the fourth power, where the proportionality factor depends on the emissivity. For a given emissivity the colours can represent a temperature. Consequently, two surfaces with the same colour in a thermographical picture will mean, that the surface temperature is the same or the emissivity of the two surfaces is different. On the other hand if the colour is different the temperature is probably different. However it must be judged whether also the emissivity is different.

5.5.2 Day time measurements

Two thermographical pictures of the set-up described in Section 5.1.3 taken on a bright summer day and on a grey day in the spring are shown in Figure 5.28. The summer picture shows a colour difference between tiles with Lotus Effect and ordinary tiles, while there is hardly any difference in the spring picture. On sunny days the absorptivity has decisive influence on the surface temperature. The fact that tiles with Lotus Effect are a little darker than the ordinary tiles could be the reason for the colour difference. On cloudy days where there is less long wave heat loss to the sky and there is no direct sunlight, the colour difference is very small.

If the emissivity of the two tile types is the same, the picture to the left in Figure 5.28 shows, that the tiles with Lotus Effect are warmer on a sunny day than ordinary tiles,. This contradicts the impression Figure 5.27 gave. The reason could be the thermal contribution from the solar radiation, expressed by the absorptivity. To rule out this factor, and with it the colour influence, thermographical measurements were also made on a clear summer night.
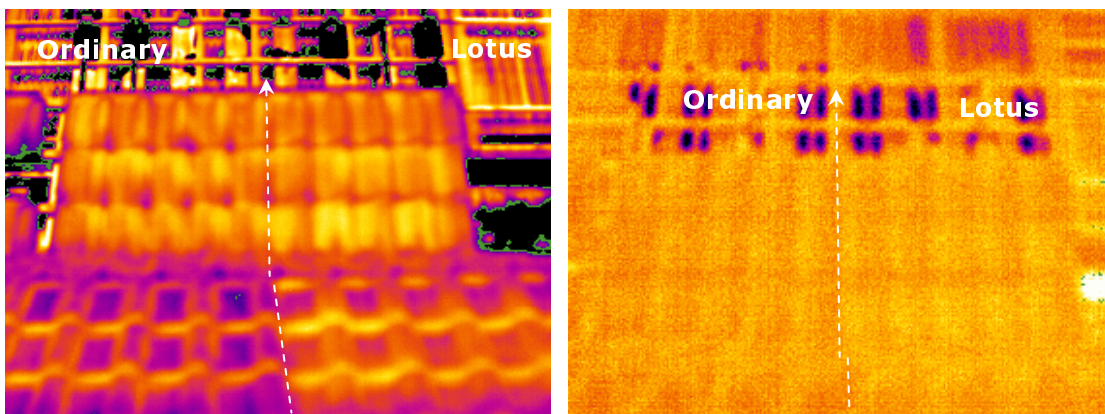
Figure 5.28: Two examples of thermography of the set-up with two different tile types. Left: on a sunny day, there is a noticeable colour difference between the two tile types. Right: on a cloudy day a difference is hardly noticeable, only the yellow parts in the lower 2/3 of the picture are tiles. The colour scale is different in the two pictures and is not shown, as the pictures only illustrate principles, however in each picture dark colours represents low thermalradiation (colder).

5.5.3 Night time measurements

As surface roughness is enhanced at surfaces with Lotus Effect, the emissivity could be changed as well. The hypothesis for this experiment was therefore:

The Lotus Effect reduces the emissivity of the surface.

To investigate this, thermographical pictures of the south oriented roofs (low and high slope) were taken during a clear summer night (14[th] to 15[th] of July). For completeness the measurements started at noon (1 pm due to summertime), again at 5 pm, 7 pm and then every hour until 6 am the following day, approximately one hour after sunrise.

The emissivity of the surface was set to be 0.92 and from this the temperature was calculated in every single pixel of the picture. To obtain an average temperature of the different roofs, two methods were used:

- Drawing a horizontal line through the middle of the four tiles in the middle row, with the line placed approximately at the same location in each picture. The average temperature of this line represents the average temperature of the roof

- Placing a square around three tiles away from the edges. The average temperature of the temperatures inside the square represents the average temperature of the roof.

The methods are shown at Figure 5.29. Neither of the methods are very precise; they highly depend on where the line or square is placed. Still, by comparing the two methods, the difference in average temperature was surprisingly small. As an attempt to get the best possible estimate of the roof temperature, the middle temperature of the two methods was used.

Provided that the emissivity of the two tiles is the same, the surface temperature and the difference in temperature between the two tile types could now be calculated. How it developed over the night is depicted in Figure 5.30.
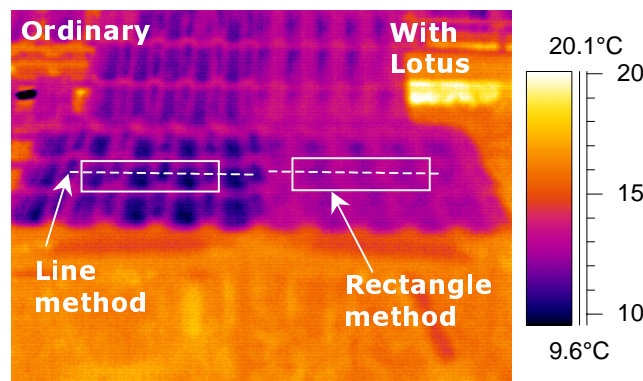
Figure 5.29: Methods to estimate average temperature of roof surface. Picture from 4 am. Line method: every pixel at the line represents a temperature, and an average is calculated. Square method: An average of the temperatures in the square is calculated. The surface temperature is estimated to be the middle of the two temperatures.

In addition to differences in emissivity, water uptake caused by dew could influence the measurements. However, the tiles on the roofs were not to be touched, instead 4 single tiles of each type were weighed to estimate the water uptake in the tiles at the roofs. The tiles were weighed every second hour from 5 pm to 5 am. The average relative weight change due to water uptake of four tiles is also shown in Figure 5.30.

The low-sloped roof radiate rather directly to the sky, while the roof with a 45° slope is more influenced by radiation from the surroundings. Any differences in emissivity would therefore be more recognisable at the low-sloped roof. In the low-sloped roof the difference between the two tile types became clear after midnight, which is the same time as the water uptake increases. The tiles with Lotus Effect were warmer than the ordinary tiles, which took up slightly more water.

The question now is, whether the temperature difference is due to differences in emissivity, water uptake or heat capacity. To evaluate this, the changes in heat and moisture conditions from midnight to 2 am are examined, the key figures are shown in Table 5.4.
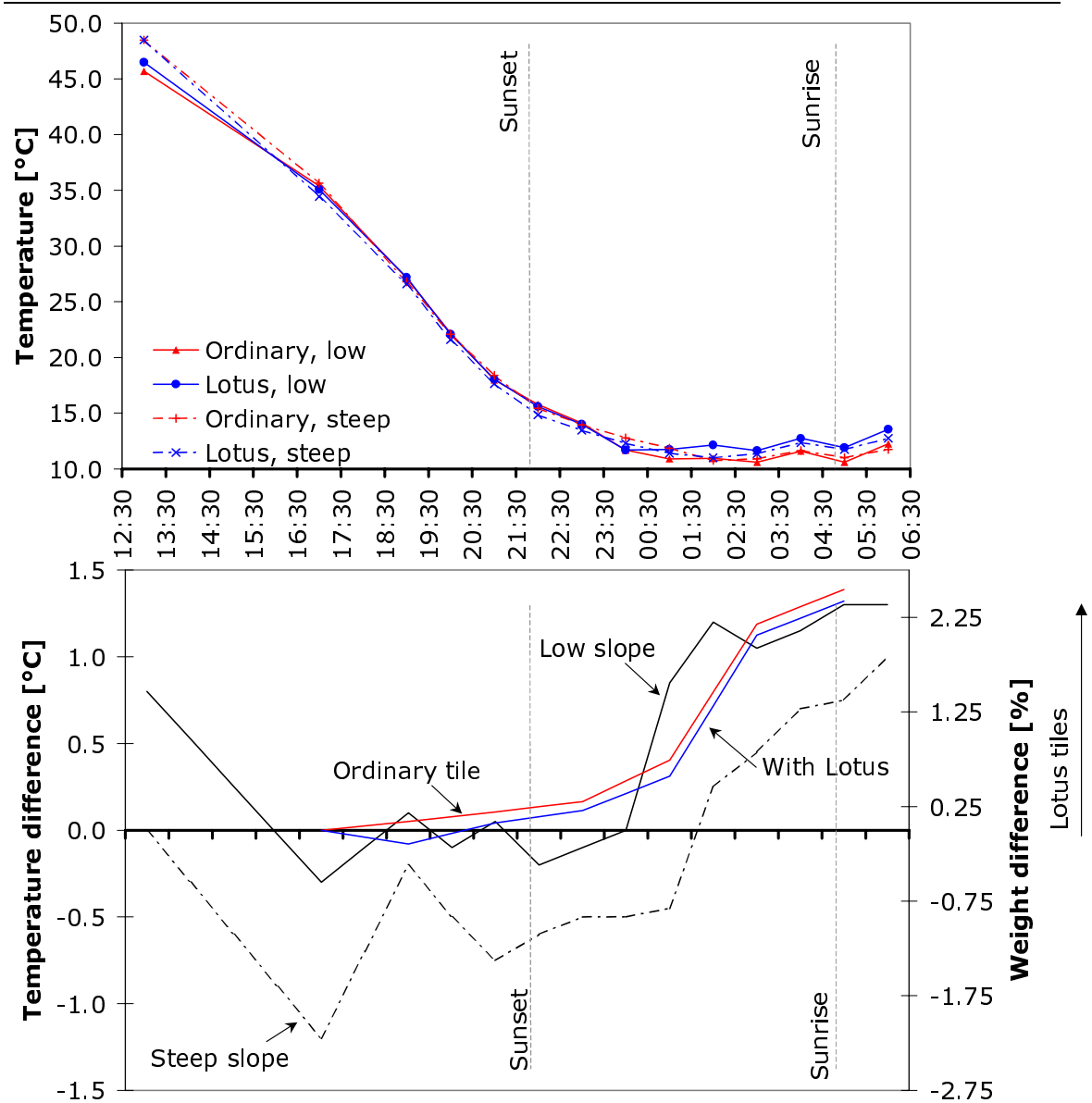
Figure 5.30: Measurements 14th to 15th July. Top: surface temperatures at two different slopes and two tile types. Bottom: temperature difference between the two tile types (Lotus tiles minus ordinary tiles) i.e. above zero the Lotus tiles are warmest. In the same picture the relative water uptake compared to the situation at 17:00 hours in similar tiles.

	Ordinary tiles			Tiles with Lotus Effect		
	00:00	02:00	Change	00:00	02:00	Change
Surface temperature measured with thermography (°C)	11.7	11.0	-0.7	11.7	12.2	0.5
Average weight of one tile (kg)	2.980	2.980	0.000	2.800	2.800	0.000
Water uptake (g)	0.958	2.416	1.459	0.425	1.740	1.315
Outdoor temperature (°C)	17.75	16.08	-1.67	17.75	16.08	-1.67

Table 5.4:   Changes in heat and moisture conditions from midnight to 2 am at the low-sloped roof.

From Table 5.4 it can be seen that the ordinary tiles had the largest total water uptake, the most mass and they became colder. The latter part though is based on the assumption that the emissivity of the two tile types is similar. Thus, in fact the surface temperature is unknown. However, the following considerations can be made:

– The outdoor relative humidity during the two hours was approximately 90% and the air temperature was 17°C, i.e. condensation would occur at surfaces colder than 15°C. The surface temperatures seem to be lower than this, which corresponds to the fact, that the tiles felt wet during handling at night.

– Upon condensation heat is released, the condensation heat $q_{condensation}$ can be described by: $q_{condensation} = g_{condensation} \cdot L$

   where $g_{condensation}$ being the amount of water condensating at a surface per second and L = evaporation heat of water = $2.5 \cdot 10^6$ J/kg, when the surface area of a tile is 0.12 m^2, 1.459 g condensate (see Table 5.4, ordinary tiles) during 2 hours this leads to:

   $$q_{condensation} = \frac{1.459 \cdot 10^{-3} kg}{2 \cdot 60 \cdot 60s \cdot 0.12m^2} \cdot 2.5 \cdot 10^6 J/kg = 4.2W/m^2$$

   Compared to the transmission loss to the ambient when the temperature difference is approximately 5°C

   $$q_{transition} = \frac{\Delta T}{0.04m^2 K/W} = 125W/m^2$$

   Which makes the condensation heat negligible

– Most water condensates at the ordinary tiles, which indicates, that these are the coldest

– The ordinary tiles have a larger mass than the tiles with Lotus Effect, which would make them likely to stay warm for a longer time. However, a lumped analysis show that the thermal effect of mass is negligible, at the temperatures in this experiment the temperature difference would be less than 0.1°C after approximately one half hour. The effect of mass will hereafter be disregarded.

If the emissivity was similar in the two tile types the temperature difference shown in the thermographical pictures is real. It would mean that two tile types, which radiate similarly and had the same temperature until midnight, change temperatures differently; the ordinary tiles continue to loose heat an extra hour, hereafter the temperature becomes more or less constant. Behaviour like this can not be explained if the radiation is similar. Consequently the emissivity must be different between the two tile types, and the scale in the pictures should therefore be different for the two tile types.

Based on the fact, that more water condensates at the ordinary tiles, these must be colder during the night than the tiles with Lotus Effect. As differences in condensated water and mass are ruled out as explanations for this, the emissivity of the tiles with Lotus Effect must be lower than that of the ordinary tile.

The hypothesis is corroborated.

However, the methods used are simple, and better measurements could have been made with instruments for emissivity measurements. Usually these measurements are conducted with an apparatus where the radiation from a sample is compared to radiation from a black body. Unfortunately, the department did not own such an apparatus, and the statement is therefore based on measurements that are not very precise.

5.6 Summary of experiments

Table 5.5 provides a quick overview over the numerous hypotheses, experiments and results. The hypotheses have been shortened compared to the text in the chapter, but the meaning should still be the same. However, it is important to

remember, that although a number of hypotheses were not corroborated by these experiments, it only means that in *this* case the hypotheses did not hold up. Whether this is because the whole theory is wrong or the circumstances about these experiments are special in a way that the theory does not apply, will be discussed in Chapter 6.

Section	Hypothesis	Experiment	Hypothesis corroborated?
5.2.1	Soiling will be more abundant at north than south facing surfaces, and most noticeable at steep sloped roofs	Set-up with two different slopes and orientated towards north and south, visual inspections.	**Yes**
5.2.2	Roofing tiles with Lotus Effect are self-cleaning; soiling will be washed off	Visual inspections and measurements with LED technique at the two tile types	**No**, but soiling is somewhat delayed
5.3.1	More water will run off tiles with a hydrophobic treatment than off ordinary tiles	Collecting water from gutters under the two tile types	**No**, on the contrary, water run off from tiles with Lotus Effect was smaller than from ordinary tiles
5.3.2	When exposed to rain tiles with a hydrophobic treatment will take up less water than ordinary tiles	Weighing of single tiles exposed to normal weather	**No**, on the contrary, tiles with Lotus Effect took up more water than ordinary tiles
5.3.3	There is a higher risk of frost damage in tiles with Lotus Effect than in ordinary tiles	Accelerated freeze-thaw test	**No**, both tile types passed the test
5.4.1.1	There is no difference in porosity of the two tile types.	Measurement of pore volume by vacuum saturation	**Yes**
5.4.1.2	The pore size distribution in the two tile types is similar	– Capillary suction – Sealed bag – Measurements with pressure plate equipment	**No**, the two first experiments corroborated the hypothesis, but the last falsified it
5.4.2.1	It is possible to detect and determine the chemical composition of the surface treatment on tiles with Lotus Effect by using XPS.	Measurements with XPS	**Yes**

5.4.2.2	– SEM images will show differences in topography – SEM used at fragments can show the penetration depth – SEM combined with EDX can show the chemical composition of the hydrophobic treatment and how it changes through a sample	SEM pictures and EDX	**Yes**, SEM is highly suitable for information on topography **No**, penetration depth or chemical composition of the treatment can not be determined by SEM/EDX
5.4.2.3	The water vapour transmission properties of the roofing tiles are not affected by the surface treatment.	Measurements with wet cup	**No**, but the treated tiles are the most permeable
5.5.3	The Lotus Effect reduces the emissivity of the surface.	Thermographical measurements	**Yes,** possibly

Table 5.5: Summery of hypothesis, experiments and results given in this chapter.

6. DISCUSSION

In the previous chapters the concept of changing surface properties for improving hygrothermal and anti-soiling performance has been discussed. Theoretical considerations and more practical observations have been reported. Based on the previous chapters, this chapter will include a discussion of which parameters have the most influence, and which are realistic to change.

The findings in the experiments will also be discussed. Although the hypotheses have been evaluated in the previous chapter, the reasons and implications of the outcome will be analysed here. Generally the experiments will be used as the starting points for broader discussion. This does not mean that the experimental findings are generalized to apply for all situations, this would be the less scientific inductive approach (see Section 1.2). Instead the experiments serve as illustrations of the general theories described in Chapters 2 and 3.

Although they have some mutual influence, hygrothermal properties and soiling will be treated separately, as it has been throughout the thesis.

6.1 Hygrothermal conditions

Changing hygrothermal properties by applying special treatments has been discussed as a promising theoretical possibility, but the experiments in Chapter 5 were discouraging; although the theoretical definition of hydrophobicity (contact angle > 90°) was visible, the water uptake was higher in the tiles with Lotus Effect than in ordinary tiles. This emphasises the point that contact angle measurements cannot be used instead of water uptake measurements, as specified in Section 2.3.3.2.

The higher water uptake in treated tiles could mean, that the treatment itself promotes the uptake; either by retaining water in the treated layer or by enhancing the capillary suction, and thereby allowing water inside the material. Both theories must be considered:

- Retaining water. If the treatment itself changes the treated layer in a way that the extra water uptake is stored in the layer. The minimum layer thickness can be calculated from the experiments by assuming that all

pores in the layer are filled with water: the extra water uptake in tiles with Lotus Effect during a heavy summer shower is approximately 150 g (see Figure 5.8). The surface area of one tile is approximately 1180 cm^2, and the porosity 0.225 (see Table 5.2), this means that the minimum thickness of the treated layer (penetration depth) would be:

$$\frac{0.15 \cdot 10^{-3} m^3}{0.118 m^2} \cdot \frac{1}{0.225} = 6mm$$

A penetration depth of this size where the hygric behaviour is very different from the bulk material would be visible when water was sprayed at a fractured cross section. However, this was not possible and the retaining treatment theory was abandoned.

– Enhances capillary suction. This would mean the opposite of hydrophobic behaviour; the treatment diminishes the contact angle instead of enhancing it. Yet, at new tiles an enlarged contact angle is visible at the surface. In the same new tiles the water uptake is increased as well. If the treatment enhances the capillary suction, the treatment would have to have different surface free energies whether it is at the surface or in the pores. In fairly new tiles, where the aging process has not changed the polymer or surface, this is unlikely.

Instead of the reason for the enhanced water uptake being in the treatment, the explanation could be in the bulk material. The assumption, that the bulk material in the two tile types is similar, could be wrong.

6.1.1 Bulk material

Improving durability by changing surface properties was discussed in Section 4.1, where it was seen as a way to prolong the service life of materials. In consequence inferior materials could be upgraded with a surface treatment. For society this could mean economic savings because otherwise unusable materials become useful and therefore more valuable again.

However, surface treatments at porous materials must be adapted to the bulk material as well as the surface. The physical and chemical consequences and possibilities of this combination of bulk material and surface treatment must be seen as a whole.

6.1.1.1 Pores

In Section 2.3.1 and 4.1.1.2 the pore shape and size distribution was described as important to moisture transport and deterioration, it was also mentioned, that the physical pores only can be changed by clogging the pores or reducing them by covering the pore walls with a treatment. The latter effect is more noticeable in very small pores as shown in Figure 6.1.

Some of the experiments described in Chapter 5 can be used to discuss whether it is reasonable to presume that the pores are narrowed:

- <u>Porosity and pore size distribution.</u> In Section 5.4.1.2 the porosity and pore size distribution of tiles with Lotus Effect and ordinary tiles were determined. Although the differences were small, the final conclusion was, that while the porosity was statistically similar (average 0.23), the pore size distribution was different; ordinary tiles had larger pores than treated tiles. Narrowing of the pores could explain the different pore size, although the porosity is similar. But there is a tendency to a higher porosity in the ordinary tiles. Furthermore, the penetration depth of the treatment should be substantial to influence the pore size distribution of the whole tile. None of the experiments indicated large penetration depths.

A   B   C
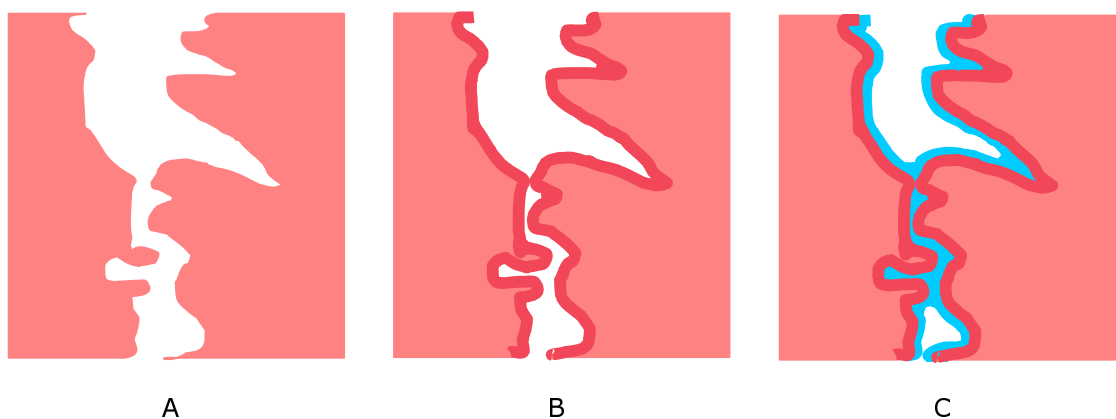
Figure 6.1:   Principle in narrowing pores when applying hydrophobic treatment. A: untreated pore. B. Treated pore, in the narrow parts the size is distinctively diminished, the treatment smoothen the pores by filling some of the corners. C: Moisture transport in the hygroscopic region, as described by the bridge theory in Section 2.2.2.

- Water vapour permeability. If the pores were simply narrowed the water vapour permeability is likely to be diminished. The findings in Section 5.4.2.3 do not support the theory, as the water vapour permeability, measured in the wet cup, was higher in the tiles with Lotus Effect than in ordinary tiles. If the pore structure was the same and the pore walls were simply narrowed and hydrophobic this would difficult to explain. But as other findings have shown this is not the case in the Lotus tiles. In Figure 2.4 two different explanations are given to why permeability increase with humidity. Although narrowing pores decreases "regular" diffusion, it might also have another effect when the humidity is high, as in the wet cup. In the terminology of the bridge theory in Section 2.2.2 narrowing of pores would probably mean more "short cuts" and therefore enhanced moisture transport. In the surface diffusion theory the moisture transport would not be that affected by narrower pores, on the contrary, one would imagine, that the treatment would smoothen the pores by filling some of the "corners," which according to Krus (1995) are supposed to be responsible for the extra transport. If these corners were filled with the treatment this would reduce the possibility of liquid transport. Toniolo et al. (2001) have by means of SEM pictures described how the sharp edged crystals in a porous calcareous stone are smoothened when treated with a polymer.

- SEM analysis. According to Carmeliet (2001) the polymer length of polysiloxane, a frequently used hydrophobic treatment, is in the vicinity of 0.01-0.1 µm. A single polysiloxane layer would therefore be invisible on the SEM pictures, only a thicker layer might have been visible. SEM analysis did not reveal any covering of pores, not even in tiles where a considerably amount of active agent had been applied (Figure 5.18). Alvarez & Fort (2001) who have used SEM to show hydrophobic treatments of dense limestone used a 10 times higher magnification to reveal penetration depths of 5-8 µm. However, penetration depths of this magnitude are, for practical purposes, of little interest and an enlargement of this size was therefore omitted.

The pore size distribution together with the SEM pictures show that the tiles have relatively coarse pores; most of them have a radius > 1µm (see Figure 5.14 and 5.17). It therefore seems unlikely, that narrowing pores with a thin layer of

hydrophobic treatment will affect the properties, especially if the penetration depth is small (tenth of μm). In the particular case of tiles with Lotus Effect versus ordinary tiles it seems to be more likely that there is a difference in pore structure of the whole bulk material instead.

However, in a more general aspect, the narrowing of pores can be relevant in bulk material with a large amount of fine pores (0.1-10 nm), such as in high strength concrete, where a considerable number of the pores are < 10 nm (Wee et al. 1995). These pores are likely not to be treated, like the pores in the calcium silicate described by Carmeliet (2001), or the pores might even be clogged. With this kind of material the size of the polymer could become decisive for the choice of active agent in the treatment.

Alvarez & Fort (2001) have treated two types of limestone with ten different hydrophobic treatments. Among other things, they came to the conclusion, that it was not the porosity but the pore size distribution which was decisive for the average penetration depth. The limestone with the smallest porosity (6.91%) but the coarsest pores (85 % < 5 μm) had the largest overall penetration depth (8.6 μm), while the other had a porosity of 8.38 % with 98% of the pores < 5 μm and a penetration depth of 5.3 μm.

Consequently, not only the porosity but the size of the pores has to be considered if a hydrophobic treatment should be used and if so, what kind of treatment would be applicable. Naturally this also depends of the chemistry of the hydrophobic agent.

6.1.1.2 Chemistry

As mentioned in Section 2.3.3.4 most commercially available silicon-based hydrophobic agents have small hydrocarbon groups, although longer and more branched polymers have better properties. However, larger groups and more branches mean larger polymers, e.g. silane is smaller than siloxane, see Figure 2.21. As smaller polymers "get in everywhere" they are generally more applicable than larger polymers. Alvarez & Fort (2001) have described how two limestones with different properties are often used on the same building as it is visually difficult to differentiate between the two materials. In such a case it is crucial that the hydrophobic agent which is chosen will treat both types, even if a better product is available for one of the materials.

Teflon or other fluorine-based agents have the same size problem, in Section 3.4.2.3 it was described how an enrichment of CF_3 groups would diminish the surface free energy, but this would also enhance the size.

However in many porous materials where a hydrophobic treatment is considered the pore size will be relatively large, and only a very small part of the pores will be noticeably affected by the molecule size of the treatment.

When a substrate is treated with a hydrophobic agent, the two components might interact. In some cases the interaction becomes disastrous, in others it enhances the durability of the treatment:

- <u>Disastrous.</u> Colour change due to chemical reactions, e.g. in Boston a 40 storey sandstone building turned black due to oxidation of iron (Charola, 2001).

- <u>Advantageous.</u> The adhesion between the substrate and the treatment will be enhanced if chemical bonding takes place; this is described in Section 3.4.2.4 as chemisorption. How this affects the adhesion of a hydrophobic treatment is shown in Figure 2.23 where silicon-based treatments react with the silicon in a substrate e.g. tile or concrete.

The result of the XPS analysis showed a very high content of fluorine at the surface of the tile with Lotus Effect; an analysis which could not be corroborated by the SEM/EDX findings. One explanation could be that the surface layer is very thin and XPS only analyse the top layer (nm thickness); while EDX goes a little deeper (μm thickness). In the case of very thin layers this might have some influence. However, a more reasonable explanation is probably that the layer was damaged as the sample was prepared for EDX analysis.

Fluorine contamination is also a possible explanation. Fluorine is not easily decomposed and will be detectable longer than most contaminants. The samples used for the XPS analysis were from a pile of new tiles where samples were taken from areas of the tiles that were unlikely to have been touched. If the fluorine findings were a result of general contamination, the ordinary tile would most likely have had a similar contamination; instead it seems reasonable that a partially

fluorinated siloxane has been used. Theoretically this would improve the performance of the hydrophobic treatment including the visual effect of droplets forming beads, which is very noticeable with new tiles, see Figure 5.22.

Teflon or other fluorine-based polymers have throughout the thesis been described as promising alternatives to the otherwise commercially very dominating silicon-based polymers. The characteristics of fluorine-based polymers are:

- Very low surface free energy due to the presence of CF_3 groups. The abundance of CF_3 groups determine how low the surface free energy becomes. Low surface free energy means high hydrophobicity.

- The solution is non-polar, which limits the physisorption, the result is an almost non-stick surface.

- The polymers are almost inert i.e. unlikely to react chemically with any substrate.

While the first two characteristics are entirely positive, the latter is ambiguous, no chemical reaction means no danger of discolouration, but also no chemisorption. The treatment may not adhere to the substrate as well as a silicone-based polymer on a silicon containing substrate.

As described in Section 5.4.2.2 a hydrophobic treatment labelled "Teflon" was donated during the project. No further information was available other than "it contains Teflon", a sparse description like that renders it unfit for scientific investigations on how fluorine-based polymers act as hydrophobic treatments. Instead the treatment was used for SEM analysis, where it was used as one of two treatments whose penetration depth was supposed to be seen at SEM pictures (Section 5.4.2.2). This failed, but before the tile was smashed to pieces for the SEM analysis, the visual appearance of the tile was examined. Figure 6.2 shows a photograph of the tile, with a close up on how water form beads at the surface.

Figure 6.2:   Left: an ordinary tile treated with "Teflon" (left) and silan (right). "Teflon" gave the tile a glossy look. Right: Water at "Teflon" formed an almost perfect spherical droplet.

Although the properties looked promising, the visual appearance would be unacceptable in most cases; this is probably a reason why the treatment is not commercially available. However, treatments using the name "Teflon" are available e.g. Zonyl (DuPont, 2001) but these are fluorinated silicon-based treatments.

6.1.2 Treatment

When it is concluded, that the bulk material is suitable for hydrophobic treatment in respect of physical and chemical nature, an appropriate active agent must be found. Chemistry aside, as it already has been treated as a part of the bulk material / treatment process the next step is to determine what treatment would have the best performance. Best, that is, in sense of functionality combined with economics and environmental concerns.

6.1.2.1 Application

Although a well-suited hydrophobic agent has been chosen, the application method can be decisive to whether the end result will have the intended effect. The major concern in application is whether the penetration depth is sufficient. Theoretically the penetration depth itself is unimportant to the hydrophobic behaviour of the treated surface. If the surface is treated, the water will run off. Nevertheless penetration depth is very important in practice, the deeper the active agent has penetrated the substrate, the more likely the whole system is to be effective. Toniolo et.al. (2001) have even established a direct link between penetration depth and long-term efficiency of a treatment in highly porous substrates. This is because the surface is subjected to mechanical abrasion and in combination with e.g. driving

rain or splash, water would overcome small penetration depths with water uptake as a consequence (Meier & Wittmann, 1999).

In porous materials with small pores it is especially difficult to obtain penetration depths of more than a few mm or, as in the example in Section 6.1.1.1, sometimes the penetration depth is only few µm.

Examples of application methods are:

- <u>Immersion</u>. Dipping the substrate in the hydrophobic liquid, often used for testing in laboratories, but also described in the patent for tiles with Lotus Effect.

- <u>Spraying or by brush.</u> Most common method for hydrophobic treatments. The liquid should be applied down and up to insure a homogeneous distribution of active agent.

- <u>Gel or crème.</u> Basically applied like liquids, but are different in their mode of operation.

- <u>Internal hydrophobic treatment</u>. A water repellent liquid is mixed into the material e.g. into concrete or mortars.

- <u>Box technology.</u> A box filled with hydrophobic treatment is fixed at the surface by vacuum, the box is left at the surface until the desired penetration depth has been reached. In practice this means pre-tests with a modified Karsten pipe (see Figure 2.12) should be used to predict the necessary time (Gerdes et al. 1998).

The key factor is the contact time, except for the internal hydrophobic treatment, where the penetration depth is the whole material. The other methods can all be varied. Immersion, of which the box technology is a special case, can have different duration. Spraying can be applied several times, as one application is similar to 20 sec. of contact time, as mentioned in Section 2.3.3.5. Gel and crème prolong the contact time, as they do not run off and can be applied in a thick layer; up to 2mm (Hankvist & Karlsson, 2001). The gel can stick to the surface for several days until it is actively removed or slowly disappears as weathering cleans the surface.

Other methods such as carpets saturated with hydrophobic liquid, placed at the surface for enhanced contact time are possibilities (Meier & Wittmann, 1999). But no reports on such treatment were found. Nevertheless, the method is used as a cleaning technique; poultice-based cleaning (Marie-Victoire & Texier, 1999). Two methods are described, one is to apply a wet poultice to the surface and let it dry, where after it crumbles and is easy to remove; this resembles the gel technique. The other is based on application of e.g. mineral wool, slightly wetted and placed by hand. Afterwards the wool is kept wet through a network of pipes dispensing the correct amount of water. This method is very work intensive and therefore expensive. But it is an alternative to the box technique, which is probably best suited to large even surfaces.

Gall et al. (1999) have described internal hydrophobic treatments in mortars as very promising. By adding relatively small amounts of active agent (3% of the cement weight in the mortars) the uptake of chloride containing water was reduced by 85 %. The method however, has some drawbacks; the hydrophobic treatment is relatively expensive and the amount needs to be optimised. It is best suited for surface layers, not whole construction parts. Furthermore the properties may disappear with time as hydration products cover the hydrophobic agent, as described in Section 2.3.3.3.

Materials immersed in hydrophobic treatments have a fair chance of obtaining good penetration depths, as the materials can be left in the solution for a long time. In water-based solutions this might not apply because a water front would precede the active agent as explained in Section 2.3.3.5; for practical purposes the method is hardly used. In the patent for tiles with Lotus Effect (European Patent Office 1998-b) it is stated that the tiles are immersed in a siloxane solution. The immersion time is not stated. On the tiles themselves it is evident that they have not been immersed and the Lotus Effect has been applied by spraying the upper surface. Figure 6.3 shows the back of a tile where the treatment has run over the otherwise untreated back. Had the tiles been immersed the whole surface, front and back, would have been treated.

Area where the treatment also is visible as stripes at the back
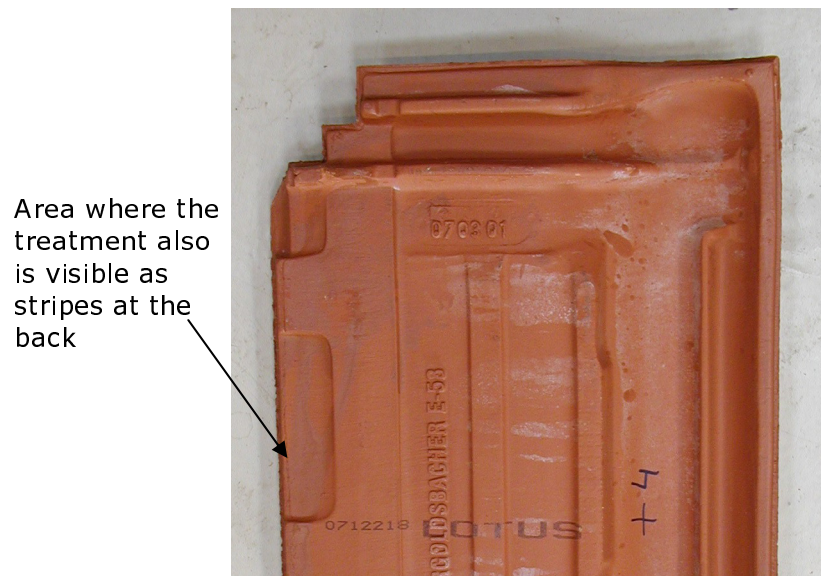
Figure 6.3: Back of tile with Lotus Effect, the treatment must have been applied in a different way than immersion. The tile has been subjected to frost test and has also a white layer probably caused by a combination of heating and wetting, see Section 5.4.3.2.

Immersion is actually used on roofing tiles e.g. the example in Section 4.2.3 where of scaling of roofing tiles was caused by a hydrophobic treatment applied by immersion (Vasic, 1997). However, it was the treatment, not the application type that caused the problem. The purpose of the immersion was to prevent both-side efflorescence but efflorescence does not functionally harm the tiles, and at visible areas it will be washed off. Using hydrophobic treatment for this reason alone seems unnecessary.

6.1.2.2 Service life

Although hydrophobic treatment penetrates the uttermost layer it does not mean, that the treatment does not degrade; it has only a limited service life and will have to be renewed. When evaluating different possible treatments for a specific case the overall service life of the treatment becomes important in order to calculate the cost in use of the treatment. As stated in Section 4.1.4.1 aesthetics can easily become the determining factor. Nevertheless not all surfaces are troubled with soiling and functionality will in these cases determine the service life. Traditionally service life has been estimated by experience and beliefs but a standard for service life prediction has been developed; ISO 15686-1 and -2 (2002) in which a more standardized method, the factor method, has been introduced. In the factor method

the estimated service life of a component is given by simply multiplying a reference service life with different modifying factors:

$$ESLC = RSLC \times A \times B \times C \times D \times E \times F \times G$$

with the abbreviations:

ESLC = Estimated Service Life of a Component

RSLC = Reference Service Life of a Component

and modifying factors relating to the specific conditions of the case:

A : Quality of components

B : Design level

C : Work execution level

D : Indoor environment

E : Outdoor environment

F : In-use conditions

G : Maintenance level

The modifying factors will have values > 0, but no upper limit. 1 corresponds to the situation in the reference case.

The factor method is not limited to any components and by simply multiplying all the modifying factors none of them stand out as especially critical. This must be seen as a weakness in the method as some components are more sensitive to changes in the conditions than others. In specific cases the critical modifying factors must be pinpointed. E.g. the penetration depth is decisive in long-term efficiency of hydrophobic treatments, and as stated in Section 6.1.2.1, the penetration depth is depending on the application, consequently must the modifying factor C be evaluated very carefully. The factor D, indoor environment, however has only little influence, but the factors are multiplied as if they are of equal importance.

In the case of hydrophobic treatments of exterior surfaces the estimation of service life is hindered by some of the factors being important but not fully understood. Generally the factors for hydrophobic treatments can be split in different groups:

- – <u>Controllable factors</u>. The factors A, B, C and G (quality of components, design level, work execution level and maintenance level) can to some degree be influenced by design, description of the project, including application instructions for the workers at the site, and plans for maintenance.

- – <u>Less critical factors</u>. The factors D and F (indoor environment and in-use conditions) will in most cases be either less important (D) or unlikely to differ from the reference conditions (F). Only in special cases will these factors will be different from 1.

- – <u>Critical factors</u>. Exterior surfaces are often fully exposed to the outdoor environment, therefore the factor E is very important while at the same time uncontrollable by the designer. The reference service life RSLC is also a crucial factor and often very difficult to determine.

In this way the problem has been reduced to the determination of the two critical factors, E and RSLC. Both factors however, are encumbered with great uncertainty. For functionality estimates the outdoor environment may simply be a comparison of the climate where the treatment is planned to be used and the climate in which it has been tested. For soiling considerations this is more difficult as these conditions can change faster than normal climatic changes.

The most difficult part is the reference service life of the component RSLC, a figure that the manufacturer of a hydrophobic treatment is supposed to deliver. To do this, it will be necessary to follow the prediction procedures described in ISO 15686-2 (2000), these are depicted in Figure 6.4.

To have an operational methodology it is necessary to develop an accelerated test, which makes it possible to predict the service life without waiting say 25 years. But such tests can only be verified by long-term testing to see if the degradation is similar. Materials used for surface treatment are changing rapidly; today it is unlikely that products like paints and water-repellents stay on the marked for a 10-year period without changes in the chemical composition. Not only do the producers try to improve the performance of their products but also environmental concerns force them to use alternative chemicals.

Defining the problem. Identifying possible degradation agents and degradation mechanisms and how to accelerate them		
Pretesting to establish the primary degradation agents, establish the agent intensity levels needed to induce property changes. Verifying adaptability of measurement and inspection techniques	**Exposure** and evaluation in order to determine ageing processes and compare long- and short-time tests	
	Analysis / Interpretation of the exposure tests with the purpose to predict a service life	Critical **review**

Figure 6.4: Methodology for predicting service life. The manufacturer should use a similar method when searching for a reliable RSLC. The testing and analysing part (middle column) will often have to be repeated, resulting in new pretesting and new tests. When standardised tests (e.g. ISO tests) are available, new pretesting may not be necessary. The figure is a simplification of a figure in ISO 15686-2 (2000).

Long-term exposure for products, which has already been removed from the market during testing can only be used to evaluate an accelerated test performed on this particular product. The result may help in developing accelerated tests but the test result itself is of very little interest.

If the factor method was used for predicting service life of tiles with Lotus Effect, the task would be:

- Defining failure in terms of frost damage, water uptake, visual change etc.

- Obtaining reference service life (RSLC) from the manufacturer including information on what climatic conditions the RSLC was determined

- Estimate how the climatic and soiling-causing conditions differ from the reference situation. This would mean determining the modifying factor E

– Estimate whether the "indoor" climate of the set-up has influence on the performance of the tiles. This would mean determining the modifying factor D.

The rest of the modifying factors would all become 1, and the estimated service life ESLC would be:

$$ESLC = RSLC \times A \times B \times C \times D \times E \times F \times G$$
$$\Rightarrow \quad \underline{ESLC = RSLC \times D \times E}$$

(6.1)

However, the manufacturer was not asked for a RSLC and failure was not defined. But it is fair to presume that visual appearance would be one of the factors as the commercial argument for the tiles was their self-cleaning properties. A conservative guess at service life would be 25 years. The climatic conditions are unlikely to differ considerably from those the manufacturer would have chosen as the tiles come from Bavaria, but intended for the whole of Germany where the climate is comparable with the Danish climate. As for the environmental factor; the set-up location was chosen as a place where soiling was likely to happen, although it was not extreme. E must therefore probably be lower than 1. Finally if the lack of indoor climate has a negative influence on the performance D should also be < 1.

After approximately 2½ years the roofs in the set-up with Lotus tiles is green, not as green as an ordinary roof but to a degree that makes it unacceptable. Estimating E and D are similar to educated guesses, but the product of these two should be 0.1 if the factor method should be used for estimating the correct service life.

Yet factor D can be eliminated if an actual house is chosen. Eight houses in Denmark have tiles with Lotus Effect as roofing and when the roofs were approximately 2 years old 7 of them were inspected. Figure 6.5 shows an example of tiles on one of these houses. This example is a house located at the north shore of a bay and close to a small forest. During this project it has been a general observation that roofs, independent of surface, in close proximity to water e.g. lakes or sea are more likely to suffer biological growth than roofs at a distance from free water. This means that, in those areas, the factor E should probably be less than 1. According to Equation (6.1), when D = 1, E would have to be 0.1. A factor that seems unreasonable, and makes one question whether the RSLC was correct.

Figure 6.5: Two year old roof with Lotus tiles. Left: north side. Right: south side, notice the same soiling pattern as at the low slope in Figure 5.3 from the field test. The roof was renewed for aesthetic reasons. The old roof of concrete roofing tiles was covered with biological growth and after cleaning it quickly resoiled. Tiles with Lotus Effect were chosen for replacement.

This example was used to illustrate the difficulties in using the factor method, despite its simplicity. Its weaknesses make it difficult to estimate the factors and to obtain realistic estimates of the service life.

The simplicity of the factor method makes it easy to understand. But it is a deterministic method giving the user a single number of years as estimated service life. But service life is a stochastic quantity and therefore only can be estimated with a degree of uncertainty which should appear in the end result. The simplicity of the method can be misleading. Before the factors are found the user must go through the whole methodology and may well find it difficult going from theory to practice when fixing the factors or the RSLC. Other and more probabilistic approaches, e.g. Aarseth & Hovde (1999) might be more complicated in their mathematics but a professional building designer should be able to overcome this obstacle. An estimated service life ± some years, reflect the reality better than a single number of years.

Neither the factor method nor the step-by-step principle by Aarseth & Hovde (1999) discriminates between different performance patterns over time. Figure 6.6 illustrates how failures can be linear over time or accelerated at different times. Nevertheless this could be important in the overall evaluation of a treatment as there is a difference in how performance decreases until it reaches a point where it is unacceptable (end of service life) whether it happens at once or gradually.
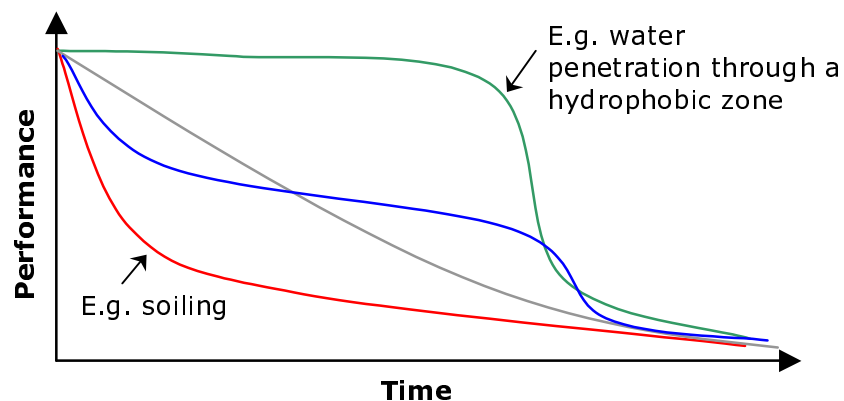
Figure 6.6:   Different performance patterns. Some failures are linear, some accelerate or decelerate at different times.

A few examples concerning surface treatments:

- The soiling rate changes with time; quickly in the beginning and then it slows down (see Figure 4.8). This could resemble the red or blue line in Figure 6.6.

- As mentioned in Section 4.1.1.3 Sandin (2003) has observed, that once water has penetrated the hydrophobic zone it is likely to happen more frequently. This resembles the green line in Figure 6.6.

ISO 15686-1 (2000) emphasizes, that the forecast of service life should be used as a guide rather than an absolute, and that the recommendations in the standard are not intended to implement contractual liabilities. Forecasts cannot necessarily be expected to be either accurate or precise. It must be concluded therefore, that the method with all its faults should only be used with care and the results critically reviewed. Although the factor method is a standard no reference to it was found in the literature concerning surface treatments, probably because it is not suitable for that use. It seems to be as good as any educated guess. The best way to evaluate the service life of any hydrophobic treatment is still a combination of testing and educated guesswork, based on scientific facts and experience. The factors of the factor method may be used as a checklist to be sure all influences have been considered.

6.1.3 Advantages of hydrophobic treatment

So far it has been established that the physical character of the bulk material in combination with the physical and chemical nature of a hydrophobic agent is

decisive in whether a surface should be hydrophobized. The service life of a treatment is highly influenced by the application, but can basically only be estimated through tests and experiences with similar combinations of substrate and treatment. When all these parameters come together is it then realistic to achieve the enhanced properties stated in Section 2.3.3 and 4.1.1?

6.1.3.1 Moisture content

The main reason for applying a hydrophobic treatment is to avoid water uptake by capillary suction. The results of the experiments reported on water run-off and water uptake in Section 5.3.1 and 5.3.2 do not support the theory. There is a difference in water uptake and run-off in favour of the ordinary tiles. More water runs off instead of being transported into the ordinary tiles. Even with new tiles where the difference in how the water forms beads at the surface is most noticeable the difference is the same. In the beginning of this chapter it was discussed if the treatment itself promotes the uptake. This was rejected, as differences in the bulk material was seen as the reason for such behaviour. It is unknown how the water uptake in the same material but without Lotus treatment would have been. But as the bulk materials are not that different, it is unrealistic that the water uptake is noticeably reduced by the treatment. As stated in Section 2.3.3.2 according to British or Dutch regulations, a treatment is only hydrophobic if it reduces the water uptake by 50% or 80% respectively.

The conclusion must be, that this treatment is not hydrophobic.

The combination of visible hydrophobic behaviour and large water uptake illustrates that measurements of large contact angles does not necessarily correspond to low water uptake as explained in Section 2.3.3.2. Therefore instead of using the theoretically term "hydrophobic" the practical term "water repellent" would be more appropriate.

Unfortunately the knowledge of the tiles and the treatment is insufficient. The findings were inconclusive for penetration depth and the chemical composition of the treatment. Furthermore it is possible that differences in the bulk material contribute to the water uptake. And the treatment is not hydrophobic. Consequently are the findings not suitable for tests on hydrophobic treatment.

6.1.3.2 Transport of chemicals

No experiments were conducted to evaluate if hydrophobic treatments prevent transport of chemicals. Based on the findings for water uptake from a free water surface, Section 5.4.1.2 it is unlikely to think that the treatment of the tiles with Lotus Effect would take up less water-soluble chemicals than ordinary tiles.

One observation did indicate some differences in behaviour towards chemicals. Only tiles with Lotus Effect became a white layer at the backside when subjected to water and heat at the front. As described in Section 5.4.3.2 only a less distinct white layer became visible after heating, and was not visible in tiles immersed in water. The layer leads to the following considerations:

- The layer looks like efflorescence, it may be salt

- The layer is water-soluble but could not be detected by SEM/EDX although the samples were prepared water-free.

- The layer only appeared on tiles with Lotus Effect which means that it is either something from the treatment or because the bulk materials are different.

- The layer only appeared on the back of tiles. At tiles exposed to water, as in the outdoor set-up or the tiles used for frost testing, this was natural, because the layer is water-soluble. But the same tendency of only occurring at the back was found at the specimens that were simply dried in an oven. An example of one of these specimens can be seen in Figure 6.7.

If the layer has been the result of salts or minerals being washed out it should not have become visible in the specimens, which were not exposed to water. On the other hand the tiles with Lotus Effect did loose more weight than the ordinary tiles when dried either in the oven or during the frost test. Maybe some of the solvents or water from the treatment was dried out, transporting salts or minerals to the surface. This could also explain why the layer was indistinct with the heated samples, but clearly visible on tiles that had been exposed to heat and moisture on the treated side. As the water uptake in the treated tiles was considerable, it might have transported salts or minerals to the backside of the tile.
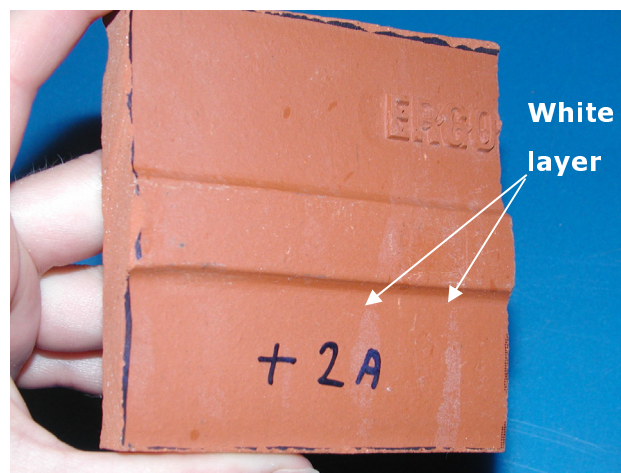
Figure 6.7: Back of tile specimen with Lotus Effect after heating to 90°C,
The tile had not been subjected to water.

Efflorescence would not occur at a hydrophobic surface as there is no capillary transport of liquids in the treated zone. Vasic's (1997) example of scaling on roofing tiles due to hydrophobic treatment (see Section 4.2.3) illustrates this as the tiles were immersed in a hydrophobic liquid to prevent efflorescence at both sides.

Although the chemical composition of the white layer could not be identified with SEM/EDX it is reasonable to believe that the white layer is a form of efflorescence caused by moisture transportation of water-soluble salts or minerals originating from the treatment or the bulk of the tiles with Lotus Effect.

6.1.3.3 Durability

Theoretically hydrophobic treatments change the capillary transport in the treated zone by reducing water uptake and transport of chemicals; both effects that influence the durability of the substrate. The experiments did not include chemical attacks and the supposed hydrophobic treatment did not reduce the water uptake. So, the experiments are unsuitable for evaluating the effects of hydrophobic treatments on durability.

However, the freeze-thaw test could be seen as an accelerated test on durability. As the previous findings revealed that the moisture uptake in the tiles with Lotus Effect was considerably higher than in the ordinary tiles the test was more about whether the treatment would hinder the drying out to an extent where it would be prone to frost damage. The test did not show any frost damage neither in the

ordinary tiles nor in the tiles with Lotus Effect. This test should be seen in combination with the water uptake in tiles as it was registered at the outdoor set-up and reported in Section 5.3.2. During heavy persistent rain the tiles with Lotus Effect took up approximately 200 g of water or $0.2 \cdot 10^{-3} m^3$. Each tile weighs 2.8 kg and the dry density of the tiles is 2065 kg/m^3 with a porosity of 23%. This means that the water in the pores corresponds to:

$$0.2 \cdot 10^{-3} \cdot \frac{2065}{2.8} \cdot \frac{1}{0.23} = 64\%$$

Which is lower than the 70-90% reported by Hansen (1995) as the critical degree of saturation of a tile. The critical degree depends on the actual material and it is unknown how close the tiles are to their critical degree.

From these considerations no frost damage was to be expected.

In true hydrophobic treatments where the water uptake is reduced by at least 50 % the risk of frost damage would be eliminated in tiles because the critical degree of saturation would never be reached.

However, in practise not all hydrophobic treatments are perfect, faults or unsuitable use of hydrophobic treatments can do more harm than good.

6.1.4 Disadvantages of hydrophobic treatment

Despite of the obvious advantages in making surfaces water repellent, there is a widespread scepticism towards hydrophobic treatments based on a conservative attitude and some failures in certain treatments (Sandin 1995). This is not surprising as the building industry is generally sceptical about new technology and processes. This could be because buildings represent a large investment and are supposed to last for many years. Most building owners therefore show little interest in experimentation or new processes. This is in contrast to the fast changing fashion in architecture, towards where some building owners are more daring.

While the risks of experimental architecture in general is beyond the scope of this thesis the following sections will focus on what possible drawbacks there are in the use of hydrophobic treatments.

6.1.4.1 Drying out

The most common concern about using hydrophobic treatments is how it will affect the drying mechanisms. A typical example is a brick wall with or without rendering where the untreated wall will take up water from the driving rain and dry out through the surface. Additional moisture contributions from other sources like rising damp, moisture from the inside or due to minor leakage which also dry out through the surface. The application of a hydrophobic treatment effectively stops the liquid transport to the surface, which means that moisture can only dry out by the much slower process of diffusion.

Künzel & Kießl (1996) undertook measurements and calculations on test elements of brick wall where a hydrophobic treatment was applied to half of the elements. The elements were discontinuous weighed for more than two years. The findings on faults were:

– Small cracks of approximately 1 mm in diameter did not have any noticeable effect on the water content. The cracks were introduced with a wire, while the mortar was still soft and one month before the hydrophobic treatment was applied to some of the elements.

– Larger faults of approximately 30 mm in diameter had a noticeable effect on the water content. Drilling holes in the facade near the end of the test period, and filling the holes with untreated mortar induced these faults.

Krus & Holm (2000) did not test elements but refined the computer simulations by adding a two dimensional calculation, which made it possible to simulate local areas around faults. They simulated brick walls where the outer 2 cm were hydrophobic due to a treatment that also reduced the water permeability by 50 %.

– Flawless treatment. Even in an extreme case of a wet wall and an indoor climate with high moisture content the wall will eventually dry out after several years.

– Faults at a joint. Locally very high moisture contents will appear around the faults as illustrated in Figure 4.2. In a "normal" brick wall the critical saturation degree is not reached. In a very absorbing brick wall, which would not be used without protection, the water content near the faults

would mean risk of frost damage, because the general water content would be high. If the joints are modelled as having a resistive layer (200 times reduced capillary transport in 1 mm) the risk of frost damage is reduced. However if the faults are caused by material loss in the joints, such a layer is unrealistic in those places, but could appear in the faultless joints. In this case the risk of frost damage is the highest.

While Künzel & Kießl (1996) express some concern about their experiments as being too optimistic (conducted at small specimens under controlled conditions by professionals), the examples of Krus and Holm (2000) are negative extremes. The combined conclusion of these two findings must be:

- Not every mm of the mortar has to be tight. It has virtually no influence on the moisture content in treated or untreated walls.

- Larger faults like missing head joints would mean increased moisture content. If the problem is a wall with failing joints then hydrophobic treatments cannot alone be a cure. Without repointing the hydrophobic treatment will not reduce the moisture content. It might even increase the risk of frost damage.

- When repair work is done on hydrophobic walls the holes cannot be left untreated.

The findings illustrate how important the application of a treatment is and underlines the importance of faults in joints.

Accordingly it is a major concern of hydrophobic treatments that they are sensitive toward workmanship and maintenance. If the factor method described in Section 6.1.2.2, despite its weakness, is used for estimation of service life, then the factors C (work execution level) and G (maintenance level) are especially critical.

Hydrophobic treatments will often be applied on site, which makes it especially difficult to ensure the required quality. Simple and controllable application methods must therefore be favoured.

Faults in the hydrophobic layer is one risk that can be minimized by meticulous process but in some cases the application of a hydrophobic agent is inappropriate as treatment would harm the construction. Apart from chemical reactions between the hydrophobic agent and the substrate, which could be avoided by choosing another agent, hydrophobic treatment should be avoided when a considerable amount of moisture forms behind the treatment itself:

−   <u>Moisture from rising damp</u>. Applying a hydrophobic treatment at a surface where moisture from rising damp would normally evaporate could mean that the damp will rise to a higher level and cause new problems.

<u>Before hydrophobic treatment</u>   <u>After hydrophobic treatment</u>

Hydrophobic layer

Accumulation of salts

Evaporation and efflorescence

Evaporation and efflorescence
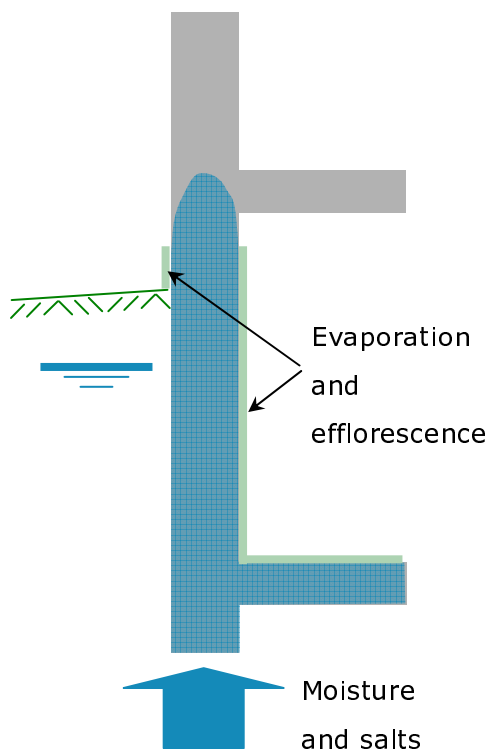
Moisture and salts
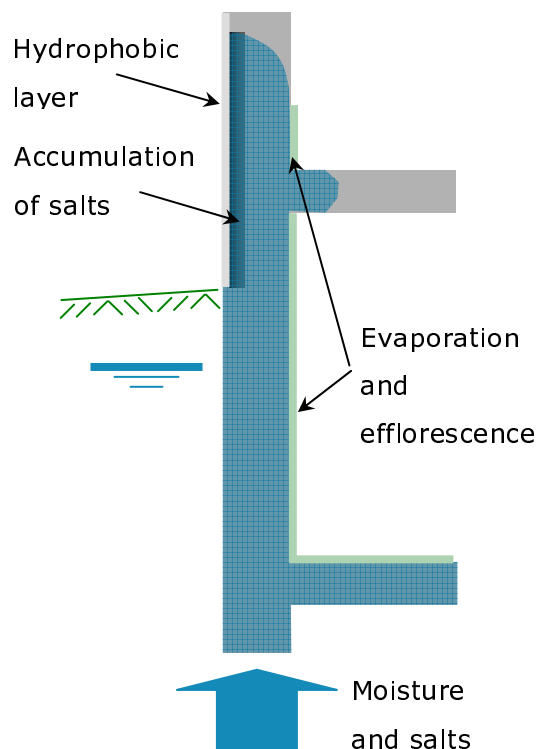
Moisture and salts

Figure 6.8:   Schematic depiction of an example where hydrophobic treatment worsens the case. In the normal case (left), rising damp transports moisture and salt to the surface where moisture can evaporate. Salt efflorescence occurs in the same area. After hydrophobic treatment the exterior salt efflorescence is stopped but inside the problem is increased. The wet zone is larger and not only the basement but also the ground floor will experience walls with high moisture content, salt efflorescence and probably mould growth. Crystallisation of salt behind the hydrophobic zone might cause scaling of the hydrophobic layer.

– <u>Salt transport</u>. Hydrophobic treatments prevent efflorescence. It was the purpose of the treatment in the example of scaling roofing tiles (Vasic, 1997) and is probably why in this study a white layer is only formed at the back of the tiles with Lotus Effect. It shows, that capillary transport is hindered and salts cannot be transported to the surface. In some cases this can be disastrous as salts will accumulate just behind the treated zone resulting in scaling of the hydrophobic layer.

Figure 6.8 show an example of rising damp with salts, illustrating a combination of two situations in which hydrophobic treatments can become disastrous. Hydrophobic treatments are also used as barriers against rising damp. In that case a hydrophobic agent is injected into the construction to form a horizontal hydrophobic layer. Treatments of this kind are beyond the scope of this thesis.

6.1.4.2 Visual appearance

Reasons for choosing a hydrophobic treatment can be functional or aesthetical. An example: the surface of a historic building must be protected against rain but the visual appearance must for aesthetic reasons remain the same. Hydrophobic treatments could meet these requirements while other actions would be visible.

However, hydrophobic treatments are not always invisible. Colour or gloss changes may appear, especially in cases where only parts of a surface have been treated. This situation occurs when hydrophobic treatments have been used as a part of an anti-graffiti treatment or because only some exposed parts are treated. Figure 6.9 shows a Swedish example of a detached wall with horizontal top side. Experience shows that brick walls of this construction in the southern Swedish climate will deteriorate due to frost damage if the topside is unprotected or the top is not sloped. To prevent frost damage the building owner chose to hydrophobiate the upper course. As Figure 6.9 shows, there is a noticeable colour difference between the top course and the rest of the wall. An additional problem is, that just below the treated zone is the moisture content apparently very high as moss growth has started.
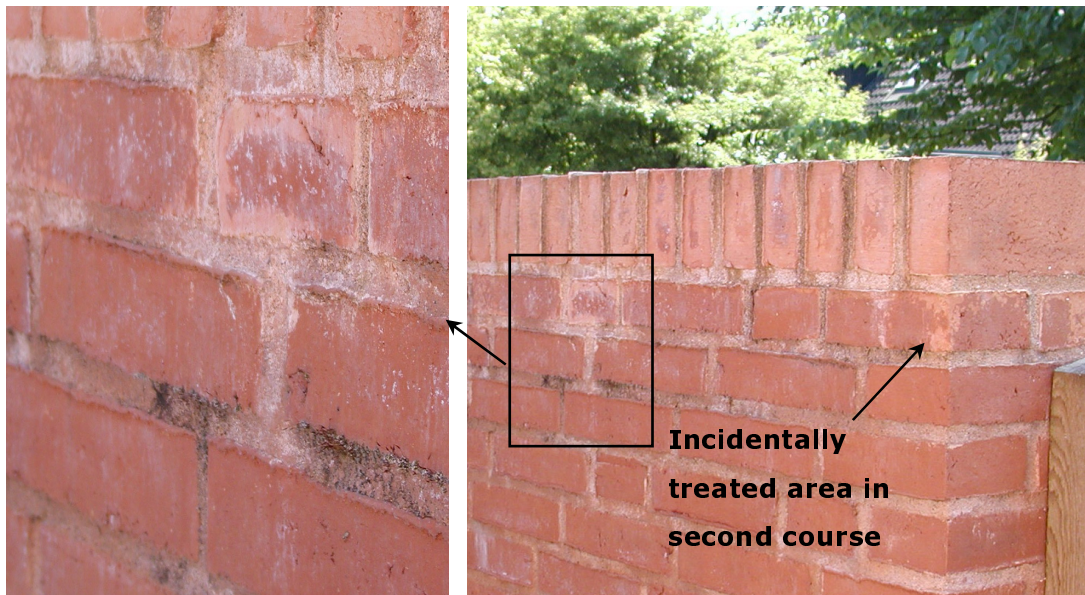
Incidentally treated area in second course

Figure 6.9: Detached wall with horizontal topside, the top course was treated with hydrophobic agent to prevent frost damage. There is a noticeable colour difference between the two areas, in some areas the treatment has run down the next course. The picture was taken when the wall was dry. Notice the moss growth under the treated zone (enlargement to the left).

6.1.5 Thermal conditions

Although there was no information on changed thermal properties of tiles due to the Lotus Effect the experiments in this study showed a small difference in emissivity and possibly also in absorptivity, although the latter was not tested. Daytime measurements of the surface temperature in the sun indicated that the Lotus tiles were warmer than the ordinary tiles. The small colour difference in the tiles, as the Lotus tiles were slightly darker than the ordinary tiles, could be responsible for this difference. But also the different surface roughness of the two tiles would act this way because increased surface roughness increases the absorptivity (see Section 2.4.1.1). In this case the size of the protrusions is approximately 25 μm which is considerably larger than the wavelength of visible light (0.4 - 0.8 μm) and therefore effective in hindering direct reflectivity as the reflected photon is likely to hit a protrusion instead of being reflected directly.

The absorptivity has no influence during the night but probably due to a lower emissivity the tiles with Lotus Effect were warmer than ordinary tiles. The

measurements were conducted during a clear summer night, with a roof of low slope (12°) the difference was approximately 1°C.

The measurements of the actual emissivity of the two tiles were not very precise, and the results did not seem reasonable. Both emissivities seem to be too high. It is therefore not possible to determine how much the Lotus Effect diminishes the emissivity.

The protrusions are only larger than the wavelength in a very small part of the spectrum of long wave radiation. The effect of the enhanced surface roughness will therefore be relatively small. There most be other reasons for the lower emissivity perhaps the hydrophobic treatment incidentally lowered the emissivity.

The development of well-performing low emissivity paints seem to be in progress, while the findings of Stopp et al. (2001) showed that the promised low emissivity of one commercially available paint could not be verified, Leonhart & Sinnesbichler (2000) have tested paints from "first and second development phase" and have found noticeable improvement in the paintings.

6.1.5.1 Possibilities

Hopefully, well-performing low emissivity paints combined with high absorptivity will become commercially available because there are some promising perspectives in their use in cold climates:

- <u>Energy savings</u>. Other researchers have found possible energy savings of up to 20 %. This however seems unrealistic in modern constructions with insulation layers. In the winter savings below 2 % seem more realistic. The difference in heat flux will in the summer be considerably larger which might cause cooling problems, see Section 6.1.5.2.

- <u>Surface temperature</u>. The surface temperature is on summer days raised approximately 15°C (week average 5°C) and in the winter approximately 1° during the day, and weekly average 0.5°C. This may be helpful in preventing biological growth, see Section 6.2.1.1. It also means shorter periods with condensation at the surface.

- <u>Moisture content</u>. In the winter the moisture content is up to 50 % lower, which is important when considering frost damage.

The most effective change in properties is lowering the emissivity as this reduces the moisture content in the winter considerably. Unfortunately this property is difficult to maintain; dirty surfaces have high emissivity and absorptivity. Therefore these achievements are probably on the optimistic side. Whether the effort in obtaining these properties is worth the gain must be evaluated individually, because the barriers are considerable.

6.1.5.2 Barriers

Although the advantages in changing absorptivity is known e.g. in the white colour of houses in warm climates a consciously change of emissivity and absorptivity is not normal, either because the problems are too great and the gains too small. The major problem in using low emissivity and high absorptivity is the increased need for cooling in the summer and the low heat gain in the winter. As the energy consumption for cooling normally is much higher than for heating the net gain could be negative.

Problems of thermal stress will in some constructions be a barrier. Facades with exterior insulation and a thin rendering on top are an example. The extra energy load will be absorbed in the thin rendering that will become very warm, which increases the risk of cracking.

Generally monolithic constructions will be more positively affected by the use of surface treatments with low emissivity and high absorptivity than constructions with more layers where the difference between exterior and interior is changed abruptly.

6.2 Soiling

If favourable surface properties in terms of hydrophobicity and low emissivity have been obtained then a long-term effect can only be achieved if the surfaces are kept clean. Regular cleaning of roofs and facades is costly and might even destroy the surface layer that has the desired properties. Self-cleaning properties would be favourable and different possibilities have been described from a theoretical point of view in Section 3.4. In this section the results from the experiment of this study will be used on soiling and cleaning in general.

The experimental set-up was only exposed for approximately 2½ years. The tiles did soil in that time but only due to biological growth. Soiling from environmental particles either did not take place or was overlapped by the biological growth.

6.2.1 Biological growth

Different kinds of biological growth have been described in Chapter 3. Despite differences in species and even genera most biological growth have similar needs for survival:

- Nourishment, which can be more or less abundant but normally always accessible

- Moisture, generally the more the better, although this may favour some species on the expense of others

- Heat, most species prefer temperatures between 5 and 30°C

- Light, except for moulds, biological growth need light to photosynthesize.

Some species are first-colonizers others will come later but which biological growth will appear at surfaces basically depend on the combination of the above.

In the soiling test with ordinary and Lotus tiles, none of the conditions above were altered artificially. The only differences that occurred were caused either by the differences in the tiles or the slope and orientation of the set-up.

6.2.1.1 Heat and moisture

Due to the sunlight one would expect that the south-facing tiles would be warmer and drier than the north-facing tiles and that both conditions that would inhibit growth. It was expected, that the north-facing roofs would soil faster through biological growth than the south-facing roof. This hypothesis was corroborated by the experiment.

Only a few surface temperatures were measured. With the south-facing tiles, on a sunny summer day these were about 50°C. Lotus tiles were approximately 1°C warmer than the ordinary tiles. The north-facing roofs with a steep slope had temperatures which were approximately 15°C lower than at the south side. Also here the tiles with Lotus Effect were approximately 1°C warmer than the ordinary tiles.
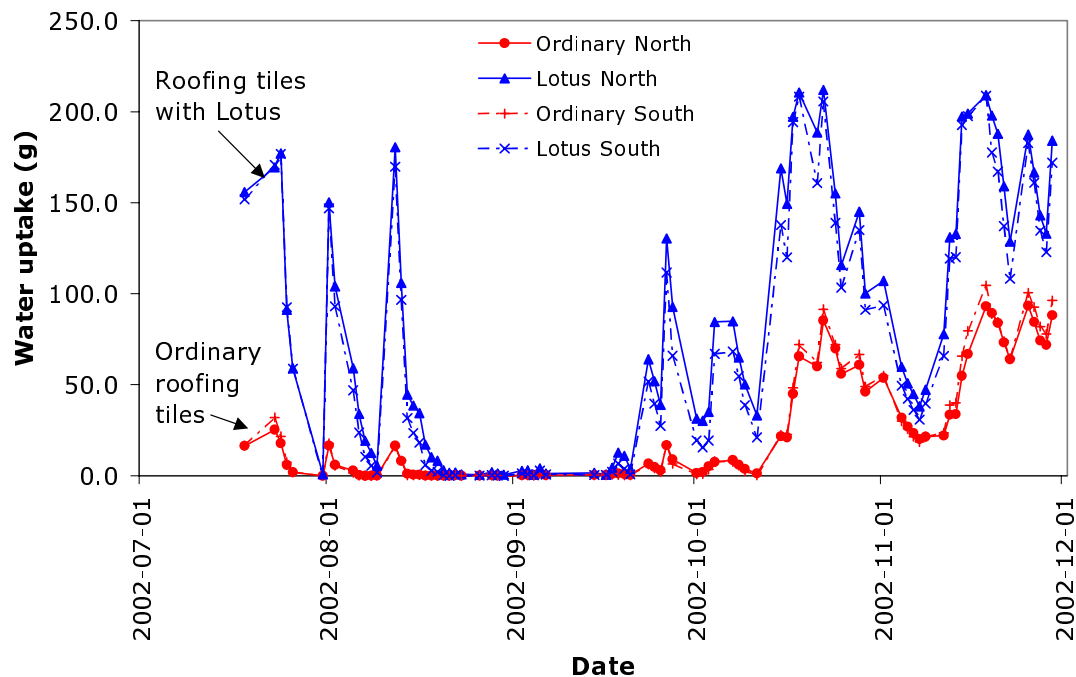
Figure 6.10: Measurements of water uptake in tiles with and without Lotus Effect, depending on their orientation. The differences in orientation are small, only the north-facing tiles with Lotus Effect are up to 20 % more wet in the autumn months than the south-facing tiles. The ordinary tiles have only small differences, where the south-facing tiles tend to be wetter.

Measurements on the moisture content of north and south-facing tiles are more abundant. Figure 5.8 showed the differences in the moisture content of ordinary tiles and tiles with Lotus Effect during almost five months. Measurements from all four roofs were pooled as there were only small differences. Figure 6.10 shows the lines split up in north and south measurements.

While the differences in the ordinary tile is very small with a tendency to larger values in the south-facing. The differences in the Lotus tiles is somewhat larger in autumn where the north-facing tiles contain up to 20% more water than the south-facing tiles.

If these findings are compared to the biological growth on the two types as shown in Figure 6.11, the difference is noticeable. The south-facing tiles, whether treated with Lotus Effect or not, are practically without soiling, while the north-facing tiles are covered with biological growth.

The result of these comparisons must be that it is the not the moisture content in the tiles but the surface temperature which is decisive for the growth of algae. It is unlikely, that other effects differ in the set-up, as it was placed in a relatively open space. The low sloped roofs soiled less than the steep sloped. This can be explained by the direct sunlight as the sun will for some time shine at north-facing roofs with a 12° slope, and considerably less at roofs with a 45° slope.

Consequently, surface properties that increase the surface temperature will also reduce the soiling. This means the perspective in high absorptivity and low emissivity are not limited to thermal performance but will also influence the susceptibility to soiling.

As the tiles with Lotus Effect also seemed warmer at the north side, based on thermographical pictures. The differences in soiling performance, as discovered with LED technique, could not be caused only by the Lotus Effect but also to some extent by the surface temperature.

In Figure 3.5 where the growth of bacteria and fungi is compared to precipitation and temperature in the Montreal area it seems as if both parameters have an influence. The bacteria growth follows more closely the precipitation line with its bimodal shape. While the fungi growth corresponds to the temperature curve. The fungi growth continues after the temperature starts to decrease, which confirms that fungi growth need better living conditions to initiate growth (spore germination), but are able to continue growth (myzel growth) at a lower level (Sedlbauer, 2001).

Assuming biological growth is independent of moisture would be wrong. The visual observations have showed, that the biological growth is accelerated in the autumn, which corresponds to the findings of Lighthart & Mohr (1994) (Figure 3.5), and coincide with the higher moisture content in October-November. At surfaces where biological growth is ongoing the higher moisture content and moderate temperatures enhance the growth.

The biological growth at the tiles in this study is limited to algae. Despite many similarities in the species and genera of biological growth other species might act

differently e.g. lichen are very robust and may not be that sensitive to temperature differences.

Tiles with Lotus Effect **Ordinary tiles**
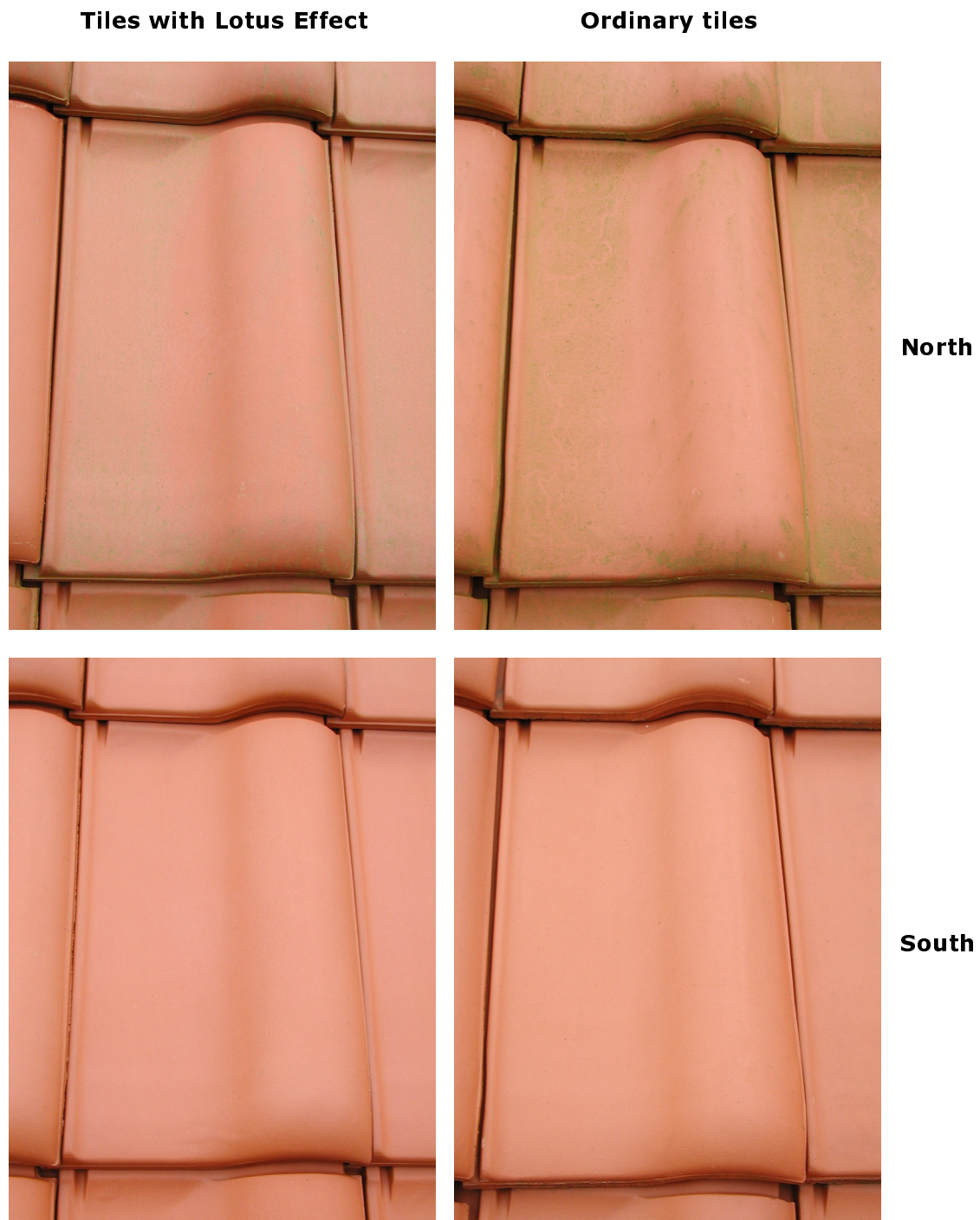

North

South

Figure 6.11: Differences in soiling depending on orientation and treatment (steep slope). South-facing tiles are clean, while north-facing tiles are green, due to biological growth. The tiles have been exposed for approximately 2½ years.

6.2.1.2 Bioprotection or biodeterioration?

The tiles used in the experiments were only exposed for approximately 2½ years. Although some were covered with biological growth the surface was not altered, as the SEM pictures in Figure 5.16 show. After longer exposure the surface would have started to deteriorate. Tiles with and without soiling could have been examined e.g. with SEM to determine if the surface change depended on soiling. Still it would have been difficult to decide whether the soiling appeared on specific tiles because the surface was different from the beginning or because the biological growth had changed it. If the difference in soiling was based on the orientation of the tiles then surface changes were likely to be caused by the soiling, or the lack of soiling. The latter outcome would mean that the soiling is protecting the surface.

Frambøl et al. (2003-d) have made thin sections of different tiles, with and without soiling. Unfortunately the aim was not to determine deterioration by soiling but the effect of surface roughness on soiling. The findings show that biological growth is more abundant on rough surfaces than smooth. But why some of the tiles are rougher than others is unknown.

The question as to whether soiling is a failure has been described in Chapter 3 where soiling was seen as a failure because it eventually will reach a point where it becomes unacceptable either for aesthetic or functional reasons. Nevertheless the concept of bioprotection (or protection by other kinds of soiling) is important when estimating the time before the failure is evident. If some soiling can be accepted and this soiling acts as protection then the service life would be substantially enhanced. An example is shown in Figure 6.12.
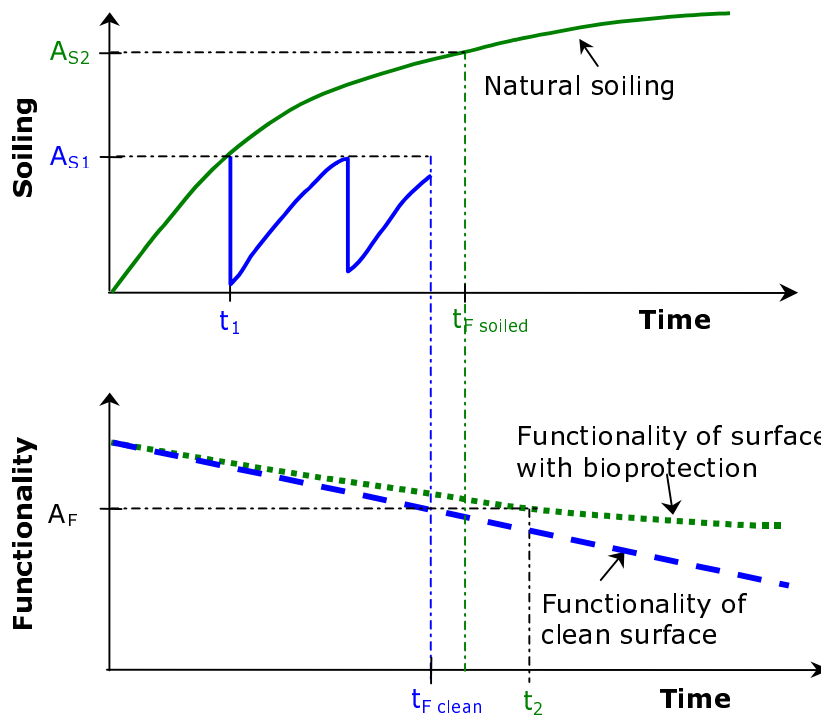
Figure 6.12: When estimating service life, criteria for failure should be defined, in this example two criteria are set: A_S defines the accepted soiling (top), A_F defines the accepted functionality (bottom). As times go, two lines will be followed simultaneously, a full line for soiling, and a dashed or dotted line for functional failing. Whichever crosses the corresponding line (e.g. full line compared to A_S values) first determines the service life. The soiling line is similar to Figure 4.8. In the cleaned case the beginning of the soiling curve will be repeated, but with a starting point lower than at the beginning, as the surface will not be fully cleaned. Time of failure is given by t_F

The example illustrates how a high acceptance level A_{S2} can result in longer service life also from a functionality point of view. In this case the surface with low soiling acceptance will have to be cleaned at the time t_1, and once again before it fails functionally at t_F. The high soiling acceptance result in a service life of $t_2 > t_F > t_1$. I.e. in case 1 the surface must be cleaned twice and at the 3^{rd} cleaning also repaired. In case 2 soiling also determines the service life but it is longer than t_F for the first case. Nevertheless will the surface probably be repaired when cleaning is initiated.

If the surface is deteriorated instead of protected by soiling then the dotted line in Figure 6.12 will be below the dashed line. Although the cleaning in case 1 will start at the same time, cleaning will prolong the time before repairs are necessary.

As the example of Figure 6.12 illustrates; before estimating service life, the criteria of failing must be defined not just single values but also underlying concepts e.g. whether cleaning is maintenance (part of factor G) or end of service life.

In service life prediction by the factor method the soiling influence will be at several factors not only the Factor E (Outdoor environment) but also in more or less controllable factors like e.g. factor A (Quality of components) in this case susceptibility to soiling and Factor B (Design level), is the design in a way that the surface is more or less exposed. Factor G (maintenance) has already been mentioned and other factors might be influenced as well.

Basically one would have to consider not only susceptibility of the surface to biological growth but also how vulnerable the substrate is to the influences of soiling, e.g.:

- A <u>porous substrate</u> with an open surface will make it easier for some endolithic microorganisms to penetrate the substrate with their hyphae, rhizines or spores. On the other hand these surfaces are often vulnerable towards abrasion against which soiling might protect.

- <u>Resistance to chemical attacks.</u> Algae and lichen release mostly acidic metabolites. Environmental soiling can also contain chemicals that might attack the surface e.g. sulphur.

- Sensitivity to <u>thermal stress</u>. Biological growth will often retain water and in doing so reduce the thermal stress.

- <u>Aesthetic change.</u> How visible would soiling be at the given surface. Would it cause aesthetic problems?

- <u>Risk of soiling.</u> This must be considered if the area where a given surface is to be used has an increased risk of soiling, e.g. high levels of NO_x or environmental particles.

Many of the investigations on biodeterioration and deterioration are based on findings for historic monuments, often made of sandstone, limestone or granite. Frambøl et al. (2003-b) point out that these monuments are often considerably older than what would be seen as normal service life. The findings on biodeterioration and bioprotection therefore represent extreme cases. The problem should really be compared to the estimated service life of the construction. Based

on this Frambøl et al. (2003-b) conclude that the deterioration processes have no functional consequences, at least not in brick walls or tile and concrete roofs. The problem is an aesthetic one.

This is true for many private houses but for the larger public projects required service life can be 50-100 years and many will be renovated after that time. Furthermore the aesthetic problem will be solved by cleaning and, as stated in Section 4.1.4.2, the combination of early biodeterioration and cleaning will increase the deterioration. Protection or deterioration resulting from soiling should therefore be considered when making service life estimates.

6.2.2 Self-cleaning properties

Instead of dealing with soiling, deterioration and recurring expensive and harmful cleaning any soiling is best prevented. The effects of low adhesive treatments have been discussed in Section 6.1.1.2. The statements about silicon-based and flourine-based polymers are not just valid for molecules but also for particles and, to some extent, to biological growth as the treatments will inhibit biological growth in finding footing at the surfaces.

Graffiti is a special kind of surfaces soiling. It is a rapid solvent-based soiling of a well-defined area; quite different from "natural" soiling. A typical precaution against graffiti is an anti-graffiti treatment, which eases the cleaning. The treatment must therefore not only be water and oil repellent but also have easy to clean properties (Weißenbach et al 2001). The wide field of anti-graffiti treatments will not be considered further in this thesis.

Instead this section will discuss the processes in natural soiling at a μm scale. Also how water runs off with the potential to remove soiling on its way. The influence of surface roughness is also discussed because this is the principle of the tiles used in the tests.

6.2.2.1 Water run-off

In Section 2.3.3.2 it was stated that contact angle measurements, which is the theoretical definition of hydrophobicity, is only of academic interest while the water uptake is what the practioner is interested in. In this case the difference is of special interest, because the main goal of the tiles with Lotus Effect is to keep the
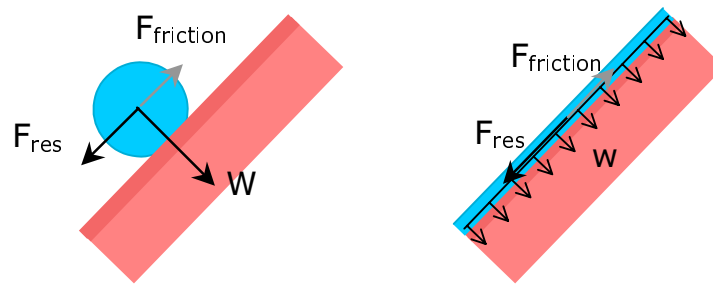
Figure 6.13: Forces acting on water running from two different surfaces, left: hydrophobic, right: hydrophilic with complete wetting.

tiles clean. For this purpose the hydrophobic effect is necessary i.e. forming of beads, which run off taking any dirt with it. Water uptake is less important if the durability is unaffected.

However, the findings show that there is less water to remove dirt from the tiles with Lotus Effect than from ordinary tiles. This might not be that critical, the difference is approximately 5%, if water beads are more effective as dirt removers than a continuous film of water.

A simple mechanical model is illustrated at Figure 6.13. Two possible situations: A: a hydrophobic surface with large contact angle; a droplet slides down the substrate. B: a hydrophilic surface with complete wetting; a film slides down the substrate. Gravity acts on the large single droplet and on the water film. Amontons' law (Adamson, 1990) says:

$$F_{friction} = \mu W \qquad\qquad (6.2)$$

where $F_{friction}$ = frictional force, W = load and μ = frictional coefficient. Consequently the frictional force is independent of the area. When the amount of water is approximately the same the only difference is in the friction coefficient.

Voué & De Coninck (2000) have on a molecular scale described how wetting and friction between liquid and substrate are interconnected as a balance of two terms:

- The <u>affinity</u> of the liquid for the solid. If the liquid-liquid interactions are smaller than the liquid-solid interactions, the liquid will wet the surface

- The <u>friction</u> between the solid and the liquid. Friction slows down the wetting process

Used in the case of water running on tiles with Lotus Effect and ordinary tiles the following considerations can be used:

- <u>Affinity</u>. The ordinary tiles are polar and the treated tiles are non-polar because of the treatment. Water is a polar liquid which means the affinity of water is higher with the ordinary tile.

- <u>Friction</u>. The friction between the surface treatment and the water is likely to be reduced compared to tile/water friction because silicon-based polymers (fluorinated or not) are often used as lubricants. On the other hand the protrusions will increase the friction.

Based on this it is not possible to determine whether the friction coefficient is lower or higher on the tiles with Lotus Effect. But at surfaces with the same texture the friction would be expected to be lower thereby increasing the downward force, i.e. the droplets will move forwards more powerfully than a film. The self-cleaning potential of single droplets is therefore larger than films.

However, at e.g. windows, which have to be transparent a hydrophobic treatment where single droplets run off would cause visible stripes on the glass. Only a film would clean the surface uniformly. To obtain this a special glass with a thin transparent coating which makes the surface photocatalytic and hydrophilic has been developed. The photocatalytic effect means that UV-radiation from daylight reacts with dirt and organic deposits, oxidises them and breaks their adherence to the surface. Due to the hydrophilic surface raindrops spread as a film on the surface ensuring that the loosened particles are washed off during normal wet weather (Pilkington, 2001).

The idea of self-cleaning properties without stripes could be appealing in other cases too. But it should only be used at non-porous surfaces otherwise the water uptake in the material would be larger because the capillary suction is enhanced.

6.2.2.2 Surface roughness

The idea of the Lotus Effect is to combine hydrophobicity with surface roughness and thereby create "super hydrophobicity", as shown in Figure 2.15. Because of the protrusions dirt particles will only have little contact to the surface. As droplets run off the surface, they are supposed to capture the particles.

The difficulty in capturing small particles trapped between the protrusions is described in Section 3.4.1.2 and the results of the experiment have not made the effect more convincing. The SEM pictures of new surfaces of tiles with and without Lotus Effect are shown in Figure 6.14.

At the top pictures in Figure 6.14 the surface of the ordinary tile appears to be rougher than the Lotus surface, but at the larger magnification in the bottom of the figure the impression is quite the opposite. Here the protrusion looks like a single particle at a surface consisting of very small protrusions. These are even smaller than the ones described in the "natural" lotus effect. With the ordinary tile the surface looks very smooth.
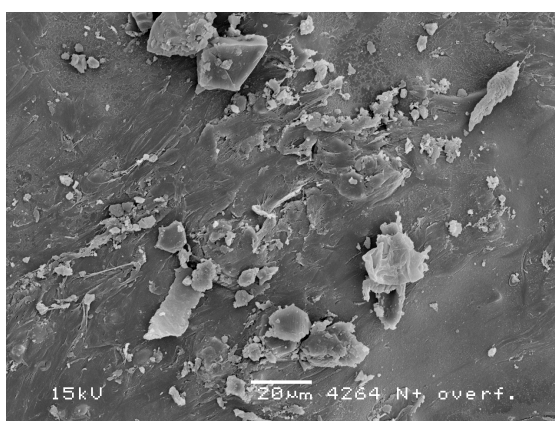
Tiles with Lotus Effect   **Ordinary tiles**
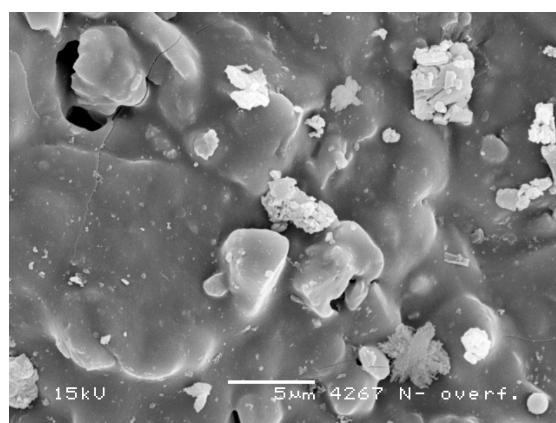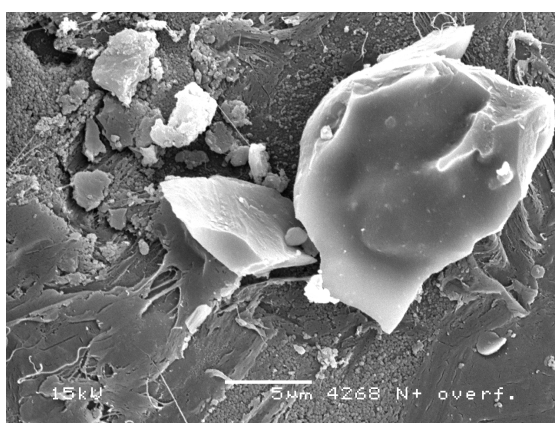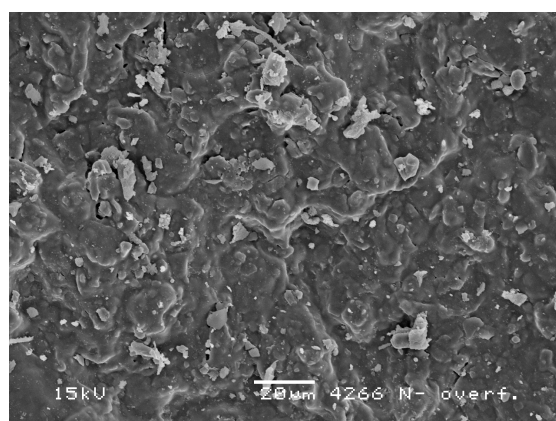

Figure 6.14: SEM pictures of Surfaces of new tiles with and without Lotus Effect. The pictures are also shown in Figure 5.16 but are also shown here in a larger size for clarification. Barr equals 20 μm in top photos and 5 μm in bottom photos.

The surface of the tile with Lotus Effect is described in the patent (European Patent Office, 1998-a) as a surface with protrusions preferably in the size of 10-50 μm with a spacing of 10-100 μm. Although the heights are difficult to determine from the pictures of the cross sections (not shown). This makes it reasonable to believe that the surface treatment used on the tiles is similar to the Lotus Effect.

The visible inspections of the tiles revealed biological growth with both types after a year of exposure. The growth seemed delayed at the tiles with Lotus Effect but was still visible. One year later the soiling was a lot more visible with both types. The delaying effect of the Lotus treatment was consequently shorter than a year. Only few measurements were made on the colour differences with the two tile types but the tendency was for the edges of the ordinary tiles to be considerably more soiled than the tiles with Lotus Effect. At more regular areas where the velocity of the water running off the tiles is larger, the differences were smaller. The measurements in the flat area (Area 2 in Figure 5.5) do not seem reasonable. They show that the new tiles are more soiled than the exposed tiles. In the LED technique the same threshold value was chosen for all pictures, but for area 2, this seems to have omitted almost all soiling. The visible inspections showed soiling in that area as well, see Figure 6.11.

When water runs off a surface with Lotus Effect the droplets might be caught in the irregularities of the edges, thereby stopping the transportation of particles. Therefore the Lotus Effect will theoretically be most effective where water runs free, i.e. at surfaces with a high slope and no interruptions. If the Lotus Effect was self-cleaning, then the middle of roofing tiles on a roof with a slope of e.g. > 25° (limit for roofing tiles without underroofing) would be clean; at least for a longer period.

But visible inspections do not support this. At the test area and at the inspected houses with Lotus tiles as roofing soiling was clearly visible at the regular parts, even more abundant in these areas. See Figure 6.15.

Figure 6.15: Tiles with Lotus Effect. Even at relatively high slopes, approximately 45° the regular parts of the tiles are soiled by biological growth after two years of exposure. Left: north side of roof near a pig farm. Right: north side of roof, notice that the protected tiles under the eaves are clean. From the same house as Figure 6.5 (located close to a bay).

The right hand picture in Figure 6.15 is interesting because it shows tiles that are protected by the eaves of another roof, although no water runs off and transports particles away, these tiles are clean. The reason must be that no biological growth starts at the tiles because insufficient water is available. Compared to the exposed parts this means that the hydrophobicity of the tiles does not prevent them from becoming wet. The amount of moisture at the surface is enough for the microorganisms to establish themselves. This corresponds to the findings of the experiments described in Section 5.2.2.

The conclusion must be that in areas with high risk of biological growth the Lotus Effect only delays soiling for a short while (less than a year). The self-cleaning properties are insufficient to prevent soiling within two years.

6.2.3 Cleaning

Because of the relatively short test period no experiments were conducted on cleaning and resoiling. The discussion on these topics will therefore be based on the findings of others, as described in Section 4.1.3 and 4.1.4, combined with the problems discussed in this chapter because cleaning is not only a soiling related problem but also influences the hygrothermal surface properties.

6.2.3.1 Acceptable soiling

From a social point of view it is the aim of the building industry to create aesthetic, functional, healthy and economical optimized buildings. Surface treatments as they have been described in this thesis influence on all four of those parameters:

- Aesthetics: the aesthetic performance of a building is highly dependent on the surface appearance

- Functionality: Treatments that improve the performance of the building envelope e.g. by preventing water ingress increase the functionality

- Health is related to functionality. The choice of surface treatment can effect the health of the building users because the water content can be altered thereby increasing the risk of biological growth on the interior surfaces.

- Important factors in economical optimization are: Durability, maintenance and operational costs. Which are all influenced by the surface treatments discussed here.

However these properties will be negated if the surface is soiled. But exterior surfaces will always soil and the acceptable amount of soiling must therefore, based on all of these considerations, be defined.

In Section 4.1.4.1 it was stated that surfaces normally change appearance long before they loose their functionality. This is true in a traditional sense in that; they do not break down, threatening the strength and stability of the structure, without very visible changes in appearance. But some of the functionality, e.g. based on differences in μm size or atomic forces is more sensitive to soiling and might be lost before the visible changes become aesthetic offensive. In service life predictions this is yet another factor to consider.

Soiling can consist of many different things, consequently can the changes induced by soiling differ. However, the general influences on the parameters discussed earlier are:

- <u>Contact angle</u>. Most "natural" surfaces are polar. Soiling would therefore tend to make surfaces more polar, which would mean *low* surface angles. The affinity of water to wet the surface is high.

- <u>Water uptake</u>. Microorganisms need moisture to grow, and will therefore *retain* water. This point is disputed by the findings of Frambøl et al. (2003-b) as stated in Section 3.1.1.2, where an alternative interpretation of their findings of enhanced evaporation from tiles with biological growth is given as well.

- <u>Adhesion</u>. Work of adhesion is given by Equation 2.11, which states that the surface free energy is the determining factor. Only a few materials have surface free energies below 30 mN/m. If the treatment was chosen for its low surface energy it is likely that soiling will *increase* the work of adhesion.

- <u>Absorptivity and emissivity.</u> Both factors are *high* (> 0.90) in dirt.

If these considerations are used at the tiles with Lotus Effect then the break down of the functionality of the Lotus Effect would be:

1. Small particles or microorganisms are trapped between the protrusions probably also at the protrusions because these are not rounded but with edges, see Figure 6.14.

2. Because of the soiling the hydrophobicity is decreased. According to Equation (2.8) the protrusions will diminish the contact angle even further when the contact angle becomes less than 90°.

3. Eventually the tiles will be reduced to tiles with small protrusions.

In the tiles investigated in this study, this process is not concluded. From the visual inspections it can be seen however, that tiles with Lotus Effect at slopes lower than 25° soil in a typical pattern (see figure 5.3 and Figure 6.5). Apparently the droplets at the rounded area of the tile do not run along the tile but across it to the flat area where it then runs off. This means that the washed off particles and microorganisms will be transported to the flat area thereby increasing the risk of entrapment in that area. The phenomenon can be seen at Figure 6.16. There is a noticeable stripe along the tile, which is the starting point of the visible soiling.
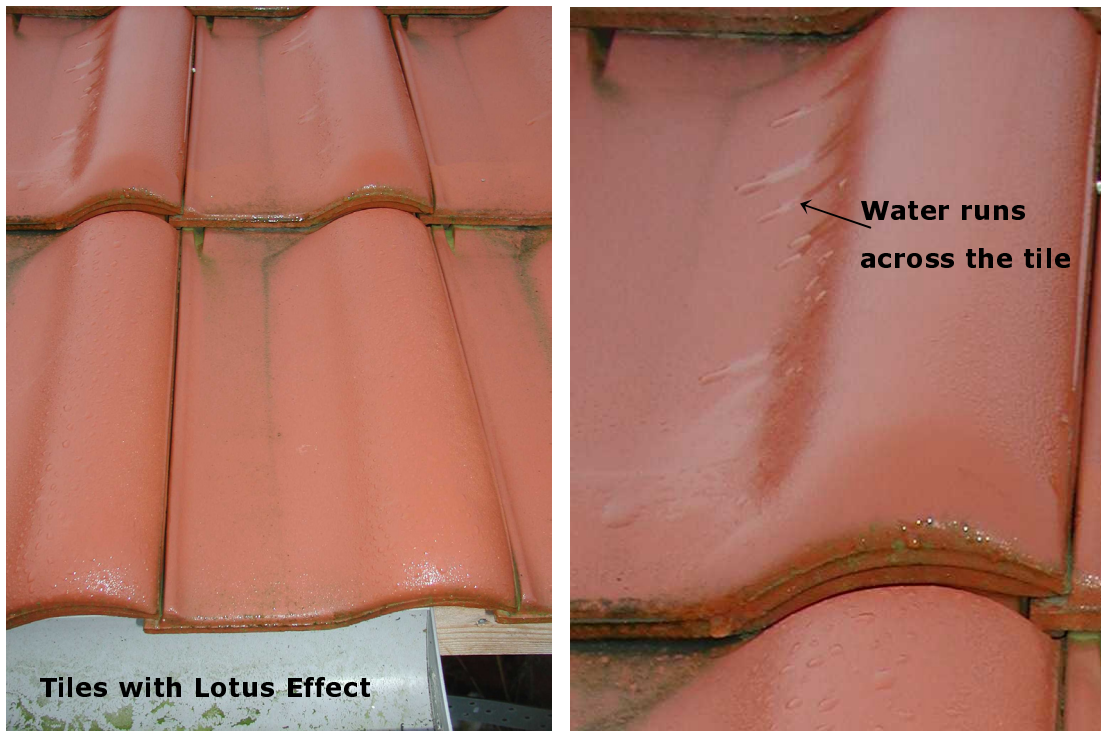
Figure 6.16: Soiling at low sloped roofs with Lotus Effect. Right a magnification of the upper left corner of the left picture. Instead of running along the tile, water droplets, transporting particles and microorganisms, run across the tile to the flat area, from where it runs off. The soiling material becomes will be concentrates in the flat areas, especially on the lower tiles. Some of the material sticks to the surface and forms a stripe of soiling.

6.2.3.2 Restoration of surface properties

If the Lotus Effect is only inhibited by soiling it should be possible to regain the effect by cleaning the surface. By primitive experiments with water and brush only very little of the visible effect of a hydrophobic treatment could be recreated. Either the effect has deteriorated and is simply not existing anymore or soiling adheres to the surface in a way that makes it difficult to remove by hand. The latter explanation corresponds to the "Hierarchy of spontaneous adsorped layers" as shown in table 3.3. The algae growth can easily be removed. It is a C-layer. Parts of the soiling are more strongly attached to the tile and cannot be removed without destroying the interface between tile and soiling (B or A-layer).

Consequently the surface will not regain its properties to the full through a cleaning. Bretz & Akbari (1997) have shown that in high albedo roofs that had lost

20 % of the high albedo through dirt. Rubbing with soap recovered 90 % of the albedo. But simply hosing the roof was ineffective. The conclusion was, that the energy savings were smaller than the cost of hiring someone to clean the roof. Because dirt accumulation can occur over a relatively short time the effect of any cleaning is of short duration.

Self-cleaning properties that are hindered by soiling are non-effective and generally not worth restoring. On the other hand, other surface properties may be more important and cleaning could be a possible way to recover these lost properties. However, as described in Section 4.1.4.2 there are many risks involved in cleaning surfaces. Mainly the risk of deteriorating the surface by the use of rough methods by attempting to not just remove the C-layer. In the case of not "just" removing soiling for aesthetical reasons but to regain surface properties it must be considered how the properties were obtained and if they will survive a cleaning. E.g. would the penetration depth of a treatment be sufficient after a surface cleaning that might not only have removed dirt but also some of the substrate. In many cases a new application will be necessary.

Finally there is the risk of accelerated resoiling after cleaning (see Figure 4.9), which makes the reasons of cleaning questionable.

Instead of a less frequent but thorough cleaning process it may be that less extensive but more frequent cleanings could minimize the risk. More preferable would be materials with self-cleaning properties, which can be combined with other properties e.g. low emissivity. This would be similar to a continuous gentle cleaning.

6.3 Parameters to evaluate before applying a surface treatment with designed properties– a summary

The discussion of the experiments in this study and findings of other researches can be summarized into the most decisive parameters, which should be evaluated before choosing a treatment with designed surface properties. However, it should be remembered that sometimes it is unadvisable to use a surface treatment. In the list it has also been evaluated if the desired properties can be obtained by the available treatments of today. This evaluation is subjective but is based on the experiments done in this study and descriptions in the literature.

Many of the parameters listed under "Things to consider" are critical in service life prediction, but the list is in no way complete.

A:	Hydrophobic treatments
Things to consider	– What is the moisture source? The treatment is primarily to stop water ingress from rain and splash – Porosity and pore size must be compared to the molecule size of the treatment – Surface free energy of the treatment; the lower the better – Possible chemical reactions with the substrate – Penetration depth; primarily obtained by the application
Pro	– Reduces the moisture content – Reduced transport of chemicals The combined result of the above is improved durability
Contra	– Changes the drying conditions as capillary transport is inhibited – Sensitive to workmanship
Realistic today	Yes, but still room for improvements

B:	Low emissivity (long wave), high absorptivity (short wave)
Things to consider	– Sensitive to soiling – The thermal capacity of the exterior layer
Pro	– Reduces algae growth – Reduced moisture content in the winter – Less hours with subcooling
Contra	– Increases cooling demands in the summer – Induces thermal stress
Realistic today	Still under development but promising

C:	Self-cleaning
Things to consider	– The susceptibility of the substrate towards soiling
	– Risk of soiling
	– Consequences of soiling
	– Surface free energy of the treatment, the lower the better
Pro	– Reduced soiling-induced deterioration
	– Expensive and damaging cleaning can be avoided
	– Achieved surface properties are preserved
Contra	– Less patina
Realistic today	Not at this point, at least not on porous materials

Table 6.1A-C: Summary of the discussion, divided in three different types of surface treatments although these might be combined.

7. CONCLUSION

The thesis started out with the hypothesis:

By changing surface properties the hygrothermal performance of the building envelope can be improved

This hypothesis has been corroborated, with the addition, that it is only possible to maintain the changed surface properties if the surface is clean and intact. Therefore soiling, self-cleaning properties and surface influence on durability have also become important factors.

Most of the findings corroborating the hypothesis are based on theory and simulations. But when applied to the complexity of the "real world" many practical problems arose. The main experiment in which ordinary tiles were compared to tiles that were supposed to have a self-cleaning hydrophobic surface was rather discouraging. Both tile types were visibly soiled during the 2½ years of the experiment and the water uptake was largest in the treated tiles. However most of the findings could be explained within the theory and the general conclusion on the experiment is that this particular surface treatment was neither self-cleaning nor hydrophobic.

Nevertheless the outcome of this project is more than this simple statement. The project has granted more general insight in the aspects – positive and negative - of designed surface properties. Moreover, the work has inspired new ideas for the further development of designed surface properties.

In the following sections positive and negative aspects are marked by + and ÷ respectively.

7.1 Reduced moisture content or transport in the uttermost surface layer

+ By applying a hydrophobic treatment, which reduces the water uptake through the treated surface by more than 50 %, the conditions of an exposed surface are similar to a protected surface with no driving rain. I.e. the moisture content will be noticeable reduced in the winter.

+ A low emissivity coating reduces the moisture level in the winter by approximately 50 %.

+ Less water uptake can theoretically be achieved by large contact angles, which is obtained if the surface free energy is low. Large contact angles however, do not always mean low water uptake.

+ Less moisture transport means less transport of water-soluble chemicals

÷ Hydrophobic treatments prevent capillary suction, which means drying through the treatment will be by diffusion i.e. a slower mechanism.

Lowering the moisture content by 50% means that the risk of frost damage is virtually eliminated.

No single hydrophobic treatment can be used for all substrates, e.g. the molecule size of the treatment must be smaller than the pore size. Unfortunately the surface free energy is generally lower in larger polymers i.e. large alkyl groups in silane / siloxane or many CF_3 groups in fluorinated polymers. Hydrophobic treatments are sensitive to workmanship and application method. The long-term efficiency is based on the penetration depth, which also depends on molecule size of the treatment. But most importantly long-term efficiency is increased by prolonged contact time.

7.2 Higher surface temperature

+ Changing the emissivity increases the surface temperature, on summer days approximately 15°C (week average 5°C) and in the winter approximately 1° during the day, and weekly average 0.5°C.

+ Absorptivity can be changed by colour or surface roughness. The darker and more rough the surface the higher the surface temperature.

+ High surface temperatures inhibits algae growth. This is why growth is most abundant on north-facing surfaces.

+ Changed surface properties to increase the surface temperature can counter the decrease in surface temperature caused by better insulation in newer buildings.

÷ Low emissivity increases the need for cooling in the summer

÷ Thermal stress at surfaces is increased by low emissivity

The possible energy savings in the winter by low emissivity roofs and walls are in modern well-insulated houses, probably negligible and at the best less than 2 %. But the reduced biological growth is important to soiling.

7.3 Reduced soiling

+ Non-polar surfaces with low surface free energy will have minimal adhesion and only small atomic forces to attract other atoms. The properties will result in almost non-stick surfaces.

+ Water running off surfaces can remove soiling. Hydrophobic surfaces are preferred as droplets are more effective than films but may leave stripes. Surface roughness can increase the contact angle if the surface is already hydrophobic.

÷ No protection from soiling, e.g. against thermal stress or abrasion.

÷ No patina. Soiling can be seen as patina, especially at older buildings this aesthetical phenomenon could be desired.

The gains in reducing soiling are aesthetical but also functional as soiling eventually will cause deterioration either by chemical attacks (environmental particles and biological growth) or physically as microorganisms penetrate the substrate. Finally reduced soiling will mean less cleaning, and thereby reduced risk of damage and cost.

7.4 Future

The thesis has been concentrated on three parameters in the outer surface layer: moisture, heat and soiling. Since the early 1970s there has been a focus on energy savings, which primarily means less heat loss through the building envelope. On the other hand this means lower surface temperatures, longer periods with subcooling, condensation at surfaces and consequently more soiling. Therefore as the heat loss problems have decreased during the last 40 years the moisture and soiling problem have increased.

In the future focus should therefore be on how to minimize moisture and soiling problems without increasing the energy consumption. Based on the findings in this thesis the most promising ideas in surface treatments seem to be:

– <u>Low emissivity coatings</u>. This would reduce the moisture content in the winter and generally reduce biological growth. However the construction must be well insulated to reduce indoor heat gain in the summer. And the surface must be robust toward thermal stress. Furthermore must the low emissivity be maintained.

– <u>Fluorine-based anti-soiling treatments</u>. The low surface free energy and non-polarity of these treatments means high hydrophobicity but also better possibilities for becoming "non-stick" than the silicon based treatments of today.

However, these ideas are based on theory and should be subjects for further research where they could be tested.

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