Experimental identification of damage mechanisms in cementitious porous materials on phase transition of pore solution under frost deicing salt attack
Experimental identification of damage mechanisms in cementitious porous materials on phase transition of pore solution under frost deicing salt attack

A thesis submitted to
Swiss Federal Institute of Technology Lausanne (EPFL)
for the degree of Doctor ès Science

presented by
Josef Kaufmann
Dept. Concrete/Construction Chemistry, EMPA

accepted on the recommendation of
Prof. Ch. Huet (examiner)
Prof. E. Brühwiler (co-examiner)
Prof. G. Fagerlund (co-examiner)
Prof. M. Setzer (co-examiner)
W. Studer (co-examiner)

CH-8600 Dübendorf, December 2000

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Preface

Serious frost deterioration problems started in Switzerland in the 1960s and 1970s owing to the increasing use of deicing salts on roads. Since then different research projects related to this subject were performed at or in cooperation with EMPA, among them the ones of Rösli and co-workers. This lead to important scientific results as well as the development of specific frost deicing salt resistance test methods.

The fact that the different frost deicing salt damage models proposed in literature still do not fully explain some fundamental experimental results, the development of new concrete types making use of additives and admixtures, an increase of durability problems and the European standardization show the actuality of this old research field.

The presented work is the fruit of a cooperation between the Swiss Federal Institute of Technology at Lausanne EPFL and the Swiss Federal Laboratories for Materials Testing and Research at Dübendorf EMPA kindly supported by Prof. F. Eggimann (EMPA) and Prof. J. Badoux (EPFL).

This EMPA report by Dr. Josef Peter Kaufmann is based on his dissertation under the guidance of Prof. C. Huet (Laboratoire de Matériaux de Construction LMC, EPFL) and W. Studer (head of the former Concrete/Binder department at EMPA).

The damage of concrete by frost deicing salt attack was studied by means of many different experimental methods, among them expansion, acoustic emission, calorimetry and ultrasonic pulse velocity measurement. New experimental arrangements allowed the measurement of the concrete behavior under saturated conditions and the study of supercooling effects. The results were consistent and lead to the development of a sequential damage model that unifies and generalizes other damage models.

This model may serve as a basis for further development of frost resistance test methods as well as new concrete mixtures with increased frost deicing salt resistance.

Without the assistance of many experts at EPFL and at EMPA, as well as without the technical support from the employees of the concrete/binder department it would not have been possible to realize this study.

The Swiss Federal Road Office (ASTRA) and cemsuisse generously supported this work. Their contribution and continued support is gratefully acknowledged.

Dübendorf, in December 2000

Dr. Michael Romer
## CONTENTS

CHAPTER 1  INTRODUCTION 11

**Part I: Background and physical mechanisms**

CHAPTER 2  ENVIRONMENTAL DATA AND ON-SITE OBSERVATIONS 17

2.1 Temperature distribution 17
2.2 Comparison between on-site conditions and fast weathering laboratory test conditions 19
2.3 Ultrasonic pulse transit time on-site 20
2.4 Conclusions from on-site experiments 21

CHAPTER 3  PHYSICAL BACKGROUND 23

3.1 Pore structure of hardened cement-bonded material 23
3.2 Physical properties of water and ice 26
  3.2.1 Structure of water and ice 26
  3.2.2 Pore size freezing/melting point relations 29
  3.2.3 Ice nucleation 31
  3.2.4 Aqueous solutions 32
  3.2.5 Growth of ice crystals in water and aqueous solutions 34
  3.2.6 Growth of ice in capillaries containing supercooled water 36

CHAPTER 4  DETERIORATION MECHANISMS 37

4.1 Microscopic damage models 37
  4.1.1 Diffusion and freezing of gel water 37
  4.1.2 Everett's arm chair experiment 37
  4.1.3 Setzer's mechanism 38
  4.1.4 Evaporation followed by sublimation 39
4.2 Macroscopic damage mechanisms 40
  4.2.1 Closed container 40
  4.2.2 Hydraulic pressure 41
  4.2.3 Thermal contraction and dilatation of ice 43
  4.2.4 Temperature shock 44
4.3 Influence of salt solutions 45
  4.3.1 Osmosis 45
  4.3.2 Crystallization effects 45
  4.3.3 Layer freezing 45
4.4 Chemical aspects 46
4.5 Salt-frost scaling 47
**Part II: Expansion experiments**

**CHAPTER 5  SPECIMENS**

**CHAPTER 6  MEASUREMENT OF EXPANSION PARALLEL TO THE FROST MEDIUM SURFACE**

6.1 Introduction
6.2 Method and apparatus
6.3 Expansion results on thick plates
   6.3.1 Non-saturated specimens
   6.3.2 Completely (vacuum) saturated specimens
6.4 Expansion results on thin plates
   6.4.1 Bending effect on thin plates
   6.4.2 Frost resistant specimens
   6.4.3 Pure water as impregnation and as frost medium
   6.4.4 Pure water as impregnation and 3% salt solution as frost medium
   6.4.5 Detailed study near the freezing point
   6.4.6 Higher concentrated salt solutions as frost medium
   6.4.7 Discussion of thin plate experimental results
   6.4.8 Hardened cement paste

**CHAPTER 7  FURTHER CLIMATIC TESTS**

7.1 Measurement perpendicular to the frost medium surface
   7.1.1 Method and apparatus
   7.1.2 Results
7.2 Temperature cycles without thawing of the frost medium
7.3 Temperature shock
7.4 Ice lens formation
   7.4.1 General remarks
   7.4.2 Expansion at constant temperature
   7.4.3 JPD arrangement- constant liquid-ice interface
   7.4.4 Conclusions for ice lens formation
7.5 Calculation of freezable water content

**CHAPTER 8  CONCLUSIONS FROM EXPANSION MEASUREMENTS**

**Part III: Physical auscultation**

**CHAPTER 9  MICROSCOPICAL DAMAGE ANALYSIS**

9.1 Microscopical methods
9.2 Results
   9.2.1 Fast weathering laboratory tests
   9.2.2 On-site exposure
13.2.1 General remarks 151
13.2.2 Results 151

13.3 Conclusions from acoustic emission 156

Part IV: Modelling and general conclusions

CHAPTER 14 QUALITATIVE MODEL FOR FROST DAMAGE 161

14.1 Scope 161
14.2 Freezing and thawing of pore solution 161
14.2.1 Freezing initiation 161
14.2.2 Ice front penetration 162
14.2.3 Liquid redistribution 162
14.2.4 Thawing 163
14.2.5 Resaturation 163
14.3 Effect of cycle repetition 163
14.4 Influence of aggregate stones 163
14.5 Influence of salt concentration 164
14.6 Comparison of on-site behavior and laboratory testing 165

CHAPTER 15 CONCLUSIONS 167

15.1 General conclusions 167
15.2 Experimental findings 167
15.3 Need for further research 170

REFERENCES 171

APPENDIX A: Expansion 181
APPENDIX B: Calorimetry 185
Summary

A wide variety of theoretical frost deicing salt damage mechanisms relied to the phase transition of the pore solution in concrete is proposed in literature. At the same time some experimental results such as the crucial influence of the thawing salt or experimental parameters like freezing rate or minimal temperature are still the subject of intense research. The damage of concrete due to the frost deicing salt solicitation is studied in this work by means of experimental methods.

The damage is separated into the cause, the ice formation within the pore system and the consequence of the phase transition of the pore solution that leads to a change of the pore system.

The ice formation is studied by means of calorimetric methods, ultrasonic pulse transit time (velocity) measurement, temperature distribution and expansion measurement.

The change of the pore system which leads to permanent residual damage is characterized by expansion measurement, microscopical analysis of loaded and unloaded specimens (SEM, confocal microscope etc.), mercury intrusion porosimetry (MIP) and acoustic emission technique.

The frost deicing salt damage mechanisms is studied under saturated conditions. The possibility of the application of a liquid layer in all performed tests allows the study of resaturation and redistribution phenomena, which are found to be crucial for frost damage. Thawing and resaturation effects also are studied in special experiments with constant temperatures and temperature cycling below 0°C.

Besides the solicitation under laboratory condition, the solicitation (temperature, humidity) and the freezing process on-site is studied.

The ice formation as well as the damage is studied extensively by means of the expansion measurement. Expansions are measured parallel and for the first time perpendicular to the concrete surface. It was very useful to use thin concrete specimens.

Two different ice formation processes, a rapid instantaneous ice formation related to freezing initiation and a slower progressive ice formation, representing a continued growth of a penetrating ice front, are found. Using a frost medium layer these processes are separated in time and are analyzed separately.

Freezing initiation in laboratory tests frequently is accompanied by supercooling leading to high ice formation rates and additional damage. It proves to be an important factor influencing the frost resistance and experimental results. Without supercooling, ice formation within concrete starts, when the temperature falls below the freezing point of the applied frost medium.

When a salt solution (NaCl) is applied at the concrete surface salt segregation is found to be an important phenomena and to be similar to supercooling.

Similar freezing characteristics as in the laboratory but without supercooling effects is observed on-site.

An analysis by microscopical methods of concrete specimens after laboratory as well as after field exposure reveals surface parallel cracks. The crack path follows the interface of the aggregates. Additionally, a degradation of microstructure is observed.

Pore size distributions are calculated from calorimetric data. Local supercooling in calorimetry experiments is found to cause significant hysteresis between freezing and thawing. This leads sometimes to misinterpretation of experimental results. Supercooling in calorimetric tests is avoided through the application of freezing germs ("ice nuclei") with very high initiation temperatures up to -0.7 °C.
A thawing phase with a presence of liquid frost medium is found to be very important for progressive damage of concrete in further frost cycles as is demonstrated in special experiments without thawing.

No indication for progressive ice lens formation is found experimentally. Neither holding the temperature constant below 0°C nor experiments with a constant liquid - ice interface within the concrete lead to continued expansions as would be expected in the case of ice lens formation.

A qualitative model for frost deicing salt damage based on the experimental findings is derived. The model distinguishes five different phases:


Each of the phases is important to cause frost damage and can not be treated isolated as it is frequently done in many well known theoretical damage models.
Zusammenfassung

In der Literatur wird eine grosse Anzahl unterschiedlicher Frost-Tausalzschadensmechanismen vorgeschlagen, die direkt oder indirekt auf der Phasenumwandlung der Porenlösung basieren. Andererseits sind gewisse experimentelle Resultate wie der dominierende Einfluss der Tausalzkonzentration oder die Beeinflussung durch experimentelle Parameter wie Gefrierrate oder Minimaltemperatur immer noch das Ziel umfangreicher Studien.


Die eigentliche Schädigung beruht auf einer Veränderung des Porensystems die sich sekundär auf andere Feststoffeigenschaften auswirkt. Diese Auswirkungen werden mittels Längenänderungsmessungen, Messung der akustischen Emission, Quecksilberdruckporosimetrie, mikroskopischen Untersuchungen an belasteten und unbelasteten Proben (REM, konfokales Mikroskop) erfasst.


Neben der Beanspruchung unter Laborbedingungen werden auch die natürliche Beanspruchung (Temperatur, Feuchtigkeit) in-situ untersucht.

Mit der Längenänderung kann sowohl die Eisbildung als auch die Schädigung studiert werden. Sie spielt deshalb eine wichtige Rolle in diesem Bericht. Dabei werden die Längenänderungen parallel wie auch, das erste Mal, senkrecht zur beanspruchten Oberfläche gemessen. Interessante Resultate werden hauptsächlich dann erzielt, wenn man die Versuche an dünnen Prüfkörpern durchführt.

Zwei unterschiedliche Eisbildungsprozesse eine schnelle, instantane Eisbildung die mit Nukleationsprozessen in Verbindung steht und eine progressive Eisbildung infolge der kontinuierlichen Eindringung der Eisfront in das Porensystem, können unterschieden werden.


Bei Anwendung einer Tausalzlösung wird Salzsegregation als wichtiges Phänomen erkannt. Ähnliche Effekte wie bei Unterkühlungen können beobachtet werden.

In-situ ergeben sich ähnliche Gefriercharakteristiken wie im Labor, aber ohne Unterkühlungseffekte.


Das Vorhandensein einer Tauphase mit einer flüssigen Frostmediumsschicht ist für eine progressive Schadensbildung unumgänglich, wie in Experimenten ohne Tauphase gezeigt wird.

Es können keine experimentellen Anhaltspunkte für eine kontinuierliche Eislinsenbildung gefunden werden.

Weder eine Langzeitlagerung unter dem Gefrierpunkt, noch in Experimenten mit gleichbleibender Flüssigkeit-Eis Grenzlinie innerhalb eines Betonprüfkörpers ergibt ein Eislinsenwachstum.

Aus den experimentellen Daten wird ein qualitatives Modell des Schadensmechanismus abgeleitet. Im Modell werden fünf verschiedene Phasen unterschieden:


Jede dieser Phasen ist bei der Schädigung durch Frost-Tausalzbeanspruchung wichtig und kann nicht isoliert betrachtet werden, wie das in den meisten anderen theoretischen Schadensmodellen der Fall ist.
CHAPTER 1  INTRODUCTION

Concrete degradation through frost is a problem that was already known to the first people that used this building material for their constructions in cold regions. Already the Romans described the use of additives to prevent from such problems. Nevertheless for a long period the concrete was thought to be, apart from some special cases of natural mineralized water or seawater attack, a non-destroyable very durable material. An expansion of the applications of concrete in all scopes of civil engineering, together with higher material requirement lead to the development of new concrete types using additives and admixtures. At the same time, an increase of durability problems is observed in the last decades.

Serious frost deterioration problems started in the 1930s and 1940s. Since then, owing to increased traffic, snow and ice are removed totally from the roads during winter and grit as means of ice control was replaced by deicing salts. Not only frost, but also frost deicing salt attack with increased deterioration was the consequence (fig 1).

Fig. 1 Typical frost deicing salt damage on bridge (A13 Splügen, Switzerland)

Meanwhile big progress in avoiding damage by the use of adequate mix designs was made. This was mostly based on practical experience. The fundamental understanding of the damage processes is still missing.

The crucial influence of the deicing salt is also found in laboratory fast weathering tests (SIA 162/1 [1], CDF test [2], Scandinavian Slab test SST [3]). The loss of small pieces of cement or mortar including porous aggregates (scaling) is up to two orders of magnitude larger when a 3% salt (NaCl) solution instead of water is applied as frost medium layer. The mass loss is found to be maximal for salt (NaCl) concentrations of 2 - 4 mass-percent.

The influence of the deicing salts is still not fully explained. The reasons for the maximum are a frequent subject of studies. The influences of other parameters like freezing rate or minimal temperature also give rise to complementary discussions.

Few is known on the behavior of concrete and the damage mechanisms on-site. The relation between damage mechanisms on-site and the mechanisms in fast weathering and other frost or frost deicing salt resistance tests is not always clear.

Many different damage mechanisms, among them Powers' hydraulic pressure theory (Powers [4]) and thermodynamic mechanisms (Everett [5], Setzer [6]), have been proposed.
Microscopic as well as macroscopic models have been developed. In special cases chemical interactions (Stark [7]) could be important. However, these mechanisms are mostly theoretical without experimental proof. The correlation between on-site behavior to test procedures only can be done if the mechanisms leading to damage are sufficiently understood.

The following work is a contribution to more than 60 years of investigation in this field by many researchers. The principal damage mechanisms of Portland cement concrete frost medium are studied experimentally both in laboratory tests and on-site. The experimental work concentrates on an open system, where the surface is exposed to an outer frost medium layer. Only few concrete mixes, mostly with a poor frost resistance and some hardend cement pastes were studied. The limitation to poor frost resistance was because of the faster response (damage) to the frost deicing salt solicitation and hence time saving which allowed the application of many different experimental techniques to the same system.

The phase transition of water and salt solutions was studied. While about 100'000 tons (1997) of NaCl (99.5%), with big annual scattering (up to 60%), only 8'000 tons of CaCl$_2$ are applied on swiss roads each year. CaCl$_2$ mostly is used at lower temperatures. In the scope of this work only the influence of sodium chloride (NaCl) was studied.

In order to be able to study the damage mechanisms, we have to distinguish between the main cause: the ice formation within the porous material, and its consequence: a change of the pore structure (damage). Many different experimental methods have been applied to characterize different aspects of the ice formation and of the damage.

The moment (time or temperature) and the amount of ice formation were studied by means of calorimetry, ultrasonic pulse transit time, temperature profile and expansion measurements. The possibility of the simultaneous application of a frost medium layer was ensured in the experiments, so that variations in function of the number of the frost cycle could be observed under saturated conditions.

The damage was characterized by expansion measurements, acoustic emission, mercury intrusion porosimetry (MIP) and microscopical analysis (SEM, confocal and conventional microscopy) of original and specimens after frost deicing salt attack.

Different methods like temperature profiles, ultrasonic pulse transit time measurement and microscopical methods were used in laboratory tests as well as on-site or on specimens with on-site exposure.

The aim of these experimental studies was to provide the practical basis for a numerical simulation of frost deicing salt damage mechanisms. The numerical simulation is the main subject of a second thesis (F.Besson) which is in progress at EPF Lausanne in the framework of the same interinstitutional project.

The here presented thesis concentrates on the description of experimental details and conclusions concerning the damage mechanisms including a qualitative model for frost damage. The experimental results also implement some conclusions concerning frost resistance testing and design of concrete mixes with adequate frost resistance. These aspects are treated in a more general project report towards ASTRA (Swiss federal road office) [143].

This thesis is arranged in four parts:

Part I Background and physical mechanisms
Part II Expansion experiments
Part III Physical auscultation
Part IV Modelling and general conclusions

Part I summarizes the practical and theoretical background. The situation on-site is analyzed experimentally. The possible damage mechanisms proposed in the literature are described.
Part II treats the most important macroscopic consequence of ice formation: expansion. Some unique experimental details allowed an improved analysis of the damage formation.

In part III different physical methods focus on the ice formation itself. Other methods like microscopical observations allowed the study of the damage in more detail.

In part IV a model of damage formation, owing to frost deicing salt attack, taking the presented experimental findings into account is developed. It is based on different well-known damage models. In addition to these isolated models, it distinguishes between five different freezing phases, each of them with different predominant damage mechanisms.

This project was realized in the scope of an interinstitutional collaboration between EMPA Duebendorf and EPF Lausanne. It was supported by grants of ASTRA (Swiss federal road office) and the "Foundation" of cemsuisse.
Part I

BACKGROUND AND PHYSICAL MECHANISMS
CHAPTER 2  MEASUREMENT ON-SITE

2.1  Temperature distribution

In order to understand on-site damage mechanisms and to improve frost resistance tests, natural frost cycles as found on-site must be studied first.

For this reason equipped specimens of laboratory concrete were fixed with a repair mortar in larger drill holes (Ø = 50 mm) at four different measurement positions in the parapet of a bridge (Hundwil, Appenzell, fig 2; w/c=0.57 AP=4%).

The specimens of mix 1 (w/c=0.5) and mix 2 (w/c=0.63) (see table 3 chapter 5) had a diameter and a height of 50 mm. The equipment of the specimens consisted of thermocouples (Ni-Cr-Ni) placed at their surface, at a depth of 10 and 25 mm and on the opposite face. The thermocouples within the cores were fixed with cement paste in small drill holes (Ø≤4mm). The thermocouples at the surfaces were glued (acrylic glue X-60). Additionally the air temperature was measured. The temperature was registered continuously (each 5-10 minutes) by means of a data logger (Grant).

![Diagram of temperature measurement on-site](image)

Fig. 2  Test arrangement for temperature measurement on-site

Temperature evolution during winter 1996/97 (typical winter) is shown in fig 3 and 4.

During the whole measurement period no sudden temperature shocks were measured.

Daily maximum and minimum values were derived. Besides some small variation due to direct sun or wind exposure, very little temperature differences were measured for different positions. While the difference between daily maximum and minimum air temperature was up to 15°C (mean value 7°C), the difference between the maximum and the minimum at the concrete surface was much smaller (maximum 7°C; mean value 3°C).

The difference between surface temperature and the temperature at the depth of 25 mm within the concrete was very modest, reaching a maximum of 1.6°C (mean value 0.2°C). It was somewhat higher for the maximum values than for the minimum temperatures owing to the heating by solar irradiation (more important in summer!).
The measured freezing rates (at 0°C) in the air was up to 2°C/h (mean value 0.6°C/h), the ones in the concrete reached only 0.5°C/h (mean value 0.3°C/h). The thawing rates (at 0°C) were up to 4.6°C/h (mean value 1.4°C/h) in the air and reached in the concrete 4.4°C/h (mean value 0.9°C/h). The differences between freezing and thawing can be explained by solar irradiation. During this period, a total of 40 frost cycles (temperature passed through 0°C) in the air, but only 20 cycles in the concrete were measured.

This number is typical for a large range of altitudes (500-2000m above sea level) in Switzerland [8].

Fig. 3  Daily records of maximum and minimum temperatures in the air

Fig. 4  Daily records of maximum and minimum temperatures of concrete. The curves at the surface and at a depth of 25 mm are practically the same

Relative humidity was measured regularly at a position below the bridge. It reached very high values throughout the winter (almost 100% RH). It was also measured in a sealed drill hole
(Ø=18mm) at a depth of 10mm from the surface of a concrete cube (l=200mm). The result is given in fig 5. In spite of big temperature variations the relative humidity in concrete was very high (98-100% RH). With falling temperature the relative humidity within the specimen rose. Only after longer warm period the relative humidity in concrete fell below 95% RH.

Hence, when the air temperature increases at constant or increasing relative humidity (of the air) or the bridge cools down during the night, the dew point at the concrete surface is reached. Liquid water supplied by melting snow also leads to an increase of the degree of saturation. The concrete therefore is assumed to be highly presaturated during winter.

### 2.2 Comparison between on-site conditions and fast weathering laboratory test conditions

The most important parameters of the temperature cycles performed in standard testing (SIA 162/1 [1], CDF test [2], Scandinavian slab test SST [3]) are compared in table 1 to the ones measured on-site.

<table>
<thead>
<tr>
<th></th>
<th>On-site</th>
<th>SIA 162/1</th>
<th>CDF</th>
<th>SST (Borås)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing rate (air)</td>
<td>0.6°C/h</td>
<td>20°C/h</td>
<td>10°C/h</td>
<td>20°C/h</td>
</tr>
<tr>
<td>Thawing rate (air)</td>
<td>1.4°C/h</td>
<td>30°C/h</td>
<td>10°C/h</td>
<td>40°C/h</td>
</tr>
<tr>
<td>max/min (air)*</td>
<td>+10°C/-5°C</td>
<td>+15°C/-15°C</td>
<td>+20°C/-20°C</td>
<td>+20°C/-20°C</td>
</tr>
<tr>
<td>Number of cycles</td>
<td>20 per year</td>
<td>28</td>
<td>28</td>
<td>56</td>
</tr>
</tbody>
</table>

*for one complete frost cycle (with thawing) within 24h

Table 1 Comparison of the test parameters in standard frost deicing salt resistance tests with the ones found on-site

The temperature change rates (of the air temperature) are much higher in the fast weathering frost deicing salt resistance tests than the ones measured on-site.

The number of frost cycles during the whole service life of a concrete structure on-site is much bigger than the total number of frost cycles applied in fast weathering laboratory tests.
2.3 Ultrasonic pulse transit time measurement on-site

Freezing process on-site also was studied with ultrasonic pulse transit time measurement (see chapter 12). Transducer and receiver were fixed (acrylic glue) on the concrete surface at a distance of 14 cm (edge to edge). One result of such measurement after a rainy morning and freezing at night, with dry weather on the following days, is given in fig 6. The ultrasonic pulse transit time was measured each 5 minutes. The transit time suddenly dropped when the surface temperature fell below 0°C. It rose to the starting level again when the thawing point was reached at the surface and remained constant during the remaining experimental period. This means that, during freezing on-site, the velocity of ultrasonic waves is increased, as can be expected owing to the solidification of water in the pores.

![Ultrasonic pulse transit time and temperature on-site](image)

The plot of the derived pulse velocity versus the surface temperature shows that the increase in pulse velocity starts as soon as the 0°C temperature is reached. This means that no significant supercooling occurred. This was a typical result confirmed in other pulse transit time experiments. Reasons for the lack of supercooling on-site may be the large outer surface area of a real concrete structure, the existence of many substances in the surrounding air (aerosols) which may serve as ice formation germs (ice nuclei). Additionally, snow rests or white frost produced when temperature falls below the dew point and below 0°C can serve as nucleation germs.
2.4 Conclusions from on-site experiments

1. Freezing in natural frost cycles is very slow compared to typical freezing/thawing rates in laboratory tests (20°C/h). Typical values for the freezing rate in the concrete were in the order of 0.5°C/h.

2. The thawing rate was somewhat higher, due to solar irradiation, reaching 1.5°C/h.

3. The temperature distribution in the outermost 5 cm of the concrete is very flat. The mean temperature difference between surface and at the distance of 5 cm is less than 1°C.

4. The minimum temperature for a real frost cycle (with thawing) under natural condition is higher than -5°C.

5. The relative humidity during winter is very high, reaching almost 100% on frost days. The concrete is therefore highly presaturated.

6. Freezing on-site is initiated as soon as the temperature falls below 0°C, with no supercooling. This shows that sufficient ice nuclei like white frost are existing.
3.1 Pore structure of hardened cement-bonded material

Hardened cement-bonded material (concrete, mortar, hardened cement paste) consists of hydration products (CSH, Ca(OH)$_2$, etc.) and pores of different shape and size. Water molecules are present as evaporable, non-evaporable and chemically bonded water. Evaporable water is water that can be removed without destruction of the hydration products (D-drying) (Powers+Brownyard [9], Powers [10]). Depending on the surrounding climate (relative humidity) and their shape and size, the pores are partly or totally filled with evaporable water. Two main physical mechanisms can be distinguished.

a) Adsorption

Molecules of a liquid or gas can be bound physically on the surface of a solid material. Surfaces have physical and chemical properties different from the inner material. Surface molecules have a higher free energy. In an early work, Langmuir [11] describes the adsorption of a monomolecular layer assuming that the forces responsible for the adsorption are like the ones for chemical bonding. A much improved model is the BET theory [12]. It describes the adsorption as a multilayer physical process caused by van-der-Waals forces. The properties of the adsorbed molecules are supposed to be the same as in the liquid. The BET theory gives a relation between vapor pressure, specific surface and amount of adsorbed molecules. In the case of water it describes the adsorption very well in the range of 5 - 35 % relative humidity.

Experiments showed that the adsorbed water is structured and that its properties are quite different from bulk water (Setzer [6]; Adolphs,Setzer [13]). The surface energy of an adsorbed layer is reduced and varies with the relative humidity (Setzer [14]). Adsorbed water is non-freezable until very low temperatures.

b) Capillary condensation

At higher vapor pressures ($P/p_S > 0.4-0.5$) capillary condensation occurs. Due to the surface tension of water the liquid-gas interface in small pores is curved. The equilibrium vapor pressure therefore is reduced so that the pores get filled depending on their pore diameter. For cylindrical capillaries the Kelvin-Laplace equation can be used:

$$\ln\left(\frac{p}{p_S}\right) = -\frac{2\gamma_{lg}}{r} \frac{v}{RT}$$

where:
- $\gamma_{lg}$: surface tension (liquid-gas)
- $v$: molar volume of water
- $R$: gas constant
- $T$: absolute temperature (K)
- $r$: radius of curvature of water meniscus = pore radius/$\cos \Theta$
- $(\Theta= contact\ angle \approx 0)$

Somewhat improved forms are found by thermodynamic approaches (Setzer,Wittmann [15]; Setzer [6]) where the prestructuring of capillary condensed water is taken into account.

Powers and Brownyard [9] separate the evaporable water into gel and capillary water according to their porous environment.
Additionally large, more or less spherical pores (10 µm ..1 mm) so-called "air pores" are formed depending on mixing and preparation. Additives such as soaps or detergents like sodium-salts with polar groups (CO₂⁻, SO₃⁻, SO₄⁻) increase the amount of air entrainment in the concrete owing to their stabilizing effect (Hermann [16]).

Capillary condensation is not possible in these pores, so that they mostly remain air filled. Their positive effect for frost resistance is well known. Already the Romans (Vitruv) described the positive effect of additives like oil-yeast or animal blood to obtain better frost resistance.

Capillary condensed water (water in capillaries) does not exist below 40-50% relative humidity. The size of capillary pores depends on the degree of hydration and reaches the size of the gel pores so that an exact separation is not possible. The sizes of cement gel and capillary pores range approximately from 1 nm to 1 µm.

From their experimental work (mostly sorption isotherms) Powers and Brownyard [9] concluded that the cement gel has the same structure independent of temperature, w/c-ratio, age etc. The non-evaporable water content was found to be proportional to the specific surface for a wide variety of Portland cements. The cement gel porosity is therefore constant (± 28 vol.-%). The specific surface of the cement gel is 200 m²/g.

Further assumptions allow a quantitative calculation of the pore structure [17]:

1. cement binds a quantity of 25% of its mass of water chemically (hydrate water). This value can be calculated from the amount of bonded water of each clinker mineral and the composition of the cement. The hydrate water has an increased density of 1333 kg/m³.
2. the cement gel water is physically bound (structured) water and has an increased density of 1111 kg/m³.

With Z [kg/m³] being the cement content, W [kg/m³] the water content and α the degree of hydration [kg/kg] and assuming a cement density ρ = 3150 kg/m³, the following relations for the mass and the volume relations in the hardened cement paste can be derived (table 2).

Owing to the higher density of the hydrate water and the water in the cement gel pores a self desiccation results when the cement gel starts forming. If no additional water is supplied, the resulting volume reduction ΔVₛ (table 2) of the total amount of the water creates empty (air-filled) space. Self desiccation is an important factor for the frost resistance of young concrete.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mass m [kg/m³]</th>
<th>volume [dm³/m³] = ( \frac{1}{\rho} ) m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrated cement</td>
<td>αZ</td>
<td>0.317αZ</td>
</tr>
<tr>
<td>Hydrate water</td>
<td>0.25αZ</td>
<td>0.188αZ</td>
</tr>
<tr>
<td>Hydration products</td>
<td>1.25αZ</td>
<td>0.505αZ</td>
</tr>
<tr>
<td>Cement gel water/-pores</td>
<td>0.22αZ</td>
<td>0.198αZ</td>
</tr>
<tr>
<td>Capillary water/-pores of whom air filled (( \Delta Vₛ ))</td>
<td>W-0.47αZ</td>
<td>W-0.386αZ</td>
</tr>
<tr>
<td>Unhydrated cement</td>
<td>1-αZ</td>
<td>0.317(1-α)Z</td>
</tr>
<tr>
<td>Total</td>
<td>W+Z</td>
<td>W+0.317Z</td>
</tr>
</tbody>
</table>

Table 2  Volume relations in hardened cement paste
The volume relations in hardened cement paste at completed hydration ($\alpha=1$) as found at EMPA (Studer [18]) are shown in fig 8. The plot is based on a diagram after (Czernin [19]).

![Diagram showing volume relations in hardened cement paste at complete hydration](image)

**Fig. 8** Volume relations in hardened cement paste at complete hydration ($\alpha=1$)

This model only can be an approximation of the real pore structure. Improved experimental techniques such as length change, improved sorption isotherms, mercury intrusion porosimetry, low temperature calorimetry, X-ray diffraction, nuclear magnetic resonance (NMR), scanning electron microscopy (SEM) etc. helped to refine the model and to distinguish between other pore classes.

Feldman-Sereda [20] assume the CSH structure to consist of colloidal layers. Water can be adsorbed between the layers ("interlayer water"). Due to the change of surface free energy and the binding forces, the amount of interlayer water contributes to important material properties and can explain creep and shrinkage. Sierra [21] has extended and partly modified this model, considering the water in the CSH more detailed.

The Munich model (Wittmann [22], Setzer [23]) is another thermodynamic model. The cement paste consists of crystalline phases and a "Xerogel" which can absorb water (fig 9). At relative humidities below 40% RH the colloidal particles touch each other. At higher relative humidities the adsorbed water molecules produce disjoining forces. This model has been extended by Setzer [24][25].

![Munich model diagrams](image)

**Fig. 9** Munich model
For the subject of the frost resistance the amount of evaporable water content that is freezable at a certain temperature is of particular interest. This amount can be measured (calorimetry, length change) or calculated from sorption isotherms. The calculation is possible using theoretical expressions for the pore size freezing point depression (see section 3.2.2) in combination with the Kelvin equation. It is also possible to reduce the sorption isotherm to the considered temperature and to use Washburn equation for its calculation (Powers+Brownyard [9], Fagerlund [26]). Washburn [27] found a semi-empirical relation between the vapor pressure of ice and a supercooled bulk water in function of temperature.

The biggest advantage of the direct measurement by calorimetry or length change is the low time requirement compared to the determination of sorption isotherms which may take weeks. A problem is the existence of hysteresis between adsorption and desorption which is generally considered to depend on peculiarities of the pore system. Larger capillaries may only be accessible by smaller pores ("neck pores"). Such an "ink-bottle" would be filled at a relative vapor pressure corresponding to the bigger pore while it would be emptied at one corresponding to the neck, which is smaller.

Similar hysteresis is reported in calorimetry and length change measurement (Bager [28][29],Beddoe [30],Powers [31]). The hysteresis here can also be explained with a similar effect, the local supercooling. The water in a bigger pore can remain liquid although its freezing point is reached, it supercools. The penetrating ice cannot nucleate the supercooled water until the water in the smaller "neck pore" freezes at lower temperature. At thawing, the pore water starts melting when the freezing point of the smaller pore is reached. The ice in the bigger pore melts when its melting temperature is reached (Fagerlund [32]).

The neck pore effect may not only be applicable to isolated pores only but to the whole pore system. The connectivity of a pore to the surface, that means the diameter of the biggest connection in the pore labyrinth is of decisive interest.

Another explanation is based on different curvature of liquid-ice interface at freezing respectively at thawing (Setzer [33], see section 11.9).

### 3.2 Physical properties of water and ice

#### 3.2.1 Structure of water and ice

In water, the average coordination number is very low for both solid and liquid but the ordering extends over several molecular diameters. This owes to the formation of intermolecular hydrogen bonds resulting from electrostatic interaction of the polar molecules (fig 10) and electric arrangements similar to covalent bonds. Many anomalous physical properties of liquid water such as the high heat capacity, the temperature dependence of the density, the melting and boiling point etc. are the consequence (Nemethy [34]). The melting point of many chemical compounds depends linearly on the number of electrons. Only substances with strong intermolecular bonding deviate considerably from this rule. The phase transition of idealized water was estimated to be -90°C (Luck [35]).

The flickering cluster model gives good explanation for the observed deviations (Frank [36]). The model is a qualitative description of water as a mixture of two states, one less dense and highly hydrogen bonded (ice like structure), the other having higher energy due to the breaking of the hydrogen bonds and being packed densely and more irregularly ("free" water molecules). The mean average cluster size ranges from 91 water molecules at 0°C/ 1atm to 25 at 70°C/ 1atm.
Fig. 10 Structure of molecule orbital of water (tetrahedral)

When water freezes below 0°C at low pressures (< 200 Mpa), Ice I (fig 11a) is formed both on slow and rapid freezing. The latent heat of 333,75 kJ/kg is set free upon the phase transition.

The ice molecules are arranged tetrahedrally and are connected by hydrogen bonds of length 2.76 Å. Owing to the low coordination number of four, relatively large empty spaces between the molecule layers result and consequently the density of ice is even lower than that of water. When ice is formed the molecular volume of water increases by 9%.

Fig. 11 a) Arrangement of hydrogen-bonded water molecules in Ice I (Nemethy [34])
b) Arrangement of water molecules in liquid phase (Frank [36])

At higher pressure (0.200 MPa), bulk water and Ice I can coexist at lower temperatures until -22°C. The pressure dependence of the phase transition temperature T can be described by the Clausius-Clapeyron equation:

\[
\frac{dT}{dp} = \frac{T}{H_0} (v_W - v_l)
\]
where: \( \frac{dT}{dp} \) : change of phase transition temperature
\( v_w(v) \) : molar volume of water (ice)
\( H_0 \) : molar enthalpy of fusion

Additionally, six different crystalline forms (differing from ice I) exist at higher pressures (above 200 MPa, fig 12).

![Phase diagram of water](image)

Fig. 12 Phase diagram of water

Another important property is the macroscopic vapor pressure above ice. As the water molecules in the ice are bonded stronger than in water of the same temperature, the vapor pressure above ice is lower than above supercooled water (fig 13). Redistribution of water in a pore system with both supercooled water and ice existing at the same time therefore must be taken into account.

![Difference of vapor pressure](image)

Fig. 13 Difference of vapor pressure above supercooled water and above ice
3.2.2 Pore size freezing/melting point relations

The water in pores of small diameters is due to surface tension effects at a lower energy level than free water. When pore water freezes, the solid-liquid interface curvature depends closely on the pore diameter and therefore the freezing and the melting point of pore water is depressed compared to bulk water.

To find a relation between pore size and freezing/melting point of the pore water, thermodynamic models have to be derived.

First thermodynamic descriptions were developed by Everett [5][37], Haynes [38] and Hill [39][40][41]. The consideration of different homogeneous layers allowed them to take surface effects into account. The validity of Gibbs-Duham equation [42] was assumed. The assumption of homogeneous layers implies the separation of two phases through a boundary region. The surface energy has to be taken into account. Two phases i and j, whose volumes are $V_i$ and $V_j$ are separated by an interface $ij$, whose surface is $A_{ij}$ and whose thickness can be ignored. The Gibbs-Duhem equations then are:

\[
\begin{align*}
S_i dT - V_i dP_i + m_i d\mu_i &= 0 \quad \text{for the phases } i \text{ and } j \\
S_{ij} dT - A_{ij} d\gamma_{ij} + m_{ij} d\mu_{ij} &= 0 \quad \text{for the interphases}
\end{align*}
\]

where:
- $T$ : temperature
- $S$ : entropy
- $\mu$ : chemical potential
- $p$ : pressure
- $\gamma$ : surface energy

The pressures $p_i$ and $p_j$ are related to the surface energy $\gamma_{ij}$ according to Laplace's equation

\[
p_i - p_j = \gamma_{ij} \frac{dA_{ij}}{dV_j}
\]

For the simple case of an ice crystal immersed in and in equilibrium with water at a hydraulic pressure $p_w$, the Laplace equation (4) can be written as:

\[
p_i - p_w = \gamma_{iw} \frac{1}{R_H} \quad \text{with } R_H = \frac{dV}{dA}
\]

and from (3)

\[
\mu = \mu(p_w) + \gamma_{iw} \frac{1}{R_{H}}
\]

For a spheric ice particle of radius $r$ the value $R_H$ is equal to $\frac{r}{2}$.

When the relation of surface to volume of a phase becomes considerable, surface effects become important and it is no longer possible to consider a defined volume for each phase (Setzer [6]). The Gibbs-Duhem equations are only approximately valid.

In his thermodynamic model, which is based on the concepts of Landau-Lifschitz [43], Setzer [6] takes into account that between the internal surface of the solid matrix and the pore ice there exists an unfrozen adsorbed water layer of some molecule thickness. He derives the following relation:

\[
(s_w - s_i) dT = (v_w - v_i) dp + (\gamma_{sw} - \gamma_{si}) \frac{V_{pore}}{n} d(\frac{1}{R_H})
\]
where: $\gamma_{sw}$ : surface energy between solid and pore-water  
$\gamma_{si}$ : surface energy between solid and pore-ice  
$V_{w(V_i)}$ : molar volume of water/ice  
$s_{w(s_i)}$ : molar entropies of water/ice  
$RH$ : hydraulic radius (= $\frac{dV}{dA}$) of ice crystal  
$V_{pore}$ : pore volume  
n : number of moles in the pore

With $(\gamma_{sw} - \gamma_{si}) = \gamma_{wi}$

and $H_0$ the molar enthalpy of fusion one can find (Setzer [44])

$$\frac{\Delta T}{T_0} = \frac{\gamma_{wi}V_i}{H_0RH}$$

where: $\Delta T$ : freezing/melting point depression  
$T_0$ : bulk freezing point

Similar equations were found earlier by different researchers (Kubelka [45], Everett [5]).

Brun [46] finds a similar equation as (7) from Gibbs-Duhem equations. In his quasi-macroscopic approach he calculates $\Delta S = (s_{w} - s_{i})$ using macroscopic values. Assuming that the solidification process is by ice nucleation (growth of a critical embryo) and by integrating (7) he obtains from calorimetric data of porous Vycor glass a temperature dependent relationship for $\gamma_{wi}$ . Additionally a layer of unfrozen water of ca. 8 Å thickness (Brun [47]) is taken into account. Finally, he obtains a relation between pore radius $R_p$ and freezing and melting point depression $\Delta T$ for spherical pores:

$$R_p = \frac{-64.67}{\Delta T} + 0.57$$  \[nm\]  \[0 > T > -40^{\circ}C\]

The apparent solidification energy can be calculated as:

$$W_a = -5.56 \times 10^{-2} \Delta T^2 - 7.43 \Delta T -332$$  \[J/g\]  \[0 > T > -40^{\circ}C\]

The form of the pores influences the curvature of the liquid-ice interface (e.g. $RH$). Therefore some corrections in the case of other pore forms have to be considered. For freezing, nucleation from spherical ice germs is assumed. Brun therefore finds no deviation from equations (9) and (10) for cylindrical pores in the case of solidification (freezing). In the case of fusion (melting) the ice fills the cylindrical pores and the hydraulic radius of the melting ice is different. He derives for the melting point depression of cylindrical pores:

$$R_p = \frac{-32.33}{\Delta T} + 0.68$$  \[nm\]  \[0 > T > -40^{\circ}C\]

$$W_a = -0.155 \times 10^{-2} \Delta T^2 - 11.39 \Delta T -332$$  \[J/g\]  \[0 > T > -25^{\circ}C\]

3.2.3 Ice nucleation

When the temperature of water is lowered below its freezing point, freezing not always starts immediately. Water can supercool to several degrees.
The degree of supercooling ("undercooling") depends on the purity of the liquid, its volume and to a lesser extent on the rate of cooling. Other factors like convection or turbulence are additional criteria.

At temperatures below freezing point small ice particles form spontaneously in bulk water, but they are not stable until they reach a critical size, so that water and ice (with different surface curvature) can be present in the pore system at the same time (fig. 14).

Assuming spherical ice particles, a relation for the critical germ radius \( R^* \) can be derived from Kelvin equation (analog to eq. 8)

\[
R^* = \frac{2\gamma_{wv} \gamma_{vT}}{H_v \Delta T}
\]  

When touching a supercooled liquid with an ice germ larger than the critical size, freezing is initiated immediately over the whole volume.

When such a germ of critical size is formed by the random motion of the water molecules, this is the so-called homogeneous nucleation. The probability of this event is proportional to the total volume of water and the time for which the liquid is supercooled. It increases rapidly with decreasing temperature. Water drops of the same size placed on a plate show typically a quasi-Gaussian distribution of the number of freezing droplets in function of the temperature (fig 15, Bigg [48]).

Below a temperature of -40°C no further supercooling of water is possible and freezing starts in each case.

Solid particle in suspension or a solid surface may also act as a nucleus. This nucleation process is then called heterogeneous nucleation (Fukuta [49]).

One of the best known and most effective inorganic ice formation germ is silver iodide (AgI). The threshold value, that means the highest temperature at which ice formation is initiated, is -4°C. The efficiency of this ice formation germ can be explained by the similarity of its crystal lattice to the one of ice. Many other inorganic substances with ice nucleation properties are known (Hallet [50], Mason [51]). Their threshold values vary in a wide temperature range from -2 to -20°C.
Several complex organic substances, notably steroid compounds, which have apparently little structural resemblance to ice, may act as germs for ice formation at much higher temperatures close to the bulk freezing point. Threshold temperatures of -1°C were observed for cholesterol, pregnenolone, diosgenin, stigmasterol and others prepared in a mica sandwich technique described by (Fukuta [52]). The substances are melted between two mica (or glass) covers and then allowed to recrystallize. One mica (glass) cover is then removed and the substrate is brought in contact with water. The ice formation capacity is studied under a microscope. The ice formation was observed to start preferentially in the shrinkage cracks of the substrate. The density of the nucleating sites and the predominant ice crystal forms depend strongly on the method of preparation.

The high nucleating ability of organic compounds is difficult to explain as they differ considerably in their unit cell dimensions and there is no close relation to the ice lattice. Rather flexible hydrogen bonding groups (OH) on the faces of the organic crystals seem to be most important. A possible orientation of OH groups at the border of the shrinkage cracks may explain their ice formation capacity.

The highest threshold value found in literature is -0.4°C for methaldehyde prepared as recrystallisation product from ethanolic solution (Fukuta [53]).

3.2.4 Aqueous solutions

The freezing and melting characteristics are changed when salts or other electrolytes are dissolved in water.

Because of the low costs, mostly sodium chloride is used as deicing salt in winter. Therefore only the system H$_2$O-NaCl is considered in detail. Similar relationships can be found for other substances.

Water around ions can be divided into three concentric regions (Frank [36], fig 16). Next to the ion, water molecules are strongly oriented due to the electrostatic field of the ion. Although the water molecules in this region are not hydrogen bonded to each other they are immobilized. Their entropy as well as their energy is low. In the following region the structure of water is broken down and the molecules are disoriented with a less structural order than in
pure water. The last region contains normal water affected only very slightly by the ion. The consequence is a lower chemical potential than pure water and hence the freezing point (fig 12) and the vapor pressure (fig 13).

Fig. 16 Schematic representation of different regions of water structure around a ion
region A: radial orientation of water molecules around a positive ion. Arrows indicate their dipole moment (for an anion: opposite orientation) region B: disorientation of molecules region C: structure which corresponds to that of pure water

The phase diagram (fig 17) shows the dependence of the freezing point from the concentration of the NaCl- solution. At higher concentrations than 30 mass-% it is no longer possible to dissolve all sodium chloride in water and pure NaCl (above 0°C) or a sodium chloride hydrate (NaCl₂H₂O) falls out. This is also the case at lower temperatures than the eutectic temperature (-21°C).

The dependence of vapor pressure (e_{sat,water} (e_{sat,salt}) = saturated water vapor pressure in the air above liquid water (NaCl-solution)) and the concentration of the NaCl-solution is given in fig 18.

Fig. 17 Phase diagram H₂O-NaCl
Owing to the transport phenomena, another physical property which is of interest in relation to frost resistance is the viscosity which also depends on the salt concentration (fig 19). It increases with higher salt content.

Fig. 19  Viscosity versus salt concentration

3.2.5  Growth of ice crystals in water and aqueous solutions

When macroscopic water is frozen, the velocity of crystallization is controlled by the rate at which the water molecules are built into the ice crystal lattice. Because of the liberation of the latent heat of crystallisation it also depends on the diffusion of heat in the vicinity of the growing interface.
When ice grows into water (not supercooled) the ice-water interface is planar. In supercooled water, dendrites branching at 120° are formed (Hallet [50]).

The velocity increases with about the square of the degree of supercooling.

Low concentrations of soluble ions like sodium chloride have almost no influence to the growth velocity. Higher concentrations lead to a loss of velocity of up to a factor 10.

The square dependence of the degree of supercooling remains. For macroscopic alkali-halide solutions still non-rational (preferred growth direction) dendrites are formed.

When an aqueous solution freezes, the ice crystals which are formed consist of almost pure water: the ions of the dissolved salt hardly are incorporated into the condensed phase. The first tenth of a millimeter of a frozen salt solution in a tube, nucleated from one side, consists of almost pure ice (fig 20). This segregation effect is used in desalination of seawater (Nesselmann [54], Tleimert [55]). The concentration of the salt within the ice depends on the growth rate and the temperature of the ice surface. By the displacement of the salt through the advancing ice, a layer of increased salt concentration at the interface of the phases results.

Tilby et al [56] measured the concentration of the solute and the growth velocity of the ice front by means of holographic methods and compared them with results from a numerical simulation.

Wang [57] observed the growth of the ice - water interface by direct optical observation. A picture motion camera observed the evolution of the ice front on a 100 micron thick concrete thin section which was moved laterally at constant velocity to keep the liquid-ice interface focused. Wang found that the rate of ice propagation in concrete cracks was 2-3 times faster than in the liquid outside and reached values of 60-70 μm/sec. This difference may be explained by the higher thermal diffusivity of the concrete (compared to pure water) which conducts away the latent heat.

When water freezes in the capillaries of cement-bonded materials ice Ih (hexagonal) is formed (Badmann [58]) as can be proven by X-ray low angle scattering. Low amount of ice Ic (cubic) was found at temperatures below -35°C.
3.2.6 Growth of ice in capillaries containing supercooled water

Due to the temperature difference between freezing point and actual temperature, the latent heat which is set free at crystallization can be removed more quickly when supercooled water freezes so that the growth velocity of ice is higher. The growth velocity of ice in capillaries (d=1,2 mm) filled with supercooled water was found to be proportional to the square of the degree of supercooling (Pruppacher [59], fig 21).

Supercooled aqueous solutions of higher salt concentration showed slower growth rate of ice. This was explained by freezing point lowering effects due to insufficient transport of solute by diffusion away from the growing interface (see fig 20). The concentration of solute at the ice front is higher which lowers the local freezing point and therefore the difference between the freezing point and the actual temperature.

![Growth velocity of ice versus degree of supercooling](image)

Fig. 21 Growth velocity of ice versus degree of supercooling (= difference between freezing point and actual temperature) (Pruppacher [59])
CHAPTER 4  DETERIORATION MECHANISMS

4.1 Microscopic damage models

4.1.1 Diffusion and freezing of gel water

Powers and Helmuth [31] found in dilatation experiments that not all phenomena can be explained by the hydraulic pressure theory (see section 4.2.2) only. Further, with frost resistant specimen they found contractions larger than thermal contraction when lowering the temperature below the freezing point of water.

These findings were explained by a larger free energy of the unfrozen water in the gel pores than of the ice in the capillary pores. The resulting water transport to the capillary ice and the subsequent phase transition cause a growth of ice lenses in the bigger pores. At the same time the gel structure shrinks.

The positive influence of the air pore content can be explained with a lower free energy of ice in the air pores, resulting from removed water due to hydraulic pressure during freezing. This ice hence attracts the unfrozen water more than the capillary ice. The unfrozen water in this case is transported to the mostly empty air pores, where it does not cause additional stress upon freezing.

4.1.2 Everett's arm chair experiment

In his arm chair experiment Everett [5] imagines two containers (A, B fig 22) each closed by a movable piston and joined by a capillary tube of radius r. Initially the cylinders are filled with liquid water at a pressure $p_1 = p_w = p_0$ and a temperature above freezing point. The temperature is then lowered to 0°C and freezing in A is nucleated. As freezing proceeds, the accompanying expansion is taken up by the movement of the pistons. When the container A is completely filled with ice and, assuming that no nucleation occurs in B (the water in the capillary and the container B remains supercooled), further removal of heat would make that the initially planar ice-water interface would become curved as the ice intends to penetrate the capillary. Owing to the curved interface, a pressure difference between the supercooled water and the ice phase is built up.

$$p_i - p_w = \frac{2\gamma_{iw}}{r}$$

Fig. 22  Everett’s arm chair experiment (left) and the equilibrium interface between water and ice (right) when

$\ldots\ldots\ldots\ldots\ldots\ p_w = p_i = p_0 \quad p_i - p_w = \frac{2\gamma_{iw}}{r}$

$p_i - p_w = \frac{2\gamma_{iw}}{r}$
Consequently the water in the lower container is to move towards the ice filled container where it can freeze, leading to an upward movement of the upper piston. With further removal of heat the curvature of the ice-water interface and the pressure difference $\Delta p = (p_i - p_w)$ would increase until the interface becomes a sphere with radius $r$ equal to the radius of the joining capillary, so that the ice can completely penetrate the capillary. For a sphere of radius $r$ is $\frac{1}{R_H} = \frac{2}{r}$, so that the maximal pressure difference that can be reached is:

$$\Delta p_{\text{max}} = \frac{2\gamma_{wi}}{r}$$

This equation is used in soil physics (Taber [60]) for the calculation of the heaving pressure of ice lenses. However, in his model no water flow would occur when the water is in the condition of a sufficiently high tension (reduced $p_w$). In the case of a porous material this could happen when a sufficient amount of water is removed of a small cavity or when other containers filled with ice are fed by the same water filled container.

The curvature of the ice-liquid interface is zero when the temperature in the ice and in the water container are near the bulk freezing point of water. It also might be difficult to speak of a meniscus when considering the adsorbed water in the smallest pores.

4.1.3 Setzer's mechanism

In his thermodynamic model Setzer calculates the pressure difference between an ice crystal of radius $R_{Hc}$ in small pores and a plane surface, that arises when the capillary condensed water freezes, to (Setzer [33]):

$$\Delta p_{\text{freezing}} = \frac{\gamma_{ai}}{R_{Hc}}$$

where: $\gamma_{ai}$ : surface tension ice-adsorbed layer

Between ice filled pores of different sizes therefore exist considerable pressure differences. Using a similar equation as equation (8), a relation for the maximal possible pressure in function of the temperature below bulk freezing point $T_0$ can be found without any information about the surface tensions:

$$\Delta p = - \frac{H_0}{T_0 \gamma_i} \Delta T$$

When the temperature is lowered and the water in the finest pores freezes, pressure differences of 30 - 40 MPa can result. The stress in the matrix depends of water transport that tends to equal the pressure difference. The water transport is related to the boundary conditions (Setzer [6]).

This thermodynamic model assumes independent ice nucleation in each pore (no ice front). Neither the 9% volume increase of the water when freezing nor the thermal contraction of the ice in the bigger pores ($\alpha_{T, \text{ice}} \equiv 55 \times 10^{-6} \text{ [K}^{-1}]$), which in most cases would change the pressure situation are taken into account.
4.1.4 Evaporation followed by sublimation

Litvan [61] proposes a mechanism where the unfrozen pore water is transported to the ice, both in the larger capillaries and outside the porous material, due to the difference in vapor pressure above ice compared to the one above supercooled water. The water transport is through evaporation followed by sublimation on the existing ice (fig 23).

Fig. 23 Litvan: evaporation of supercooled water in the fine pore with subsequent sublimation on the ice in a coarser pore

Due to this desorption and the formation of an interface meniscus, tensions in the pore system and near the surface arise. However, such a transport requires strong thermodynamic imbalance for instance due to a strong supercooling or to a big temperature gradient.

4.2 Macroscopic damage mechanisms
4.2.1 Closed Container

In the simplest case every small "unit cell" of the cement paste can be looked upon as a closed container (Fagerlund [62], fig 24) where no water transfer is permitted from the place where ice is formed. In real concrete this may be the case when the concrete contains no air-filled space or when the permeability of the pore walls is very low.

Fig. 24 Closed Container ("unit cell")

When the temperature falls below 0°C, and no supercooling occurs, pure water starts freezing. When no fracture of the surrounding dense wall occurs, the 9% volume increase upon the phase transition of water increases the pressure. This lowers the freezing point of the remaining water (see phase diagram). If the container temperature does not fall below the new freezing point, no more ice is formed and the pressure remains constant. From the Clausius-Clapeyron equation or from the phase diagram we obtain:
(17) \[ p = 10 \Delta T \]

where: \( p \) : pressure [MPa]  
\( \Delta T \) : freezing point depression [K]

When the internal pressure is evenly distributed across the container wall the tangential stress is:

(18) \[ \sigma_t = 10 \Delta T \frac{w_f^3}{(1 - w_f^3)} \]

where: \( \sigma_t \) : max. tangential stress [MPa]  
\( w_f \) : total freezable water \([m^3/m^3]\]

The maximal tolerated freezable water content can be calculated using the tensile strength of the concrete as the maximal allowed tangential stress. The above calculations assume complete water filling. Damage can be prevented by a certain amount of empty pore space, mainly by air-pores.

Neglecting the compressibility of ice and water (considered in Schröter [63]) a relation for the critical degree of saturation can be derived (Fagerlund [64]):

(19) \[ S_{\text{eff,CR}} = 0.917 + 3 \frac{\varepsilon_b(1 - 2\nu)}{(1.09 P (1 - k_T))} \]

where: \( S_{\text{eff,CR}} \) : effective critical degree of saturation  
\( \varepsilon_b \) : linear relative ductility \([m/m]\]  
\( \nu \) : Poisson ratio  
\( P \) : total Porosity \([m^3/m^3]\]  
\( k_T \) : non-freezable water \([m^3/m^3]\]  
\( k_T \) : fraction of P

Thus the minimum air pore content to avoid damage can be calculated using:

(20) \[ S_{\text{eff}} = \frac{w_f}{w_f + a} = 1 - \frac{a}{P(1 - k_T)} \]

where: \( S_{\text{eff}} \) : effective degree of saturation  
\( a \) : air-pore content \([m^3/m^3]\]

The model might be useful when a large amount of freezable water is concentrated in a relatively small volume, like in porous aggregates (Fagerlund [65]), for the interfacial zone, for material with low tensile strength like fresh concrete or in cases where the permeability is very low, in high performance concrete with low water/cement ratio.

The closed container model predicts lower air pore content than known to be necessary for frost resistant concrete. One possible explanation is that excess water caused by freezing has to flow to escape places (empty air pores). This water flow creates hydraulic pressure.
4.2.2 Hydraulic pressure

The hypothesis of hydraulic pressure was first described by Powers [4], mainly as to explain his observations of the protective influence against frost/salt deterioration of air voids. According to Darcys law, he calculates (Powers [66]) the resulting hydraulic pressure caused by the expelled water due to the 9% volume increase of the water in the sphere of influence around an air pore (fig 25).

![Diagram of an air bubble and its sphere of influence]

Fig. 25 Air bubble with radius \( r_b \) and its sphere of influence with radius \( r_m \)

The amount of expelled water from a sphere element is:

\[
\Delta V = (1.09 - \frac{1}{S'}) \Delta w_f 4\pi (r')^2 \Delta r'
\]

where: 
- \( S' \) : degree of saturation of matrix (without air)

By the application of Darcys law:

\[
\frac{dp}{dr} = \frac{\eta}{K} \frac{dV}{dt} \frac{1}{a}
\]

where: 
- \( p \) : hydraulic pressure [Pa]
- \( a \) : area through which flow takes place = \( 4\pi r^2 \)
- \( V \) : total flux through a volume element [m³/s]
- \( \eta \) : viscosity [Pa s]

and integration over the sphere Powers derives for the maximal hydraulic pressure:

\[
P_{\text{max}} = \frac{\eta}{3} (1.09 - \frac{1}{S'}) \frac{UR}{K} \phi(L)
\]

where: 
- \( U \) : rate of ice formation [\( \frac{g}{g K} \)]
- \( R \) : freezing rate \( \frac{dT}{dt} \) [K/s]
- \( K \) : permeability [m²]
- \( w_f \) : freezable water content
- \( r_b \) : radius of air bubble [m]
- \( r_m \) : radius of sphere of influence of cement matrix [m]
L is the so-called air void spacing factor. The material is supposed to be damaged when the hydraulic pressure reaches its tensile strength. No water is expelled when the degree of saturation is lower than 0.917 and the generated hydraulic pressure is then zero. Only slight lowering of $S'$ reduces the hydraulic pressure significantly. This leads to the existence of a critical degree of saturation (Fagerlund [67]).

Powers model calculation was for uniform sizes of air pores. Further theoretical analysis to consider other aspects as the important case of a penetrating ice front (Warris [68]) can be derived from more general integration of Darcy's law. Analog to the case of a hollow sphere, a critical slice thickness can be calculated (Fagerlund [69]).

The existence of a critical distance was demonstrated on concrete specimen of different thickness (Fagerlund [67]). Only the specimens thicker than a certain amount showed severe damage after freeze/thaw solicitation.

Besides the shape and distribution of air pores, other concrete properties such as permeability and freezable water content are highly influencing its frost deicing salt resistance. The permeability depends mostly on the total porosity but it is reduced by ice formation in the coarser pores. The effects on the maximal pressure by the rate of ice formation with the varying temperature are discussed by Fagerlund [70].

An important factor is that smaller air pores can get filled with water (Fagerlund [71], Schröter [63]) or secondary hydration products (ettringite, etc.) (Kukko [72]).

In the first case the spacing factor is increased as well as the degree of saturation, whereas in the second case only the spacing factor is increased while the degree of saturation remains equal.

The real material neither consists of hollow spheres nor of slices but of water saturated matrix enclosing more or less spherical air filled pores of different sizes. There are many individual flow paths for each matrix element to the nearest escape boundary, giving rise to a hydraulic pressure. Due to the big complexity of the system, the critical flow path for crack formation hardly can be calculated theoretically. On the other hand it can be determined easily in experiments by the determination of the critical degree of saturation.

The concept of hydraulic pressure stimulated many other researchers to develop methods of frost resistance testing of concrete based on a critical distance of air voids (Dobrolubov [73], Pigeon [74][75], Pleau [76]). The mean distance between air pores is measured on polished, mostly impregnated concrete surfaces or thin sections by means of image analysis equipment. For experimental studies it is of most importance to vary the spacing factor independent of the total air pore volume content.

Power suggested from experimental data that an air pore spacing factor of less than 0.25mm would prevent the concrete from damage (Powers [77]). Indeed a balance between air pore content and capillary properties (water/cement ratio) has to be found [74][75][76]. On the other hand, scaling of very thin concrete layers (typically 0.1 mm) in frost deicing salt resistance tests hardly can be explained by hydraulic pressure. Powers [4] himself calculated the ice formation rate to be very high and hardly to be found in real concrete structures. In the case of supercooling such high velocities are easily reached as can be seen in fig 21.

In the model one assumes that the air pores remain empty so that they can serve as escape boundaries. In practice this is only the case for undercritical saturation. With higher degree
of saturation, these pores get filled by excess water. Assuming an advancing ice front, the distance to the next empty escape boundary increases continuously as the excess water fills the previously empty pores. The maximal hydraulic pressure therefore can reach critical values without big ice formation rate but this is only for inner concrete layers. In the case of an advancing ice front and overcritical saturation, surface parallel cracks at a depth of some spacing factors would appear.

4.2.3 Thermal contraction and dilatation of ice

Different thermal contraction coefficients of the concrete phases, aggregate stones (4.20 $10^{-6}$ [1/K]) cement paste (10..11 $10^{-6}$ [1/K]) (Dettling [78]) and ice lh (55 $10^{-6}$ [1/K]) can cause internal stress, especially when big temperature variations occur.

In combination with a redistribution of pore water the high thermal contraction/dilatation coefficient of ice gives rise to another possible damage mechanism. Considering a water filled porous material at a temperature below zero degrees the bigger pores will be ice filled after nucleation has started, whereas the liquid in the smaller pores remains unfrozen (see section 4.1). Due to the resulting pressure difference the water in the smaller pores tends to migrate to the larger ice filled pores (fig 26).

Fig. 26 Thermal contraction of ice when lowering the temperature (1) and refilling with water (2) which freezes. This causes tensile stress in the surrounding material when the temperature rises again (3) and the ice expands

The pressure that the ice exercises on the pore walls may hinder this migration. When the temperature then is lowered, further the ice will contract more than the cement stone matrix due to its higher thermal contraction coefficient. Now, the migration of water can equal the loss in pressure or fill the empty pore space and an additional amount of water is allowed to freeze in the bigger pores. When the temperature rises at thawing, the higher dilatation coefficient of ice causes tensile stress. Calculations (Grübl [79], Podvalnyi [80], fig 27) estimate the stress to:
Fig. 27 Resulting tensile stress in cement stone upon thawing because of different coefficients of thermal contraction

4.2.4 Temperature shock

When concrete is covered with an ice layer and this layer is thawed by deicing salts a temperature shock, e.g. a sudden temperature lowering at the concrete surface to satisfy the energy requirement for the phase change of the ice, appears. Walz [81] reports deterioration of concrete where the ice was separated from the deicing salt by means of a plastic foil.

Harnik and Rösli [82][83] studied the amount and the extent of the temperature shock in laboratory and under field conditions. With different ice layer thickness and deicing salt concentrations they found temperature changes in laboratory tests of up to 14°C. With eutectic concentrations of sodium chloride the shock was the most severe. The ice layer thickness gave contradictory results. The maximal tensile stress was calculated to:

\[
\sigma_{\text{max}} = 0.24 \Delta T \quad \text{[N/mm}^2\text{]} \\
\text{where:} \quad \Delta T \quad \text{: Temperature lowering [K]}
\]

A resistance factor \( W_T \) to temperature shock can be defined (Manson [84]):

\[
W_T = k \frac{\lambda}{\alpha_T} \frac{\beta_t}{E}
\]

where: 
- \( k \) : proportionality factor
- \( \lambda \) : thermal conductivity
- \( \alpha_T \) : contraction coefficient
- \( \beta_t \) : tensile strength
- \( E \) : modulus of elasticity

Nevertheless, Harnik and Rösli only found minor temperature shocks of 1-2 °C during their extensive field studies.
4.3 Influence of salt solutions

4.3.1 Osmosis

Scaling (Verbeck [85]) and expansion (Fagerlund [69]) of concrete submitted to frost deicing salt attack are found to depend on salt concentration. A pessimum for frost resistance is found for NaCl concentrations of 2-4%. This is often explained with the aid of osmotic pressure models.

When the concrete pore solution starts freezing coarser pores freeze first. In the presence of sodium chloride solutions (or alcalihydroxides), segregation effects are assumed to increase the salt concentration in the pores containing ice bodies. The lower salt concentration in the unfrozen smaller pores and the difference in diffusion coefficient of water and salt ions lead to an osmotic pressure. The pore walls are supposed to act as semipermeable membranes. In tests with hardened cement paste plates and sodium silicate solutions pressures up to 1 N/mm² can be found (Mc Connel [86]). Theoretical considerations derive pressures in the same order of magnitude (Hartmann [87]).

So far, no experiments to measure the osmotic pressure in frost deicing salt tests are reported.

The pessimum is explained by the osmotic pressure on the one hand, which increases with increasing salt concentration. On the other hand, the content of freezable water decreases (Klieger [88]) with higher salt concentration so that a decreasing hydraulic pressure results (Fagerlund [69]). This is in spite of increasing viscosity (fig 19).

At constant temperature the osmotic pressure would lead to a continuous expansion. This is not found in the experiments performed in the scope of this work.

The theoretical and practical pressures are small compared to the tensile strength of concrete. Neither the difference of scaling with water which is up to two orders of magnitude smaller than with 3% salt solution (for standard concrete) nor the difference between inner damage and surface scaling in frost deicing salt resistance tests (Jacobsen [89]) can be explained with osmosis effects only.

4.3.2 Crystallization effects

At very high salt concentrations (eutectic) crystallization of the deicer salt is possible. Decreasing solubility at lower temperatures supports crystal growth during freeze/thaw cycling. For NaCl no volume increase due to crystallization is found (Hartmann [87]). Nevertheless oriented growth could lead to a pressure upon the pore walls. Additionally, soluble mineral from the cement stone matrix may recrystallize if present at high concentrations.

4.3.3 Layer freezing

Chloride profiles of building walls often show lower chloride content at the surface. A maximum chloride content is found at certain distance from the surface. According to freezing point depression by the salt solution (Raoult’s law) the different concrete layers would freeze at different temperatures depending on their chloride content. Therefore freezing in the concrete layer with the highest chloride content would occur when certain amount of pore solution on both sides already would have frozen. Permeability would be reduced and higher hydraulic pressure could result (Meier [90]).

The theory implies a sufficient amount of freezing germs in the inner concrete to start nucleation. More probable is that freezing is only initiated at the surface. Additionally the layers with comparable chloride content would be rather thick so that the shortest path to the next air void is small compared to the region of retarded freezing.
4.4 Chemical aspects

The decreased frost deicer resistance of low concentrated solutions and the similar behavior of chemically very distinct deicers (chlorides/organic solvents) confirm that the deterioration rather is due to physical effects than chemically.

Nevertheless deterioration by chemical attack can not be neglected in certain cases. For example for blast furnace cement concrete chemical aspects are important. While a good frost resistance can be achieved, decreasing frost deicing salt (NaCl) resistance was found for increasing granulated slag content, even with high air pore content. This was attributed to carbonation and the formation of metastable calcium carbonate modifications like argonite and vaterite that are soluble in NaCl solutions.

Additional calcium hydroxide or the application of a draining formwork improved the frost deicing salt resistance of blast furnace cement concrete (Stark [7][91][92]).

While the frost damage of NaCl solutions is thought to be mostly physically, this is not the case for other deicing salts like CaCl₂, MgCl₂ or KCl which can be found as impurities in stone salt (Fuji [93], Radcke [94]).

High salt concentrations can cause leaching and remineralizing. Calcium hydroxide (Ca(OH)₂) can be dissolved into CaCl₂ and the corresponding metal hydroxide.

For example:

\[ \text{Ca(OH)}_2 + \text{MgCl}_2 \rightarrow \text{CaCl}_2 + \text{Mg(OH)}_2 \]

In a further reaction step the calcium chloride can react with the tricalcium-aluminat or the tricalcium-aluminhydrates to form Friedl's salt:

\[ \text{CaCl}_2 + \text{C}_3\text{A} + 10\text{H}_2\text{O} \rightarrow \text{C}_3\text{A-CaCl}_2\cdot 10\text{H}_2\text{O} \]

Many other reactions are possible; an overview is given in (Glock [95]).

Recently secondary ettringite formation is discussed more intensively. This reaction is supposed to be supported by thermodynamic conditions at low temperatures (Stark [7]). Low concentrated NaCl solutions (0.58%) transform monosulphate hydrate \((\text{C}_3\text{A-CaSO}_4\cdot 12\text{H}_2\text{O})\) at temperatures between -5°C and -20°C into ettringite, Friedl's salt and sulfate-chloride monophase (Dorner [96]). Higher concentrations do not form ettringite. The volume expansion due to ettringite formation from the monophases in mostly elder concrete is therefore not attributed to high chloride content in building concrete in winter, but may lead to more severe damage in spring when chloride concentration is lowered by rainfall.

In concrete with calcareous aggregates secondary ettringite was observed after freeze-thaw cycling. The proposed reaction (Renaud [97]) is

\[ 6\, \text{Ca}^{2+} + 2\, \text{Al(OH)}_4^- + 4\, \text{OH}^- + 3\, \text{SO}_4^{2-} + 26\, \text{H}_2\text{O} \rightarrow \text{Ca}_6[\text{Al(OH)}_6]_2(\text{SO}_4)_3\cdot 26\text{H}_2\text{O} \]

Freezing and thawing cycles are supposed to entail the water circulation provoking the apparition of many ions in the solution. The dissolution of portlandite \((\text{Ca(OH)}_2)\) liberates \(\text{Ca}^{2+}\) ions. \(\text{SO}_4^{2-}\) ions are liberated from CSH gel in the case of calcareous concrete or by dissolution of primary ettringite in siliceous concrete.

Chemical leaching also leads to increased pore volume and higher capillary pore content. Higher freezable water content results and hence increased damage by physical effects. Air voids and microcracks may get filled with secondary hydration products (Kukko [72]). A larger spacing factor could result.

Organic deicers, used as non-metalcorrosive substances for deicing of landing pistes of aircrafts, affect the viscosity and surface tension of the solutions and lead to higher saturation of the concrete. In alkalic environment hydrolyse reaction can start. The hydrolyse products can attack the cement stone matrix.
4.5 Salt-frost scaling

Experimental observations on salt-frost scaling, mostly in the scope of frost resistance testing in laboratory by means of fast weathering methods, lead to the development of many theories to explain this kind of surface damage. Some of these mechanisms are included in the general description of the mechanisms that can lead to frost deicing salt damage in the previous sections, mostly as special cases. A short review of some experimental findings of other researchers and some of the proposed mechanisms on this specific aspect are given below.

Verbeck and Klieger [85] found increased scaling (compared to pure water application) for both organic (alcohol, urea) and salt deicers (NaCl, CaCl₂) and they concluded that scaling is rather a physical than a chemical effect. Without the application of a liquid layer at the surface scaling was much less. Nevertheless, in special cases chemical damage mechanisms are important. For example, scaling is increased in cementitious materials containing high amounts of slag cement owing to carbonation (Stark [7]). The positive effect of deicers often is attributed to a higher degree of saturation close to the surface owing to osmosis or reduced vapor pressure.

Verbeck and Klieger also reported scaling to be maximal at a certain "pessimum" deicer concentration. In the case of a sodium chloride solution the pessimum is reported at a concentration of about 3 mass-% (Fagerlund [135]). Powers explained the existence of a pessimum by superimposed hydraulic pressure and osmosis.

The amount of scaling also is influenced by the freezing rate (Fagerlund [70], Studer [136], Sellevold [137]), the minimal temperature (Suder [136], Jacobsen [89]) and inner salt concentration (Snyder [138]). Snyder referring to Hartmann [87] explains salt frost scaling with steep salt and temperature gradients and freezing initiation in different material layers. Petterson [139] explains the increased scaling when saturating specimens with pure water and applying salt solutions on their surface with supercooling of the inner pore solution and increased hydraulic pressure when freezing is initiated in the outer liquid.

Different researchers report a water uptake during frost deicing salt testing by means of fast weathering laboratory tests (Fagerlund [135], Auberg [101], Jacobsen [89]). Setzer [25][140] explains the water uptake by a pumping effect as a consequence of micro ice lens formation. Lindmark [141] explains scaling by progressive osmotic micro ice lens growth, similar to the frost heave in soils. Both mechanisms assume the existence of an outer liquid phase at the specimen surface during the period when ice exists within the concrete.
Part II

EXPANSION EXPERIMENTS
CHAPTER 5  SPECIMENS

The subject of this work was to study the damage mechanisms of ordinary Portland cement concrete on frost deicing salt attack. The influence of different material parameters was only of secondary interest, so that just a few different concrete mixes were studied in detail. This allowed the application of various different experimental techniques.

Concrete cubes (200x200x200 mm$^3$) of the following mixes were fabricated (table 3):

<table>
<thead>
<tr>
<th>Sand 0/4 mm</th>
<th>Mix 1</th>
<th>Mix 2</th>
<th>Mix 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>640</td>
<td>722</td>
<td>722</td>
</tr>
<tr>
<td>Gravel  4...8 mm</td>
<td>320</td>
<td>266</td>
<td>266</td>
</tr>
<tr>
<td>8...16 mm</td>
<td>340</td>
<td>285</td>
<td>285</td>
</tr>
<tr>
<td>16...32 mm</td>
<td>700</td>
<td>627</td>
<td>627</td>
</tr>
<tr>
<td>Cement CEM I 42.5</td>
<td>300</td>
<td>300</td>
<td>325</td>
</tr>
<tr>
<td>Water</td>
<td>150</td>
<td>189</td>
<td>145</td>
</tr>
<tr>
<td>W/C-ratio</td>
<td>0.5</td>
<td>0.63</td>
<td>0.45</td>
</tr>
<tr>
<td>Bulk density</td>
<td>2447</td>
<td>2452</td>
<td>2383</td>
</tr>
<tr>
<td>Total porosity n</td>
<td>11.01</td>
<td>14.62</td>
<td>15.72</td>
</tr>
<tr>
<td>Air pore content</td>
<td>1.09</td>
<td>0.99</td>
<td>3.69</td>
</tr>
<tr>
<td>U$_{50}$ (drying at 50°C)</td>
<td>3.77</td>
<td>5.78</td>
<td>5.53</td>
</tr>
<tr>
<td>U$_E$ (water storage)</td>
<td>9.92</td>
<td>13.64</td>
<td>12.03</td>
</tr>
<tr>
<td>S$_{crit}$ (critical degree of saturation)</td>
<td>0.901</td>
<td>0.935</td>
<td>0.86</td>
</tr>
<tr>
<td>S$_E$ (cap) (degree of sat. at water storage)</td>
<td>0.902</td>
<td>0.932</td>
<td>0.76</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>$\Delta m_{30}$ (mass loss after 30 frost cycles)</td>
<td>1200</td>
<td>800</td>
<td>40</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>43.5</td>
<td>43.1</td>
<td>43.9</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>32600</td>
<td>35200</td>
<td>36600</td>
</tr>
</tbody>
</table>

Table 3  Mix design and material properties

After fabrication the concrete cubes remained in the moulds for 2 days (20°C / 70%RH) before they were demoulded and then treated individually.

Additionally hardened cement paste with water/cement ratios of 0.26 ; 0.4 ; 0.5 and 0.8 were studied. The pastes with a higher w/c-ratio (0.4 ; 0.5 ; 0.8) were produced in the scope of a thesis at EPFL (Houat [98]) with the aid of a special mixing technique. Mixing was done under vacuum in a rotating tube.

The studied mixes mostly had a medium to poor frost resistance. The limitation to relatively poor frost resistance was chosen because of the faster response (damage) to the frost deicing salt solicitation and hence time saving which allowed an improved experimental analysis.
CHAPTER 6  MEASUREMENT OF EXPANSION PARALLEL TO THE FROST MEDIUM SURFACE

6.1  Introduction

When water freezes its volume increases 9%. The ice therefore needs more free space to accommodate and if this is not sufficiently provided the concrete will expand due to the pressure that the ice is exerting on the pore walls. This expansion can be measured and gives useful information about the moment of ice formation, the amount of ice that is formed and finally the deformation and permanent residual damage due to crack formation.

Special attention was put on the measurement of the expansion of the outermost concrete layer (1 to 10mm) with the possibility of the application of a frost medium layer like in the fast weathering tests. Expansion of the concrete parallel and perpendicular to the concrete-frost medium interface was measured to study the degree of uniformity of the expansion.

Most researchers (Powers [9], Litvan [99], Erbaydar [100]) who have studied the dilatation of concrete worked with specimens that were preconditioned to a certain degree of saturation, mostly water saturated or vacuum saturated. As will be demonstrated the simultaneous application of a frost medium layer allows the separation in time of different freezing effects. Very little research has been previously carried out studying dilatation keeping a frost medium layer on one concrete surface and in especially in the direction perpendicular to this surface.

6.2  Method and apparatus

The test specimens were concrete plates (200x200x50mm$^3$ or 150x150x10mm$^3$). An adhesive aluminum tape fixed on their side faces allowed the application of a frost medium layer (ca. 3 mm) on the upper surface of the specimens. In most cases the specimens were stored under water before the application of a frost medium. Other preconditioning is mentioned in the text.

The expansion was measured continuously by means of two inductive displacement transducers (HBM W1T3, class 0.2) that were fixed on an invar frame with little thermal contraction ($\alpha_{in} = 1 \times 10^{-6}$ m/Km). The displacement transducers were protected against humidity by plastic foils. To prevent frost medium loss by evaporation a thin polyethylene foil covered the whole apparatus. On two opposite lateral faces steel plates ($\sigma$=10mm; h=3mm) were fixed just below the tested surface. The dilatation was measured between the centers of the two steel plates parallel to the frost medium surface (fig 28). In the experiment one steel plate was kept fixed to the invar frame, the corresponding displacement transducer was used for control purpose only. The opposite concrete side was allowed to move freely so that the expansion of the whole plate actually was measured by one displacement transducer only. The temperature was measured with thermocouples (+/− 0.1 °C) which were fixed on the concrete surface by means of acrylic glue in the frost medium layer ("frost medium temperature") and on the opposite concrete surface. Additionally, in the case of the thick plates, a thermocouple was fixed at the center of the specimens.

The whole apparatus was then put into an air driven clime chamber and submitted to frost cycles. Cooling and freezing rate, in the air, was kept constant at 10°C/h. Due to the smooth cooling in an air chamber and the very small variation of air temperature (+/− 0.2 °C) supercooling to a few degrees of the frost medium layer was frequent. Temperature and output voltage of the displacement transducers (after signal amplifier) were registered each 15 seconds by means of a Grant datalogger. The data were analyzed afterwards on a PC.
The total measured expansion includes the expansion of the specimens, the expansion of the invar frame and the expansion of the displacement transducers. The expansion of the invar frame was calculated from the invar temperature and the thermal expansion coefficient for invar ($\alpha_{th, \text{invar}} = 1 \, \mu\text{m}/\text{mK}$).

The expansion of the displacement transducers was derived from a calibration experiment. The total expansion of a steel plate (length = 40mm) with well-known thermal properties ($\alpha_{th, \text{steel}} = 10 \, \mu\text{m}/\text{mK}$) was measured. Fig 29 shows good linearity of the measured total expansion. The expansion of the displacement transducers was calculated by subtraction of the expansion of the steel plate and addition of the expansion of the invar frame (calculated with the invar temperature) to the measured total expansion.

In all experiments the expansion of the specimens was calculated taking the expansions of the invar frame ($l_{\text{invar}} \times 0.33 \times T_{\text{invar}}$) and a linearised expansion of the displacement transducers ($0.33 \times T_{\text{invar}}$) into account.
6.3 Expansion results on thick plates

6.3.1 Non-saturated specimens

First, thick plates (200x200x50mm³) were used as specimens. This dimension was chosen, as it is a standard in frost deicing salt resistance tests performed at EMPA [1].

In this case mostly only the thermal expansion of the plate was measured. Only slight deviations from thermal expansion below freezing point, even for high water/cement ratio (mix 2, w/c=0.63) and with a 3% salt solution as frost medium layer, were observed. While the expansion above freezing point underwent minor changes with little remaining expansion (permanent residual damage), the differences below freezing point were more important.

Fig. 30 Expansion versus frost medium temperature of mix 2 (w/c=0.63) with frost medium 3% salt solution (5 frost cycles)

6.3.2 Completely (vacuum) saturated specimens (thick plates)

More interesting result were obtained when the degree of saturation of the specimens was increased. Some specimens hence were impregnated under vacuum once with water, once with a 3% NaCl-solution. The same liquid as used for the specimen impregnation was applied as frost medium. The impregnation under vacuum allowed the filling of the larger air inclusions. The specimens resulted completely saturated.

In fig 31 the expansion in function of the temperature in the frost medium is plotted. The difference between the temperature at the center of the specimens and the temperature in the frost medium layer was less than 2°C.

In both cases the specimens first contract thermally until the freezing point of the frost medium layer is reached. While this is at 0°C for water it is at -2°C for the salt solution. A steep expansion of the specimen is observed when freezing is initiated. With decreasing temperature, expansion continues, somewhat steeper for the salt solution, until a maximum at about -15°C is reached. A slight contraction until the minimal temperature at -25°C follows. When the temperature rises again, an almost linear expansion, with similar coefficient as the thermal contraction above 0°C, is observed till -10 or -5°C. A contraction until 0°C follows which curves again into thermal expansion above 0°C. Some further contraction (especially compared with freezing) above the melting point of the frost medium may be attributed to relaxation effects caused by closing of microcracks.
A strong hysteresis is formed. Different freezing and melting points of the pore solution could explain this hysteresis. Another possible explanation would be damage formation including a mechanism described above in section 4.2.3, which is based on the high thermal contraction coefficient of ice Ih (55*10^{-6} m/K). Contraction of the pore ice and the refilling of the empty space by migration of water in smaller unfrozen pores due to lower chemical potential would result in a linear expansion at thawing with continuous damage formation. Above -10°C the specimen length decreases as the pore ice melts.

While the measured expansions for both frost medium are quite similar, major differences are observed at the second frost cycle. The expansion below freezing point reaches higher values for specimens with deicing salt attack. The differences result from larger expansion increase during the freezing while the thawing branches of the expansion with water and with a salt solution are almost parallel.

One possible explanation may be that a higher degree of specimen saturation is reached with the salt solution as impregnation and as frost media. This might be attributed to a better refilling of damaged zones with salted medium by osmosis effects.

The steep rise of the expansion near the freezing point of the salt solution suggests another possible explanation. The ice formation rate with the salt solution was higher due to segregation effects. The pore water therefore partly could have frozen like supercooled water. A similar effect could be caused by the application of a frost medium that has a lower freezing point than the storage liquid.

Fig. 31 Expansion of completely saturated specimen (mix 1, w/c=0.5) with water or 3% NaCl solution as saturation liquid and frost medium versus temperature in the frost medium

The effect of the application of a high concentrated salt solution after six frost cycles with pure water as frost medium layer is demonstrated in terms of time in fig 32. A drastic increase of the expansion at freezing results.
Fig. 32. Effect of 15% salt solution applied as frost medium to a vacuum (water) saturated specimen after six frost cycles with water as frost medium (mix 2, w/c=0.63)

6.4 Expansion results on thin plates

6.4.1 Bending effect on thin plates

Owing to the freezing gradient one may expect that the expansion measurement is influenced by a bending effect. While bending was not observed for thick (50mm) plates it was important on thin (10mm) plates.

In order to estimate bending of the thin plates in the expansion tests, the expansion of thin concrete plates (150x150x10 mm³) of mix 2 (w/c=0.63) was measured in an additional experiment on both surfaces, the frost medium interface and on the opposite side (bottom) by means of a shrinkage meter (fig 33). On each side, two steel cylinders (Ø=10mm h=10mm) at a distance of 10 cm were fixed with an acrylic glue onto the concrete surfaces. The expansions were measured after 6, 14 and 28 frost cycles at minimum (≤-10°C) and at maximum temperature (≤10°C) in standard deicing salt resistance test (SIA 162 Test Nr 9 [1]). The specimens were taken out of the climatic chamber for a short time for measurement. The freezing rate in the frost medium was ≤20°C/h. Analyzing the results obtained at the minimum temperature a thermal contraction of ≤10 µm/Km has to be taken into account.

The specimens were previously impregnated with pure water (1 week under water). Pure water and salt solutions of a concentration of 1-10 mass-% NaCl were applied as frost medium. In order to prevent the frost medium from supercooling some cholesterol was sprinkled on it. Two different specimens were measured for each frost medium.

Although this experiment was not very precise (temperature control, etc.) the results are very interesting as they show a strong bending of the concrete plates.
In table 4 the expansion measured on side A and B at maximum and at minimum temperature and the mass of scaled material (in g) is given.

With pure water as frost medium layer only minor differences between the expansion of side A and B was observed. While side B (frost medium interface) contracted slightly, side A expanded. The amount of scaled material was very small.

With salt solutions of a concentration of 1-3 mass-% as frost medium layer, bending became important. While the frost medium side (B) expanded, the opposite side (A) contracted. This contraction certainly is the result of the big expansion in the outermost concrete layer. The mass loss due to scaling also is high.

For a salt concentration of 10%, the bending effect was only found for one specimen where a big crack was observed which possibly has influenced the result. The other specimen showed much less bending. Nevertheless the mass loss was important.

Owing to the important bending of the thin concrete plates it was not possible to quantify the influence of the composition of the frost medium layer in the expansion measurement parallel to the frost medium interface.

In fig 34-41 the surface damage (frost medium surfaces) is shown. Biggest surface damage is found with a 1-3% salt solution as frost medium layer, while with pure water or with a 10% salt solution only minor surface damage was found.

In the case of a 10% NaCl solution as frost medium a more detailed surface analysis reveals fine white lines around the aggregate stones, branching from one aggregate to another (fig 42). The salt remaining on the concrete surface after evaporation of the frost medium forms these lines.

This suggests that large amount of frost medium was concentrated in the cracks, preferably formed at the interface between the aggregate and the cement paste matrix. Inner damage therefore is important when applying a high concentrated salt solution as frost medium. Surface scaling and inner damage are two independent forms of frost deicing salt damage.
### Table 4

Expansion (µm/m) on frost medium side (B) and bottom side (A) and amount of scaled material (g) with different frost media (mix 2, w/c=0.63)

<table>
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<th>28 FC min</th>
<th>6 FC max</th>
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<td>-20</td>
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<td>Specimen 2 side B</td>
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• * could not be determined
Concrete surfaces (frost medium interface) after 28 frost cycles (mix 2, w/c=0.63)
6.4.2 Frost resistant specimens

When 50 mm thick plates were measured, only very high saturation leads to significant expansions due to the phase transition of the pore solution in concrete.

First experiments where the expansion of a 10 mm thick layer perpendicular to the concrete-frost medium interface was measured (see section 7.1) gave very encouraging results. The idea was that these expansions should be isotropic and therefore it should be possible to detect them on thin plates of 10 mm thickness in a parallel test arrangement, either.

Expansion measurement parallel to the frost medium surface with thick plates may not be very sensitive to the surface layer since the measured length changes are the result of the expansion of the whole specimen. Thinner plates have two advantages: i) concentration of the effects on the outermost layer where scaling occurs; ii) reduction of the influence of the purely thermal contraction of undamaged lower concrete layers.

The tests were performed on specimens that were previously saturated under pure water (no vacuum) during 1 week. A very important point was the waterproofing of the concrete side opposite to the frost medium layer with an adhesive aluminum tape to prevent the concrete from drying through the high wind velocities in the climatic chamber. Indeed only thermal expansion was found without vapor barrier indicating a lower degree of specimen saturation.

When specimens with high frost resistance (high content of entrained air) were measured, almost only thermal contraction of the thin plate was observed (fig 43).
6.4.3 Pure water as impregnation and as frost medium

Measuring specimens with lower frost resistance reveals very interesting behavior with increasing number of frost cycles. The case with pure water as frost medium (prestorage: 1 week under water) is shown in fig 44.

When the frost medium layer freezes (indicated by arrows) a double peak in the expansion versus time curve is observed. The first peak is small but very steep, the second increases
rapidly with increasing number of frost cycles. When the frost medium is allowed to evaporate, these peaks disappear and only the normal thermal contraction is found.

The first peak can be attributed to supercooling of the frost medium that is followed by rapid ice formation as will be shown below. It does not appear when no supercooling occurs (4th frost cycle).

A plot of the expansion versus the temperature of the frost medium (water) is done in fig 45. While the first frost cycle shows only thermal contraction behavior (although the saturation was 1 week under water) the following cycles show increasing expansion after freezing is initiated. With frost medium water, remarkable expansion is already observed at 0°C indicating that the pore water starts freezing already at this temperature. This suggests that the presence of enough freezing germs provided by the freezing frost medium layer prevents the concrete pore solution from supercooling. The pore solution freezes according to pore size - freezing point relation when the ice front penetrates, so that the expansion increases continuously with lower temperature.

The maximal expansion and the remaining expansion after each further cycle (permanent residual damage) increase with increasing number of frost cycles. This increase can be explained with an increased degree of saturation after each cycle. Additional water uptake in frost deicing salt resistance tests has been observed by other researchers (Jacobsen [89], Auberg [101]). It is most probable that microcracks and even smaller air voids are refilled with frost medium and lead to a higher saturation and therefore increased expansion and hence damage. The refilling may happen below the freezing point through migration of unfrozen pore water towards lower vapor pressure or/and by migration of frost medium at temperatures above freezing point. Owing to the shorter distance to the liquid, the outermost concrete layer certainly is refilled easier.

A more detailed analysis for the increase of the maximal and the remaining expansion ($\Delta L_{\text{remain}}$) is given below.

![Fig. 45](image)

**Fig. 45** Expansion versus frost medium temperature of mix 2 (w/c=0.63) with pure water as impregnation and as frost medium (7 frost cycles)

The seventh cycle is given in detail in fig 46. The curve looks similar to the ones obtained for vacuum saturated thick plates. After a thermal contraction above freezing point and supercooling of the frost medium to -3.5°C, an instantaneous expansion (only one
measurement point) when freezing is initiated is observed. Some relaxation follows before a progressive expansion until -11°C begins. The specimen then contracts almost linearly until minimal temperature. Upon heating it expands linearly again with a higher coefficient. Flatter increase is observed at -10°C and a peak is reached at -5°C.

A hysteresis between freezing and thawing is found. This hysteresis may be explained by progressive damage formation during freezing and thawing or by water migration towards bigger pores. A further explanation is different freezing and melting points of pore water owing to pore shape effects (Setzer [33], see section 11.10).

Because of the linearity of the freezing and the melting curve a damage mechanism as described in section 4.2.3 (thermal expansion of ice and water migration) seems to be most probable.

Between -5°C and 0°C the specimen contracts sharply on melting of the pore ice. Above 0°C it first expands somewhat more than thermally, perhaps due to refilling of cracks and then mostly thermally with slightly lowered thermal coefficient. Above 5°C the value for the thermal contraction reached the same value as for freezing. Some relaxation effects may be the reason for this behavior.

![Graph](image)

**Fig. 46** Expansion versus frost medium temperature of mix 2 (w/c=0.63) with pure water as impregnation and as frost medium (7th frost cycle)

In order to allow further analysis, the difference $\delta L$ between the freezing and the melting expansion of the frost cycle is calculated for several frost medium temperatures (fig 47). The first point below freezing point is calculated at -0.1°C, the first above freezing point at 1°C.

The resulting curve represents the sum of hysteresis effects due to freezing/melting point shift, damage formation at freezing and damage formation at thawing. At temperature above 5°C it represents the total remaining expansion $\Delta L_{\text{remain}}$ (permanent residual damage) after one cycle.

The difference increases, at positive temperatures, slightly with decreasing temperature. As mentioned above, this could be due to some relaxation. Below the freezing point the difference first increases sharply to reach a maximum at -4°C. The value for the difference at
this point is almost as high as the biggest difference at positive temperatures. The same value as for the remaining expansion (above 5°C) is already reached at -3°C which is very close to the freezing point of a 3% salt solution which is known to produce maximal scaling in frost deicing salt resistance tests (Verbeck [85]). At lower frost medium temperatures the difference diminishes to become linear at temperatures below -11°C.

Fig. 47  Difference of expansion between freezing and thawing $\delta$L versus frost medium temperature (mix 2, w/c=0.63, impregnation and frost medium water, 7th frost cycle)

6.4.4  Pure water as impregnation and 3% salt solution as frost medium

In the case of a 3 mass-% sodium chloride solution as frost medium (prestorage: 1 week under water) the double peaks at freezing in the case of water become well pronounced single freezing peaks indicated by arrows (fig 48). As before, this peak increases with increasing number of the frost cycle.

Fig.48  Expansion versus time of mix 2 (w/c=0.63) with frost medium 3% salt solution (pure water impregnation)
Plotting this curve versus frost medium (interface) temperature reveals some additional details (fig 49). After a thermal contraction, the specimen starts expanding when the frost medium begins freezing at -2°C. The same remarks as in the case of water as frost medium are valid in this case, too. The same shape is found for the hysteresis.

Some small freezing of eutectic concentration of the salt solution, reached by the segregation effect, can be observed at -23°C.

The peak expansion and the remaining expansion increase continuously with increasing number of frost cycle.

The generally lower values with the salt solution were not expected, but can be attributed to bending of the specimen as was discovered afterwards.

![Graph](attachment:fig49.png)

Fig. 49 Expansion versus temperature of mix 2 (w/c=0.63) with frost medium 3% salt solution (pure water impregnation)

One single cycle is plotted in fig 50. The eighth cycle is chosen since similar values as with frost medium water are observed. The progressive expansion after freezing initiation becomes much steeper and no relaxation is found.

The difference $\delta L$ between melting and freezing expansion of one cycle is calculated and plotted in fig 51. The curve looks very similar to the one obtained with water as frost medium.

The maximal value for temperatures beyond freezing point is found at -5°C. The biggest difference is that the initial value just below freezing point almost reaches the remaining expansion $\Delta L_{\text{remain}}$ (damage) which is found at positive temperatures $>5$°C. Exactly this value is reached at -3°C. Below -10°C the linear behavior is found again, as well as the relaxation just above freezing point.

All above remarks were made for specimens of mix 2 (w/c=0.63). Analog results were obtained for lower water/cement ratios (mix 1, w/c=0.5, see appendix A).
**Fig. 50** Expansion versus time of mix 2 (w/c=0.63) with frost medium 3% salt solution, (pure water impregnation, 8th frost cycle)

**Fig. 51** Difference of expansion between freezing and thawing $\delta L$ versus frost medium temperature, 8th frost cycle (mix 2, w/c=0.63, frost medium 3% NaCl solution, pure water impregnation)
6.4.5 Detailed study near the freezing point

A detailed study of the specimen expansion near the freezing point is done with mix 1 (w/c=0.5).

In fig 52 the temperature on the concrete - frost medium interface and the specimen expansion are plotted for pure water as frost medium and as impregnation. The water supercools to -3°C before ice formation is initiated. The temperature then rises immediately to 0°C as the crystallization heat is set free. At the same time the specimen expands very fast. Similar expansion was found for wet specimen without frost medium and big supercooling (Grübl [102], Erbavdar [100]).

Some part of this instantaneous expansion \( \Delta L_{\text{INST}} \) results from the thermal expansion due to the temperature rise. No instantaneous expansion peak is found when no supercooling of the frost medium occurs. Supercooling is a statistical phenomenon and can not be predicted as the amount and the activation temperatures of ice nucleating germs in the frost medium layer are not known. Due to the supercooling the rate of ice formation is high (Pruppacher [59]) so that hydraulic pressure could explain the other contribution. The relaxation that follows immediately would be typically for pressure decrease by water flow.

The temperature then remains constant as further ice in the frost medium is formed and the equilibrium between liberation of crystallization heat and heat transfer to the climatic chamber is maintained. The specimen in the meantime shows some further contraction. This could be caused by inner water transport and shrinkage or simply could be an inaccuracy of temperature measurement of the temperature of the invar frame or of the temperature of the displacement transducer. These differences are especially big during this time period, in other tests the expansion even increased somewhat.

When the temperature falls again, as all frost medium is frozen, a second progressive expansion \( \Delta L_{\text{PROG}} \) starts. Some variations of the temperature on the interface may be responsible that it starts somewhat earlier in this example. The progressive expansion reaches a second maximum at -10°C. Further ice formation in the specimen owing to pore size distribution leads to probably hydrostatic pressure and volume expansion.

As can be seen, two well-separated expansion peaks are observed. The separation in time of these peaks was achieved by the use of a frost medium layer. It cannot be observed without it.

When a 3 mass-% sodium chloride solution instead of pure water is applied as frost medium (impregnation with pure water) the separation of the two peaks almost disappears (see fig 53). The temperature curve shows, after little supercooling, an instantaneous rise which even forms a little peak, which is somewhat higher than the following plateau. The freezing plateau is not as flat as in the case of pure water. Both indicate some ion segregation when using a salt solution. Independent from the small supercooling, the expansion shows very steep initiation peak when the ice formation in the frost medium starts. Very small relaxation is found afterwards. The second peak, the progressive expansion, is much smaller than in the case of water as frost medium.

An explanation can be given as follows. As the freezing point of the salt solution is lower than for pure water, the pore water becomes supercooled. When freezing in the frost medium is initiated, all the pore water with a freezing point higher than the one of the frost medium, freezes at the same time. The effects of instantaneous and progressive expansion are superposing.

No relaxation effects are visible.

An explanation may be that the temperature continuous falling after freezing is initiated and further ice is formed which leads to further expansion (second peak).
Fig. 52  Pure water as impregnation and as frost medium: Specimen expansion and frost medium temperature near freezing point versus time (mix 1, w/c=0.5, 7th frost cycle)

Fig. 53  3%NaCl solution as frost medium (pure water impregnation): Specimen expansion and frost medium temperature near freezing point versus time (mix 1, w/c=0.5, 7th frost cycle)

In this example the specimens were previously stored under water. A storage in the same salt solution would lower the freezing point of the pore solution for the same amount as for the frost medium layer. Nevertheless, segregation effects which occur when freezing is initiated could make the pore solution in the outermost layer appear as supercooled (Tilby [56]). This probably may explain the scaling of thin flat plates.
6.4.6 Higher concentrated salt solution as frost medium

The effect of higher concentrated salt (NaCl) solution as frost medium is shown in fig 54. The specimen also was stored during 1 week under water (no vacuum) before the frost medium was applied. Very well pronounced initiation peaks, indicated with arrows, were found. When a salt solution (same concentration) is used as storage medium too, steep peaks are observed either, but this is then after a larger number of the frost cycle. The initiation peaks are not as high and the progressive expansion becomes more important than with water as prestorage medium.

![Graph showing expansion of mix 1](image)

**Fig. 54** Expansion of mix 1 (w/c=0.5) with frost medium 15% NaCl solution (pure water impregnation)

6.4.7 Discussion of thin plate experimental results

Some further analysis of the peak expansion at freezing $\Delta L_{\text{max}} f$, the relaxation at thawing $\Delta L_{\text{max}} th$, and the remaining expansion $\Delta L_{\text{remain}}$ (at 5°C) (see figs 46 and 50) reveals more details. $\Delta L_{\text{max}} f$ and $\Delta L_{\text{max}} th$ are used because they represent typical values describing the expansion behavior at freezing and at thawing.

In fig 55 the peak expansion $\Delta L_{\text{max}} f$, the relaxation at thawing $\Delta L_{\text{max}} th$, and the remaining expansion $\Delta L_{\text{remain}}$ (at 5°C), applied for each thermal cycle, of a specimen of mix 2 (w/c=0.63, fig 50) with pure water impregnation (1 week under water) and a 3% NaCl solution as frost medium are compared. $\Delta L_{\text{max}} f$ and $\Delta L_{\text{max}} th$ increase almost linear with the number of the frost cycle. The remaining expansion $\Delta L_{\text{remain}}$ increases less.

This suggests that the degree of saturation increases with the number of the cycle. Opened microcracks probably are refilled with frost medium during the cycle. This could be through migration of non-frozen pore solution held in smaller pores (redistribution of pore water at temperatures below the freezing point of the frost medium) or by inflow of frost medium when the specimen is thawed.

The remaining expansion $\Delta L_{\text{remain}}$ is larger than $\Delta L_{\text{max}} f$ in the first five frost cycles. The peak expansion of the freezing branch of a frost cycle hence can be smaller than the total
damage induced during one frost cycle. This means that not the whole permanent residual damage is caused by the phase transition when freezing, but that an additional part of damage is formed when the temperature rises again after the minimum temperature has been reached.

Similar behavior was found for other frost media and for other specimens with other mix design.

![Graph showing the comparison of peak expansion at freezing, relaxation at thawing, and remaining expansion versus the number of the frost cycle.](image)

**Fig. 55** Comparison of peak expansion at freezing ($\Delta L_{\text{max f}}$), relaxation at thawing ($\Delta L_{\text{max th}}$) and remaining expansion ($\Delta L_{\text{remain}}$) versus the number of the frost cycle (mix 2, w/c=0.63, pure water impregnation and 3% salt solution as frost medium)

The influence of supercooling of the frost medium is demonstrated on three specimens with pure water as impregnation and as frost medium a) mix 2 (w/c = 0.63), b) mix 2 (w/c = 0.63) some cholesterol prepared with the mica sandwich technique was added to prevent the frost medium from supercooling and c) mix 1 (w/c = 0.5) without cholesterol.

The instantaneous expansion $\Delta L_{\text{inst}}$ (see fig 52) depends significantly on the degree of supercooling ($\Delta T$), when supercooling is superior to -2°C (fig 56).

Without damage and other mechanical effects, the thermal expansion $\Delta L_{\text{th}}$ due to the sudden temperature rise when freezing is initiated is $\Delta L_{\text{th}} \approx 1.5 \times \Delta T$. This gives at most 7 $\mu$m in place of the values ranging up to 20 $\mu$m observed on fig 56.

Other factors like the number of the frost cycle also have some influence on the first expansion peak ($\Delta L_{\text{inst}}$) as obtained on freezing. This is shown in fig 57.

The second expansion peak $\Delta L_{\text{prog}}$ (see fig 52) hardly depends on the degree of supercooling (fig 58). This is not surprising as $\Delta L_{\text{prog}}$ is related to progressive ice formation when the temperature falls further after the entire outer frost medium is frozen.

The number of the frost cycle has big influence (fig 59). $\Delta L_{\text{prog}}$ increases almost linearly with increasing the number of the frost cycle.
For the remaining expansion $\Delta L_{\text{remain}}$ attributed to permanent residual damage, some influence of the degree of supercooling can not be excluded (figs 60 and 61). This suggests that the big instantaneous expansion due to high degree of supercooling causes additional damage.
Fig. 58  Progressive expansion $\Delta L_{\text{prog}}$ (in $\mu$m) versus degree of supercooling ($\Delta T$)

Fig. 59  Progressive expansion $\Delta L_{\text{prog}}$ (in $\mu$m) versus number of the frost cycle
When a salt solution was used as frost medium, the degree of supercooling generally was lower. The first expansion peak $\Delta L_{\text{inst}}$ was well pronounced even without supercooling. Nevertheless some influence of supercooling was observable.
6.4.8 Hardened cement paste

Some additional experiments with pure water as impregnation (storage 1 week under water) and as frost medium were performed with hardened cement paste of different water/cement ratios (w/c=0.8; 0.5; 0.4; 0.26). Only small amount of material was obtainable so that just smaller plates (100x50x10 mm³) could be measured. As the equipment was not built for such specimens, some minor experimental fixing problems resulted.

The specimens with water/cement ratio 0.26 were prepared in a conventional mould. It showed only thermal contraction behavior. Specimens with higher water/cement ratio, prepared with a special vacuum technique (no air pores!, Houst [98]), behave similar as the concrete specimens of mix 1 and 2.

In fig 62 the result of a specimen of hardened cement paste with w/c = 0.8 is plotted. The most important similarity with concrete is that the pore solution also starts freezing at 0°C. Nevertheless some differences are obvious. After some supercooling, an important instantaneous expansion ($\Delta L_{\text{inst}}$) at 0°C, increasing with the number of the frost cycle is found.

The remaining expansion ($\Delta L_{\text{remain}}$) of the first frost cycle is much larger than the instantaneous expansion. The permanent residual damage mostly is formed at lower temperatures. But already after three frost cycles, the instantaneous expansion reaches the same value as the remaining expansion. At the same time the hysteresis between freezing and thawing becomes smaller with increasing the number of the frost cycle.

This means that most of the damage with higher number of the frost cycle is caused by the instantaneous expansion at the freezing initiation. Hydraulic pressure, mainly caused by freezing of water in refilled microcracks is thought to be the most important damage mechanism in this case.

At lower temperature the specimen expansion continues and reaches the freezing maximum not earlier than at -20°C.
This suggests that the very high water/cement ratio (w/c=0.8) and the low strength of the material might permit ice lens segregation or progressive crack growth at lower temperatures.

![Graph showing expansion of hardened cement paste w/c=0.8](image)

**Fig. 62** Expansion of hardened cement paste w/c=0.8 with pure water as impregnation and as frost medium versus frost medium temperature ($1^{st}$ - $3^{rd}$ frost cycle)
For hardened cement paste with lower water/cement ratio w/c = 0.5 and 0.4 the expansion maximum at freezing is observed much before the minimal temperature is reached. Very similar result as for concrete specimen is found (fig 63). In this case the smaller specimens did not allow a very precise measurement.

Fig. 63 Expansion of hardened cement paste w/c=0.5 with pure water as frost medium versus frost medium temperature (1.-4. frost cycle)
CHAPTER 7  FURTHER CLIMATIC TESTS

7.1  Measurements perpendicular to the frost medium surface

7.1.1  Method and apparatus

The scaled (removed) material in laboratory frost deicing salt resistance tests mostly consists of flat particles (ca. 5x5x0.2mm³) which may be the result of significant expansion perpendicular to the frost medium surface. The idea was therefore to measure the concrete expansions perpendicular to the frost medium surface.

A special test arrangement was chosen (fig 64) which allowed the application of a frost medium layer. In this test arrangement it was possible to use thick (50 mm) concrete specimen which do not deform (no bending).

![Test arrangement for measurement of expansion perpendicular to the frost medium surface](image)

Special tapered concrete specimens were cut. From cores (Ø=50 mm, h=50 mm) a ring of 7.5 mm of concrete to a depth of 10 mm was removed. After that, an aluminum tape was fixed (glued) around the remaining part which allowed keeping a frost medium layer on the
surface. Then an invar cylinder (⌀=3 mm, h=6 mm) was fixed on the concrete surface by a glue (Araldit). An invar frame which was pasted onto the lower concrete surface permitted the exact positioning of an displacement transducer (HBM W1T3 class 0.2) over the invar cylinder.

The displacement transducer was protected against humidity by a plastic foil. By means of this apparatus the expansion of the topmost 10 mm of concrete could be measured with the application of a frost medium layer. The apparatus was designed in a way that the invar cylinder (the measurement position) could be placed at almost any desired point on the tested surface.

To find an adequate measurement position the inner structure and the aggregate distribution of the concrete was studied by means of X-ray computer tomography first.

In order to calibrate the thermal contraction of the apparatus and the invar cylinder, it was fixed on a plane steel cylinder so that only the contraction of the equipment was measured. The expansion of the concrete specimen was derived taking the expansion of the apparatus into account.

The whole apparatus was put into a climatic chamber where the freezing rate of the air was set to 10°C/h.

The specimens were stored under water (1 week, no vacuum) prior to measurement. The bottom side of the specimen was then protected against humidity loss.

The temperature was measured in the air, at the center of the specimens, at their bottom, at a distance of 10 mm from the concrete - frost medium interface within the concrete and in the frost medium layer. With high degree of supercooling temperature differences of up to 4°C between center temperature and frost medium temperature were measured. The differences between frost medium temperature and the temperature at a depth of 10 mm within the concrete was only 1-2°C.

7.1.2 Results

The measurement perpendicular to the frost medium surface demonstrates that the expansions in the outermost concrete layer are volume dilatations and probably isotropic.

Owing to the very inhomogeneous material, no quantitative conclusions can be made. The absolute values varied in a wide range. Qualitatively the same results as for the measurement parallel to the frost medium surface with thin plates were obtained.

Although it was an initial objective of this work, the influence of the aggregate stones could not be studied in a reliable manner by special positioning of the invar cylinder.

Another problem was frost damage formation (scaling) which made the invar cylinder tilt, feigning a sharp contraction of the expansion. This mostly occurred just at freezing initiation. When the entire frost medium at lower temperatures was frozen and the invar cylinder became fixed by the ice, the typical low temperature behavior (with a hysteresis) was found.

As an example, the expansion of a specimen of mix 2 (w/c=0.63) with a 3 mass-% NaCl solution as frost medium (pure water impregnation) is plotted in fig 66 in terms of time and in fig 67 in terms of temperature.

The measurement position was chosen in a region with only small aggregates (fig 65) and hence increased porosity. The absolute expansion values therefore are much higher than the ones obtained measuring parallel to the frost medium surface. An additional contribution may come from the generally higher degrees of supercooling, because less frost medium was applied in this test arrangement.

As the whole frost medium layer freezes very fast, especially with high degree of supercooling, the instantaneous expansion \( \Delta L_{\text{inst}} \) and the progressive expansion \( \Delta L_{\text{prog}} \) were not well separated.
After some supercooling the specimen expands when freezing is initiated in the frost medium. Progressive ice formation is observed at lower temperatures. The peak expansion at freezing is shifted towards lower temperatures compared to the results of the measurement parallel to the frost medium surface. The measured values lay in the range of microns so that the influence of experimental scattering cannot be excluded.

Fig. 65 X-ray computer tomograph image of specimen (mix 2, w/c=0.63)

Fig. 66 Expansion perpendicular to the frost medium surface in terms of time (impregnation with pure water; frost medium 3% NaCl-solution, mix 2, w/c=0.63)

Like in the experiments where the expansion was measured parallel to the frost medium surface, the peak expansion at freezing increases linearly with increasing number of the frost cycle, while the remaining expansion increases much less and approaches a constant value.

A detail near freezing initiation is shown in fig 68. The expansion after freezing initiation is much smaller than the progressive expansion. In comparison to the test arrangement
parallel to the frost medium surface, a much smaller amount of frost medium freezes, so that the freezing plateau gets very narrow. A higher ice formation rate results.

Fig. 67 Expansion perpendicular to the frost medium surface versus frost medium temperature (pure water impregnation; frost medium 3% NaCl solution, mix 2 w/c=0.63)

Fig. 68 Specimen expansion and frost medium temperature of the 7th frost cycle in terms of time (pure water impregnation; frost medium 3% NaCl-solution, mix 2 w/c=0.63)
With higher salt concentration (10% - 15% NaCl) of the frost medium, almost no perpendicular expansion near the freezing point of the solution was found. An expansion peak that appeared at -21°C (eutectic salt concentration) indicates segregation effects.

7.2 Temperature cycles without thawing of the frost medium

After 15 cycles of freezing and thawing, the maximal air temperature in the climatic chamber was limited to +2°C so that the frost medium temperature remained below -1.5 °C (fig 69).

The corresponding expansion was measured parallel to the frost medium surface. The temperature change rates were +/-10°C/h. This experiment was performed with pure water as frost medium and a thin specimen (150x150x10 mm³) of mix 2 (w/c=0.63). The specimen expansion (in µm) during the 16th cycle (starting above 0°C) and the following ones (without thawing) is plotted in fig 70 in terms of time. A steep expansion is observed at the beginning of the freezing part of the 16th cycle only. As the 16th cycle is going on to low temperatures, the same typical behavior, already observed in chapter 6, is seen. During the temperature increment the same kind of hysteresis is also seen.

During the following temperature cycles below 0°C (2.-4. cycle) mostly thermal contraction with just a small hysteresis and no further damage is observed.

This can be explained by a lack of accessible water. As the specimen is protected against humidity loss by an aluminum tape at its bottom side and by the ice layer at its top surface, only minor water uptake is possible at temperatures below the freezing point of the frost medium. Microcracks therefore cannot be refilled with frost medium and even could serve as escape regions for excess water. Water transport due to vapor pressure differences also would be limited in this case. This means that a damage model involving redistribution of pore solution would not be applicable under such conditions.

At the end of the test, the frost medium layer was thawed and partial dimension recovery (with a permanent residual expansion) was observed.

![Graph](image-url)

**Fig. 69** Temperatures in the experiment without thawing of the frost medium
Fig. 70 Expansion (in µm) versus frost medium temperature for the 15th and the following cycles (no thawing) with water as frost medium (mix 2, w/c=0.63)
The 15 first cycles are with thawing like in chapter 6

These observations are in contradiction to other expansion studies (Miura [103]) who found a purely thermal contraction of the concrete specimens down to very low temperatures (until -20°C). Additionally, big hysteresis and increasing damage with increasing number of the temperature cycles was found. In their experiment they studied big concrete blocks (100x100x400mm³) which were sealed and frozen from all sides without a frost medium layer.

One possible explanation may be given as follows: Let us assume that an ice front penetrates the specimen from all concrete sides and that the pore solution (alkali-hydroxide solutions; NaOH, Ca(OH)₂) segregates due to its low solubility. Only low concentrated pore solution would freeze immediately, expelling a high concentrated (probably eutectic) pore solution towards the specimen center where it may fill previously empty pores (air pores). If the critical degree of saturation of the specimen is not exceeded no damage would occur. The specimen would contract thermally. When the temperature reaches the freezing point of the expelled eutectic pore solution (freezing points around -25°C) additional ice would be formed which leads to expansion and damage, especially because most pores already are filled with ice which reduces the permeability. During temperature cycles below 0°C most of the pores filled with pure ice remain frozen while the high concentrated pore solution freezes and thaws. Nevertheless the damage in low temperature cycling would be less than with a thawing phase, as no additional water is supplied to refill the microcracks.

In our expansion experiments, the pore solution was frozen only from one side and the specimens were smaller. The fact that in our experiment the freezing initiation (with water as frost medium) was very close to 0°C support the theory of the segregation of pore solution.

The difference in behavior in the two cases can thus – at least mostly – be considered as a size effect, which will have to be kept in mind in the transfer from laboratory tests to field behavior of real structures. However, in order to obtain definitive conclusions about this further research will be necessary.
7.3 Temperature shock

When concrete is covered with an ice layer and deicing salts thaws this layer, a (decreasing) temperature shock (Rösli [83]) occurs. The mechanism is described in section 4.2.4. Some experiments to measure the expansion of concrete surfaces due to this sudden temperature fall have been performed by Glock [95].

A result of our own, obtained from expansion measurement parallel to the frost medium surface with a thin concrete plate (mix 2, w/c=0.63), is given in fig 71.

A eutectic NaCl solution (3 mm, -0.5°C) was poured on a 3 mm thick ice layer (-2°C) on the surface of an already frozen concrete specimen. Just after the application of the salt solution the temperature falls suddenly, while the specimen expands at the same time. This can be interpreted as additional ice formation in the finer concrete pores owing to this temperature fall (progressive expansion $\Delta l_{prog}$).

After that, thermal contraction behavior is predominant, but the amount of the contraction is less than it would be for pure thermal contraction ($\equiv \Delta T \times 10^{\mu m/Km}$) so that further ice is supposed to be formed in finer pores. These results are in good agreement with Glock ([95]). However, the observed expansions remain small as compared to the ones obtained during a normal freeze/thaw cycle.

![Graph showing temperature and expansion over time](image)

**Fig. 71** Temperature in frost medium layer and specimen expansion due to the application of an eutectic NaCl solution on an ice layer

7.4 Ice lens formation

7.4.1 General remarks

Ice lens segregation is one of the possible damage mechanisms, which is most discussed. In fact, only few experiments have been carried out to prove the ice lens segregation or to qualify its importance for frost or frost deicing salt deterioration of concrete. Ice lenses should continue to grow at constant temperatures below 0°C if sufficient liquid is available. The mechanism is described in section 4.1. The macroscopic consequence would be a
continuous expansion of the specimen. For instance, Powers and Helmuth [31] found in some dilatation experiments progressive expansion, depending on w/c ratio and air pore content of the specimen (fig 72) when they held temperature constant after freezing was initiated. They concluded that not all this phenomenon can be explained by their hydraulic pressure theory only and proposed a damage mechanism based on the differences in vapor pressure above ice and above supercooled water, thus resulting in the progressive formation of ice lenses.

In order to verify this, we performed some expansion experiments especially designed for that purpose.

![Figure 72](image)

**Fig 72** Effect of holding temperature constant after freezing starts (reprinted from Powers [31])

### 7.4.2 Expansion at constant temperature

First, some expansion tests at constant temperatures were performed. Specimens of different mixes (mix 1,2,3) previously impregnated with pure water or a 3% NaCl solution during two weeks (not vacuum) were sealed and then kept at different constant temperatures below 0°C (-5°C, -10°C, -20°C). In all cases the specimen length did not change significantly during more than one week of storage, independent of storage temperature or impregnation medium.

Then a test analog to the experiment of Powers and Helmuth [31] was performed. The expansion parallel to the frost medium surface with water as impregnation and as frost medium of a specimen of mix 2 (w/c=0.63) was measured. The temperature and the expansion in terms of time are given in fig 73. After 10 freeze/thaw cycles, starting above 0°C, the temperature first was lowered at a rate of 10°C/h.

Typical expansion behavior was found, with instantaneous expansion at freezing initiation and progressive expansion when the temperature fell again after all the frost medium was frozen (after the freezing plateau at 0°C). When the temperature in the frost medium layer reached -4°C (after 6h) the temperature in the climatic chamber was kept constant, so that the frost medium temperature remained at -4°C during 2 hours. The expansion stopped and even a small dimension recovery was observed. While the temperature was kept constant no further expansion occurred. According to the hydraulic pressure mechanism, some further dimension recovery would be expected because the pressure would cease due to capillary flow. It seems that the ice hinders the contraction physically or that a hydrostatic model (closed container) is more appropriate.

When the temperature was lowered again, a further expansion was observed, probably due to freezing of more pore solution in finer pores. This further expansion is not as big as it would have been without an interruption of the temperature cycle.
This might be due to redistribution of water during the phase of constant temperature. In other experiments where the constant temperature was higher (below 0°C), the expansion was more important after the temperature was allowed to fall again.

Similar results were found for other constant temperatures and frost media and in test arrangements where the expansion was measured perpendicular to the frost medium surface.

Fig. 73 Effect of holding frost medium temperature after freezing initiation constant (mix 2, w/c=0.63, frost medium water)

These results do not confirm the results of Powers and Helmuth [31] who found a progressive expansion after holding the temperature constant. It has to be admitted that in their experiment the freezing initiation was at -20°C (high degree of supercooling) and that the temperature was hold constant just below freezing was initiated (fig 72). Possible inaccuracies in temperature measurement (e.g. temperature distribution in the specimen) could have caused similar progressive expansion.

7.4.3 JPD arrangement - constant liquid-ice interface

In a special test arrangement similar to the arrangement in frost deicing salt resistance test of J.-P. Daxelhofer [104] the possibility of progressive ice lens formation in concrete at a constant zero degree isotherm was studied.

A concrete specimen (90x90x50 mm³, w/c=0.8) was mounted on an invar frame so that its length could be monitored continuously by a displacement transducer. The top surface was kept at constant temperature above freezing point by circulating tap water. The specimen was placed in a water (resp. ice) filled vessel which was put in a Lauda bath at temperatures below 0°C. The specimen was therefore in contact with ice at its bottom side and with water on its top side (fig 74). It was insulated at its lateral sides to establish a plane zero-degree isotherm.
The test result is given in fig 75. For practical reasons the whole specimen was frozen before the test started. The top temperature therefore first was below freezing point. After 20 hours the top water was allowed to circulate and assumed after some regulation a constant temperature of +17 °C (+/- 0.3 °C). This temperature was kept constant through the whole test. As a consequence of the increase of the surface temperature (after 20 h) the bottom temperature also increased slightly and some expansion of the specimen was measured. Then the bottom of the concrete specimen also assumed a constant temperature of -17°C (+/- 0.1°C) for about 18h.

The specimen length changed very few in this phase of constant zero-degree isotherm. No expansion, even some slight contraction was found in this phase. No progressive ice lens growth was detected even for a concrete specimen of very high water/cement ratio (w/c = 0.8).

After 48 hours the temperature in the Lauda bath was varied between -30°C and -40°C analog to the J.-P. Daxelhofer frost resistance test with temperature change rate of 10°C/h. At -30°C the temperature was kept constant during 30 minutes and at -40°C during 1 hour. The bottom temperature thus varied between -17°C and -12.5 °C. The specimen length also changed cyclically but the maximum and the minimum values increased linearly, indicating an increasing permanent residual expansion.

After eleven such temperature cycles, the Lauda bath temperature was kept constant again. The specimen length remained constant, again.

Finally, the bath temperature was increased to allow the pore solution of the specimen to thaw. First, the thermal expansion of the specimen was bigger than the melting effects but then the specimen contracted rapidly due to thawing.
This means that the damage was not caused by progressive ice lens formation but that it was caused by an upward and downward move of the zero-degree interface owing to temperature cycling causing freezing and thawing of the concrete.

Fig. 75 Temperature (at top, bottom and in the Lauda bath) and expansion versus time in ice lens test

7.4.4 Conclusions for ice lens formation

In the presented experiments no indication for progressive ice lens formation was found. Neither holding the temperature constant below the freezing point of the frost medium, nor a constant liquid-ice interface (ice on one side and water on the other side) resulted in progressive expansion as is expected if progressive ice lens formation would occur.

However, a redistribution of liquid cannot be excluded by the performed experiments, as this would be possible without a dilatation of the surrounding matrix. Even further ice formation in empty pore space (air inclusions, around thermally contracted ice) is possible.

7.5 Calculation of freezable water content

When the temperature is lowered during a frost cycle, not all pore water freezes at the same time, owing to the different pore sizes and pore size - freezing point relation (section 3.2.2).

The freezable water content (in function of the temperature) is characteristic for each material. A calculation from expansion data is done.

It may be sufficient for hardened cement paste to calculate the freezable water content from dilatation data (Powers [9]) by:

$$ w_f = \frac{\Delta v}{B_t} $$
where: \( \Delta v \) : net expansion
\[ B_t \] : expansion resulting from 1g of water at the existing temperature

However, it is necessary for concrete to take the withstanding aggregate matrix into account. The frost resistant aggregate stones do not expand in the same way as the pore solution upon the phase transition and their modulus of elasticity must be considered.

To calculate the freezable water content from net expansion (measured minus thermal), a 1D model as follows may be used: The concrete volume is assumed to consist of cubes of unit volume. The freezable water is supposed to fill a smaller cube that is situated at the center of the unit volume cube. When the freezable water content per unit volume is \( x \), the cube length is therefore \( x^{1/3} \). When the water freezes, it exercises pressure on the concrete cube that makes it expand. The expansion is supposed to be symmetrical and the problem can be reduced to a 1D one. Transversal deformation is not taken into account so that the expansion is somewhat overestimated and therefore the freezable water content is underestimated in the order of 10%. The model includes the strain of the ice and of the concrete matrix.

\[ \begin{align*}
\sigma_1 A_1 = \sigma_2 A_2 & \quad \text{with} \quad A_1 = 1 - x^{2/3} ; \quad A_2 = x^{2/3} \\
\end{align*} \]

\[ \begin{align*}
\varepsilon_1 = \varepsilon_3 = \varepsilon_2 = \varepsilon + (1-x^{1/3}) \left( \frac{\sigma_2}{E_c} \right) + x^{1/3} \left( \frac{\sigma_2}{E_i} \right) \\
\end{align*} \]

\[ \begin{align*}
\varepsilon_1 = \varepsilon \text{ meas} - \varepsilon \text{ therm} = \left( \frac{\sigma_1}{E_c} \right) \\
\end{align*} \]

where:
\[ \varepsilon \] : expansion due to phase transition
\[ \cong 0.03 x^{1/3} \]
\[ \varepsilon_{1,2} \] : total expansion of layer 1,2 (fig 76)
\[ E_{i,c} \] : modulus of elasticity of ice, concrete
\[ \sigma_{1,2} \] : tension of layer 1,2

Fig. 76 1D model for calculation of freezable water content

1. Equilibrium of forces
2. Compatibility

\[ \text{(27) equilibrium of forces} \]
\[ \text{(28) compatibility} \]
When the ratio \( k = \frac{E_c}{E_i} \) is close to 1 (matrix and ice behave equal), \( \varepsilon_1 = 0.03^*x \). This corresponds to the volume expansion of the pore water without interaction of the surrounding matrix as can be expected in that case. In fact, taking \( E_i = 9700 \text{ N/mm}^2 \), \( k \) may vary in the range of \( 2 < k < 5 \).

The model neither does include the freezing point depression due to pressure (Clausius-Clapeyron) nor the thermal contraction of the ice.

The calculation of freezable water content is only possible from experiments with completely saturated (vacuum saturated) specimen where all pores are water filled. Non-filled empty pores (air pores) may serve as escape regions for excess water and the expansion of the specimen would not correspond to its freezable water content.

Another difficulty is the big remaining expansion (permanent residual damage), as it is not known a priori at which temperature this damage occurs. It is most probable that a part of the damage is formed during freezing and another part during thawing. Because of the remaining expansion it is not possible to calculate exact freezable water content in function of temperature neither from melting nor from freezing curve by means of the above model. One should try to measure the expansion of a specimen without measuring the permanent damage. A possible way might be a method applied by Powers and Brownyard [9]. They measured the volume expansion in a toluene vessel and found very little remaining expansion. The toluene probably was able to penetrate the damaged zones and to refill them, so that no net remaining volume expansion was found. This also might be the reason why they found a hysteresis between freezing and thawing which was, apart from the supercooling, very small.
Nevertheless a calculation of the freezable water content was done from freezing curves presented here of resaturated specimens (water as impregnation and as frost medium, expansion parallel to the frost medium surface) with \( k = 4 \) and \( \rho_{\text{concrete}} = 2400 \text{ kg/m}^3 \). This is possible as almost no supercooling occurred. The results are presented in table 5.

<table>
<thead>
<tr>
<th>temperature (^\circ\text{C})</th>
<th>mix 1 (wc=0.5)</th>
<th>mix 2 (wc=0.63)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td>0.012</td>
<td>0.013</td>
</tr>
<tr>
<td>-5</td>
<td>0.017</td>
<td>0.023</td>
</tr>
<tr>
<td>-10</td>
<td>0.019</td>
<td>0.027</td>
</tr>
<tr>
<td>-15</td>
<td>0.019</td>
<td>0.029</td>
</tr>
<tr>
<td>-20</td>
<td>0.019</td>
<td></td>
</tr>
</tbody>
</table>

Table 5  Freezable water content [in g/g\(_{\text{dry}}\)] calculated from expansion test

These values can be compared to the ones of porosimetry data. The amount of pore water that is evaporated through drying at 50\(^\circ\text{C}\) is \( U_E - U_{50} \) (see table 3). This amount can be considered as a rough estimation of the capillary water content.

For mix 1 this value corresponds to 0.026 g/g\(_{\text{dry}}\), and for mix 2 to 0.032 g/g\(_{\text{dry}}\).

We see that the calculated amounts of freezable water (at -20\(^\circ\text{C}\)) agrees (within the limitations of the calculation) well with the content of water that is evaporable by drying at 50\(^\circ\text{C}\). About 80% of this water already freezes at temperatures above -10\(^\circ\text{C}\).

The water in the small gel pores (\( U_{50} \)), that only can be removed by drying at higher temperatures (drying at 110\(^\circ\text{C}\)), does not contribute to the calculated amount of freezable water. Therefore it can be considered as water that is non-freezable (until -20\(^\circ\text{C}\)).
CHAPTER 8  CONCLUSIONS FROM EXPANSION MEASUREMENTS

1. Expansion of concrete specimen with the simultaneous application of a frost medium layer was measured. Because of the higher probability for ice nucleation in the big volume of the frost medium layer, strong supercooling is prevented.

2. In the case of thick concrete specimens significant deviations from thermal behavior only is found for specimens impregnated under vacuum. It is not found for specimens previously stored under water during one week.

3. Important difference from thermal behavior of not completely saturated specimen is found for the outermost surface layer only.

4. In the case of thin specimens significant bending is observed.

5. Expansion increases with increasing number of the frost cycle. Hence water uptake and increase of the degree of saturation is important.

6. Two different expansion peaks separated in time by the freezing of the frost medium layer at constant temperature are found.

   A first very fast expansion (instantaneous expansion) is observed when freezing of a supercooled frost medium is initiated. Without supercooling this peak is not observed. Strong supercooling can cause additional damage.

   A second progressive expansion is found when all frost medium is frozen and the temperature falls further.

   When the frost medium is a salt solution both freezing processes occur at the same time resulting in only one more pronounced expansion peak.

7. These expansion effects are also observed when measuring perpendicular to the frost medium surface. The expansion is therefore a volume effect.

8. Big hysteresis between freezing and thawing is observed. The hysteresis, not found in calorimetry (chapter 11) and ultrasonic test (chapter 12), is probably due to damage formation. The biggest difference between freezing and thawing is found at a temperature of about -4°C.

   Permanent damage is caused both during freezing and during thawing.

9. Owing to the damage formation and the remaining expansion after freezing, the calculation of freezable water content from the performed experiments is difficult.

   The estimated amounts of freezable water content are similar to the ones calculated from calorimetric (chapter 11) and from ultrasonic data (chapter 12).

10. Temperature cycling below freezing point of the frost medium yields no hysteresis and no remaining deformation. Water migration from unfrozen frost medium layer is necessary to obtain an increase of concrete deterioration.

11. No indication for progressive ice lens formation was found.

12. Results for hardened cement paste and for concrete are similar.

13. The results of expansion tests suggest that scaling is the result of rapid ice formation when freezing is initiated. In the case of salt solutions as frost media ion segregation effects possibly are involved.
Part III

PHYSICAL AUSCULTATION
CHAPTER 9 MICROSCOPICAL DAMAGE ANALYSIS

It is of primordial interest to directly observe the damage of concrete due to frost deicing salt attack in laboratory tests as well as in field exposure by microscopical methods.

However, the big variation of aggregate distribution and type, local saturation conditions and local critical degree of saturation, porosity and preexisting damage (shrinkage etc.) made a quantitative analysis of frost damage by microscopic methods difficult.

As a consequence, in this work a qualitative analysis of inner frost damage on a series of single specimen was done only. Two types of concrete were studied: with non-porous stone aggregates, and with porous aggregates like brick and limestone. The latter were performed on the specimens fabricated and submitted to frost test by Olbrecht [105].

As shown by other workers (Kukko [72], Jacobsen [89]) scaling and inner damage have to be studied separately although they might be a different consequence of the same damage mechanism.

9.1 Microscopical methods

Binocular, polarization microscopy and confocal (laser) microscopy was applied to study the crack paths. The different methods all proved to have advantages as well as disadvantages for the frost crack study, which should be discussed first.

The binocular method allows only pure optical analysis. The resolution is relatively poor (\( \approx 5 \mu m \)). The advantages are its big depth of field, the 3D impression of observation that allows easier crack path study and the possibility of minor specimen preparation and study under natural condition. A big disadvantage is the documentation of the observed details. The 3D impression hardly can be documented.

Binocular method allowed the study of frost damage perpendicular and parallel to the surface where the frost medium was applied. Macroscopic frost cracks, even in the interface between aggregate and cement matrix could be studied without impregnation.

Polarization microscopy uses reflected or transmitted light. A resolution of \( \approx 0.5 \mu m \) can be achieved. The refractive properties of the different mineral phases (incl. hydrated cement) allow their identification in thin section analysis (transmission). The use of fluorescent resins
allows improved crack identification and homogeneity analysis (w/c-ratio, defect regions). The preparation of the thin sections can cause structural changes of the surface and hence artifacts. This is particularly problematic for concrete, because of the different phases that are polished at different rates and the possibility of pullout.

Thin sections of slices parallel or perpendicular to the frosted surface were studied. Some difficulty to prepare good thin sections was observed. Especially cracks along aggregates often were badly preserved.

In confocal microscopy a laser beam scans over the specimen and records the reflected or transmitted intensity on a TV screen. An examination in dry or wet conditions is possible. The confocal technique also allows 3D analysis. The resolution is down to 0.3 µm and therefore similar as for optical microscopy.

A further advantage is the digital form of the result which permits effective storage and documentation of results, including zooming, image analysis and focussing, together with 3D reconstruction facilities.

Frost cracks were studied on specimens (70x50x20 mm³) cut parallel or perpendicular to the frosted surface which were then impregnated with a fluorescent resin, cut again (70x50x10 mm³) and finally polished on diamond disks with a final roughness of 2 µm. The impregnation was necessary for a good specimen preparation. The fluorescent allowed the characterization of density variations by the application of polarization filters when using an Ar-laser beam.

9.2 Results

9.2.1 Fast weathering laboratory tests

In the special case of frost damage it was very difficult to polish the specimens without impregnation. Figure 79 shows a crack at the cement-aggregate interface in a polished specimen as seen in a binocular (parallel observation). Some scaling of material near the original crack is caused by the polish procedure. The crack seems to be surrounded by a weaker concrete layer.

Figures 80 and 81 show the concrete surface after 30 frost cycles (swiss laboratory fast weathering test [1]) as observed by binocular microscope perpendicular to the frost medium surface. Cracks owing to the frost deicing salt attack were found at the interface of the aggregates. Air inclusions did not stop the crack path but even seemed to have some attraction for the cracks that simply passed through them. This conforms to the theoretical analysis presented in Huet [106] and Walpole [107]. Air pores, apart from their positive influence for frost resistance, are material defects and therefore weak positions.

In optical microscopy analysis no changes of the mineral phases at the crack borders of specimens subjected to frost deicing salt attack was observed.

Studies with confocal and normal microscope of concrete cuts parallel to the surface (observation perpendicular) revealed cracks in the interface around the aggregates.

In cuts perpendicular to the surface (observation parallel) typically surface parallel cracks were found (fig 82). No cracks were found at depth lower than = 10 mm for the studied concrete mixes.

Crack pattern was along the aggregate stones and then branching parallel to the surface into the cement matrix. The opening of cracks near the surface was very big, up to 100 µm. Some of the parallel cracks later joined together due to larger aggregates across their path (fig 82, seen after fluorescent impregnation, left side). At the (left) branching point, no visible microstructural detail that might be a reason for separation was observed. The crack therefore must have grown from the right side, starting at the interface of the aggregate.

For concrete with recycled brick stone as aggregate, typical frost cracks passed through the aggregate (fig 83). This was also the case for non-frost resistant aggregate. In those cases
cracks around and through the aggregate were observed. This also conforms to the theoretical analysis presented in Huet [106].

Figure 84 shows a typical crack path through an air pore. There is a tendency for the air pores to attract the cracks. However, cracks passing along the pores were frequently observed also. This is certainly due to the three-dimensional extension of the frost cracks.

Figure 85 shows a detail at the border of the very large crack of fig 82 at a higher magnification. The crack border is sharp and not frayed. Only a few microcracks branching off perpendicularly were found. Some short microcracks are observed at small distance from the main crack, but without joining it.

Several attempts were made to study crack growth and crack evolution. Special specimens were cut perpendicularly to the frost medium surface partly before or after a certain number of frost cycles and then polished to study initial cracks. Then the polished face was sealed and the specimens were resaturated and subjected to frost cycles again, with the frost medium perpendicular to the sealed face.

Crack propagation could not be studied in this way for two main reasons. First, the cutting changed the saturation and other local condition so much that even initial cracks did not continue to grow. Second, a three-dimensional crack formation was observed: a whole concrete layer was scaling off.

A typical three-dimensional profiling of a cut perpendicular to the frost medium (observation parallel) of a previously flat (polished) specimen after 5 frost cycles is shown in fig 86. The elevated positions consist of cement matrix. The low ones consist of two aggregates, one at each side. Only a very flat profile was measured before frost attack.

Fig. 79 Crack at the interface of an aggregate after polishing without resin mix 2 (w/c=0.63) (binocular, observation parallel)
Cracks at the interfaces of two aggregates after 30 frost cycles, mix 2 (w/c=0.63) (binocular, observation perpendicular, no polishing)

Crack on the interface of an aggregate branching into an air inclusion after 30 frost cycles, mix 2 (w/c=0.63) (binocular, observation perpendicular, no polishing)
Fig. 82  Typical crack pattern after 30 frost cycles, mix 2 (w/c=0.63) (confocal microscope, fluorescent, observation parallel)
Fig. 83  Crack going through a porous aggregate (recycled brick, concrete w/c=0.5) (standard microscope, fluorescent, observation parallel)

Fig. 84  Detail of crack going through an air pore after 30 frost cycles, mix 2 (w/c=0.63) (confocal microscope, fluorescent, observation parallel)

Fig. 85  Detail of vicinity of big crack after 30 frost cycles, mix 2 (w/c=0.63) (confocal microscope, fluorescent, observation parallel)
9.2.2 On-site exposure

Typical frost damage found in practice (on-site) is the so-called pop-out, the scaling of the whole concrete layer over a non-frost resistant aggregate. Fig 87 shows a whole scale of this type with a part of such aggregate situated at the bottom (A). The main crack goes through the aggregate. Such damage is hardly found in laboratory fast weathering tests, even with the same aggregate type.

However, frost damage was studied microscopically on specimens of the same concrete mixes as used in laboratory fast weathering tests, which were exposed to on-site conditions. Drill cores of the laboratory mixes were put into drill holes of a bridge on-site (Hundwil, Appenzell, 900m above sea level) and fixed with repair mortar (see fig 2 section 2.1). After one and two years of exposure, the drill cores were removed, then impregnated, newly cut and finally polished.

Already after one year of field exposure, similar crack pattern as found in the laboratory fast weathering frost resistance tests were observed for positions 1 and 3 (fig 88). The cracks were situated parallel to the exposed surface until a depth of 3 - 7 mm.

The specimens of position 2 showed only minor cracking. While in position 1 and 3 sufficient liquid water is available by rainfall or melting snow, the position 2 was much dryer. After two years of exposure for some specimens the layer in position 3 was completely removed.
9.2.3 *Hardened cement paste specimens*

The crack pattern of a hardened cement paste specimen (w/c=0.8) after only 4 frost cycles of our own laboratory test with frost medium water (impregnation: 1 week under water) is shown in fig 89.

Almost isodistant cracks at a distance of 1 -1.5 mm parallel to the surface were observed. A first crack was found at a depth of $\approx 0.25$ mm (not seen in fig 89). Even with higher magnification no finer cracks between two cracks were found. Similar result was found for lower w/c-ratio (0.4 and 0.5); However, larger distances between the cracks (2-3 mm) were found in those cases.

Further analysis with the confocal microscope at higher magnification, somewhat out of focus, revealed a texture of the cement paste between two cracks in form of small circles around 10$\mu$m in diameter (fig 90). These "structures" (possibly fine microcracks) could not be detected before the subjection to frost cycles. The dimensions of the circles are in the order of typical cement particles.

An attempt to characterize these "structures" with scanning electron microscopy (SEM) failed, as the specimen preparation (drying at 50°C in vacuum) produced similar "structures" identified to be small cracks, even on a never frozen specimens (fig 91). A study of these never frozen specimens by means of confocal microscopy after processing in the SEM showed similar texture as fig 90. This confirms that conventional SEM introduces artefacts, and that an environmental SEM (ESEM) is needed for this kind of studies.
Fig. 89  Hardened cement paste (w/c = 0.8) after 4 frost cycles with water (confocal microscope, no impregnation, observation parallel)
Fig. 90  Detail of hardened cement paste (w/c = 0.5) after 6 frost cycles with water (confocal microscope, no impregnation, observation parallel)

Fig. 91  SEM picture of never frosted specimen after drying at 50°C in vacuum
9.3 Discussion

The observed depth of 5-10 mm of the surface parallel cracks in frosted concrete (laboratory and on-site) is far above the observed thickness of scaled material in laboratory accelerated weathering tests (0.1 - 0.2 mm) or the Powers spacing factor for frost resistance, which is about 0.12 mm.

In the case of hardened cement paste the distances between two cracks (1-1.5 mm) are, with the exception of the first crack (0.25 mm), much larger than expected from hydraulic pressure theory. Pure water was applied as impregnation (1 week under water) and as frost medium, so that no influence of deicing salt was present. According to Powers [9], for w/c=0.63 a value of $L_{\text{max}} = 0.3$ mm (freezing rate 20°C/h) would be reasonable. On the other hand effective freezing rate might be much smaller owing to the liberation of crystallization heat when the frost medium layer freezes and hence a temperature plateau is formed.

The small distance of the first crack might be explained with modest supercooling of the frost medium and therefore higher freezing rates.

9.4 Conclusions

1. Beside the observed damage of concrete by scaling, inner cracks parallel to the frost medium surface were found. The crack path follows the interface between the cement paste and solid stone aggregate. A depth of 8 mm is typical for concrete. The crack pattern preferably goes through the air pores and the porous aggregates.

2. Specimens that were exposed to natural conditions on-site show similar crack pattern.

3. In the case of hardened cement paste specimens, cracks parallel to surface with uniform distance (1-2 mm) from each other are observed. A detailed study by means of confocal microscopy showed that a texture similar to cement particle distribution in fresh cement paste is visible after frost attack with pure water.

4. Scaling was found to be due to volume expansion of the scaled material. This was observed on polished faces perpendicular to the frost medium surface.
CHAPTER 10 MERCURY INTRUSION POROSIMETRY (MIP)

10.1 Method

In order to characterize changes of pore size owing to frost deicing salt attack, one of the most widely used methods to determine pore size distribution: mercury intrusion porosimetry (MIP) was applied. Mercury is forced to penetrate the pore system of the specimen. A cylindrical capillary of radius \( r \) is filled with mercury when the pressure of the mercury is higher than the pressure according to Washburn-equation (Washburn [108])

\[
\frac{2 \gamma \cos \Theta}{\rho} = r
\]

where:

- \( \rho \) : pressure of mercury
- \( \Theta \) : contact angle
- \( \gamma \) : surface tension

and when this pore is connected to the surface from which the mercury is penetrating by other bigger pores. Most pores do not fulfill the second condition. Air voids for example are only accessible by smaller pores. Pores that are connected to the surface by smaller pores only are called inkbottle pores. The volume of an inkbottle pore is filled with mercury through the smaller neck pore and the volume is therefore interpreted as to belong to the smaller pore size. The pore size is therefore always underestimated in mercury intrusion porosimetry.

The assumptions on pore form, surface tension and contact angle are further difficulties of the MIP method. Another problem is the preconditioning of the specimen. To fill a pore properly with mercury the pore has to be emptied prior to experiment.

The degree of saturation has big influence on the result of the measurement. On the other hand the drying of a concrete specimen can cause severe damages and therefore change the result. An adequate drying method has to be applied. Nevertheless the MIP method allows estimating pore size in a very wide range from some nanometers to some hundreds of microns.

10.2 Specimens and their preparation

The aim of the MIP studies was to study the evolution of pore size distribution in frost deicing salt resistance test and to confirm the DTA results (chapter 11) comparing the pore size distribution measured with both methods.

The investigated specimens were concrete cylinders (\( d=15 \) mm; \( h=30 \) mm) taken (drill cores) two years after fabrication of mix 2 (\( w/c=0.63 \)) and mix 3 (\( w/c=0.45 \)) (table 4). The influence of frost deicing salt attack on pore size was studied comparing never frozen specimens with specimens that were taken from concrete plates previously subjected to 10, 20 and 30 laboratory frost cycles (swiss laboratory fast weathering test [1]) with a 3% sodium chloride solution as frost medium layer. All specimens had cut surfaces.

Additionally, hardened cement pastes with \( w/c \)-ratio 0.4, 0.5 and 0.8 were studied. The specimens in this case were small cubes with a diameter of 10 mm.

All specimens first were immersed in polyethylene during 1 week and then dried at 70°C until mass constance.

The maximal mercury pressure was 2000 bar. The surface tension of mercury was assumed to be 0.48 N/m² and \( \Theta=130^\circ \).

10.3 MIP results
The effect of repeated frost cycling was studied with the MIP method. In fig 92 the MIP pore size distributions (intrusion) for the specimens of mix 2 (w/c=0.63) after different number of frost cycles are compared. The result for two different specimens without frost solicitation is added. Both never frozen specimens give quite similar pore size distributions. Even for concrete specimens with big maximal grain size it is possible to get well reproducible results. The pore size distribution has a maximum at a pore radius of about 50 nm for all studied specimens. This is in good agreement with earlier MIP result (Moro [109]).

With increasing number of frost cycles a second maximum at radius between 0.4 µm and 1.5 µm becomes more and more pronounced. As the w/c-ratio in these specimens is high (w/c=0.63) and the air pore content relatively low (1 Vol.-%), they are not frost resistant and inner damage is observed with MIP in the range of 0.4 - 1.5 µm. It is difficult to interpret these values. The appearance of some sharp single peaks at different pore sizes may support an interpretation that these pores actually represent bigger cracks that are observed by MIP like inkbottle pores with smaller neck entrances.

![MIP pore size distribution in function of frost cycle number of mix 2 (w/c=0.63)](image)

Fig. 92

Fig 93 shows the MIP pore size distributions (intrusion) of specimens of mix 3 (w/c=0.45). This concrete has a high air void content and proved to have a high frost resistance. Again, a first pore radius distribution maximum is found at about 50 nm. The total volume of the pores in this region is similar to the one of mix 2 (w/c=0.63). A second well pronounced maximum is found at radius between 0.4 µm and 1 µm. It can be assumed that this maximum represents the high air void content.

From microscopy data the mean radius of air voids is known to be bigger than 100 µm. The air voids can be filled with mercury through capillaries only. Once filled, the air voids are the starting point for an additional net of big connected capillaries which then are filled and connect other air voids and so on. An inkbottle effect results.
The air voids of these specimens (mix 3) are represented in a similar pore region as the damage in the specimens of mix 2 (w/c=0.63) after a frost deicing salt attack. This supports the interpretation given above, that the increasing pore volumes with increasing number of frost cycles at radius between 0.4 µm and 1.5 µm (fig 92) actually represent bigger cracks.

Owing to the high frost resistance of mix 3, the pore size distribution undergoes only minor changes for specimens with increased number of frost cycles.

Fig. 93    MIP pore size distribution in function of frost cycle number of mix 3 (w/c=0.45)

The MIP intrusion result for the hardened cement paste specimens are given in fig 94. Again, a first pore size distribution maximum is found at a pore radius of 50 nm. For water/cement ratio 0.4 and 0.5 this peak cuts off sharply so that very low pore content above 0.1 µm is found. Taking into account that the volume fraction of cement stone in concrete is only about a quarter, the pore volumes are comparable to the amounts measured for concrete specimens.

The specimen with w/c-ratio 0.8 shows significantly higher pore contents. A second pore size distribution maximum is observed near 0.15 µm. As the cement mixing was under vacuum no air voids are present in this case. Some microcracking may be the reason for this maximum.
10.4 Conclusions from MIP measurements

1. Direct measurement of pore size distribution by mercury intrusion porosimetry (MIP) was done. Two pore size maxima at radius $r_1 \equiv 50 \text{ nm}$ and at $r_2 \equiv 0.4 - 1.5 \mu\text{m}$ are found.

2. The maximum at the larger radius $r_2$ is attributed to air pores. This difference to their real dimensions is explained with an ink bottle effect.

3. For non frost resistant concrete, an increase of pore volume in the same region ($r \equiv 0.4 - 1.5 \mu\text{m}$) is found with increasing number of frost cycles. These pores are interpreted as bigger cracks formed due to the frost deicing salt attack.

4. Finer pores ($r < 100 \text{ nm}$) are not affected by the frost deicing salt attack.
CHAPTER 11 CALORIMETRIC MEASUREMENT

When water freezes the crystallization heat is set free. When ice melts this energy is consumed. This energy change can be measured by means of calorimetric methods. These methods therefore allow determining the amount of liquid that undergoes a phase transition in function of temperature or time. The amount of excess water can be estimated. It therefore is a useful tool to study freezing and thawing of water in porous materials.

The method itself does not destroy the specimen and is not influencing the freezing process.

As seen in chapter 3, the phase transition of liquid in small pores behaves different from bulk liquid. The pore size freezing/melting point relations (section 3.2.2) allows a further analysis of calorimetric data and the calculation of pore size distributions.

It has to be mentioned that the pore liquid in cement bonded materials never is pure water but contains a certain amount of dissolved ions which lower the freezing/melting point (Raoult's law).

11.1 Methods

The measurement of the exchanged heat can be done either by differential thermoanalysis (DTA) [110-114,28,29] or differential scanning calorimetry (DSC) [30,115]. With the DTA method the temperature differences between the specimens and a reference, which are placed symmetrically in a sample holder that is cooled/heated at constant rate, is measured. Other DTA apparatus measure the heat flux from the specimen to a sample holder, which consist of a metal plate.

In the DSC experiments the specimens and the reference are arranged symmetrically and they are cooled or heated separately at constant rate so that no temperature differences between reference and specimen occur. The difference in the heating power is registered.

For some own preliminary tests a DSC of Perkin Elmer (DSC 7) was used. Unfortunately only specimens of less than 40 µl could be measured. As we intended to study concrete, the use of another apparatus (DTA - type) which allowed the measurement of substantially bigger specimens, cylinders of 18 mm diameter and a height of 10 mm, was necessary.

The measurement principle of this DTA apparatus is described below (fig 95):

![Diagram](image)

Fig. 95 Test arrangement for DTA measurements

The specimens in a specimen holder (Al) are placed onto heat flow meters that are mounted on a cylindrical metal (copper) block. Up to four different specimens (3 specimens + 1 reference) could be placed. They were separated from each other by a thermal insulation. The specimens were covered with an adhesive aluminum tape to prevent them from moisture exchange. The whole cell was covered by a cap which was fixed (vacuum dense) on the metal plate. Between the insulation and the cap remained a small air filled space. The whole calorimeter then was placed into a Lauda bath filled with ethanol. While the metal
plate was in contact with the ethanol, the specimens were not. The bath temperature was controlled by an external control unit and PT-100 temperature sensors, which allowed cooling or heating the bath at constant rate. The bath temperature was varied between -49°C and +10°C.

A data logger captured the output voltage of each of the four flow meters. The bath temperature and the temperature of the copper block were measured by means of thermocouples (+/- 0.1°C). The data was then analyzed on a computer.

The freezing/thawing rate of the bath was constant so that we can write:

\[ \frac{dT}{dt} = \alpha = \text{const.} \]

where: \( T \) : temperature  
\( t \) : time

In the standard DTA experiments a cooling rate of 5°C/h was chosen. The minimal temperature was -49°C. Other workers showed that little additional ice is formed below -50°C (Sellevold [113]).

If \( dQ \) is the quantity of heat absorbed by the specimen during time \( dt \), the heat flow \( jQ \) passing the heat flow meter is expressed by \( dQ/dt \). The signal \( V \) of the heat flow meter (output voltage) is given by:

\[ V = S \frac{dQ}{dt} \]

\[ = a S \frac{dQ}{dT} \]

where: \( S \frac{dQ}{dT} \): constant, sensitivity of the heat flux meter  
\( S \frac{dQ}{dT} = c_{pA} \): apparent heat capacity \([\text{J/gK}]\)

The apparent heat capacity composes of the heat capacity of the specimen and a term representing the liberation or consumption of crystallization heat owing to the phase transition. In order to derive the apparent heat capacity owing to the phase transition only, the measured apparent heat capacity of a reference specimen was subtracted from the measured apparent heat capacity of the specimen. The reference specimen was a concrete specimen that was preliminary dried at 110°C during 24h and then insulated on all sides with an aluminum tape. The apparent heat capacity of the reference was measured in each DTA experiment at one of the four specimen places.

The influence of the sample holders and of temperature variations could be extracted in this way. A constant proportionality factor \( (k) \) derived at fix temperature \( T_k \) was used to take the difference in heat capacity and mass of the specimen into account.

\[ c_{pA} \text{corr} = c_{pA} - c_{pA \text{ ref}} = \frac{V_{\text{corr}}}{a S g_{\text{ssd}}} \]

with \( V_{\text{corr}} = V - V_{\text{ref}} \times k \)

\[ k = \frac{V(T_k)}{V_{\text{ref}}(T_k)} \]

freezing: \( T_k = 0°C \)

thawing: \( T_k = -40°C \)

where: \( g_{\text{ssd}} \): dry specimen mass \([\text{g}]\)
The sensitivity $S$ of the apparatus was determined by a calibration experiment with copper specimens of well-known mass and physical properties.

**DTA apparatus:**

![Diagram of DTA apparatus]

The calorimeter can be idealized as a system with two containers at different temperatures (fig 96).

The heat flow in this case can be written as:

\[
\dot{Q} = \frac{dQ}{dt} = -\lambda \frac{A}{\Delta x} \frac{\Delta T}{\Delta x} = c' \Delta T
\]

where: \(c' = \frac{-\lambda A}{\Delta x} \approx \text{const}\)

\(\lambda\) : thermal conductivity

\(A\) : flow area

Applying this to the calorimeter output we get:

\[
V = S c' \Delta T
\]

This allows calculating the specimen temperature $T_{sp}$ in function of the copper block temperature $T_{co}$ (calorimeter temperature) and the output signal $(V)$. The value for $c'$ is found by a calibration experiment.

\[
T_{sp} = T_{co} + \Delta T = T_{co} + \frac{V}{Sc'}
\]

The validity of the calculation was proved with an experiment where a thermocouple was placed at the center of a specimen and the calculated specimen temperature was compared.
to the measured value. The difference between measured and calculated value, even near the phase transition point, are very small (fig 97).

![Graph showing calculated versus measured specimen temperature](image)

Fig. 97 Calculated versus measured specimen temperature [°C]

11.2 Specimens and their preparation

Although the specimens had to be small to be measured with the described DTA apparatus, only cylinders of 18 mm in diameter and a height of 10 mm, special attention was put on measuring real concrete with maximum grain sizes of up to 32 mm. This was only possible selecting the specimens after cutting, avoiding big aggregate stone. This selection was done by eye. This certainly is not very precise and somewhat hazardous, but the observed scattering between specimens of the same mix and at the same moisture conditions was much smaller than for example, the influence of uncontrolled supercooling effects. Nevertheless, principal behavior could be studied with good reproducibility. Additionally, hardened cement pastes with much better homogeneity were measured.

For calorimetric measurement mix 2 and 3 (table 4 chapter 5) were used. The concrete cubes (200x200x200 cm³) were stored in water after demoulding (2 days). At an age of seven days, drill cores with a diameter of 18 mm were taken from a lateral face. These cores then were cut into cylinders of 10 mm height. The specimens having moulded or cut surfaces (distance 0, 12 or 24 mm from mould) were stored separately in water. The drilling and cutting was executed below water. Six month later, the specimens were dried in climatic chambers of 70%, 90%, 94%, or 97% RH (at 20°C). The specimens were dried step by step, remaining at least one month at each higher relative humidity. The 94% relative humidity was achieved in closed glass recipients above a saturated KNO₃ solution - the 97% relative humidity above a saturated K₂SO₄ solution at 20°C. Some specimens remained below water and are called "virgin" in this report. The specimens were more than 6 month in the final storage conditions.

Before measuring they were weighted (M_A) and then covered with an aluminum adhesive tape to protect them from humidity changes. After the DTA experiment, the aluminum foil was removed and some porosimetry data of the specimens were determined, storing them during 1 d under water (M_E) and then drying them during 2 hours at 50°C (M_50) and finally at 110°C (M_110).

Some specimens were resaturated with water or sodium chloride solutions.
11.3 Influence of supercooling

11.3.1 DSC experiments

Apart from freezing /melting point depression by dissolved salts or pore size, the lack of nucleation germs may cause severe supercooling. The probability of supercooling depends of the amount of water. When the amount of studied material is limited, which is normally the case (Meier [110]), supercooling is frequent. The crystallization heat is then set free randomly and not at the temperature that would correspond to the freezing point of the pore water. This may lead to misinterpretation of test results. The temperature region around 0°C is of particular interest: A pore with a radius of 10 nm (capillary pore) signifies, after Brun [46], a freezing point depression of only 6 °C. Therefore supercooling of bulk water to -6°C could be misinterpreted as to be the result of the phase transition of water in capillary pores of 10 nm radius.

Own DSC results of small amount of cement stone (40 µl) show a typical phase change (freezing) at about -20°C and another at -40°C (fig 98). Similar results were found by (Beddoe [30]).

In own DSC experiments with small amount of water (water droplets) also a phase transition (freezing) around -20°C was detected (fig 99). As the studied water amount of 0.5 - 5mg still is big enough to neglect the freezing point depression due to the surface tension, only supercooling can explain the low phase transition temperature. We think that for this reason the freezing peak at -20°C for hardened cement paste specimens (fig 98) also has to be attributed to strong supercooling (Kaufmann [116]). For this purpose supercooling has to be prevented in calorimetric experiments.

Fig. 98 DSC freezing result of scaled material of mix 2 (w/c=0.63)
11.3.2 **DTA experiments**

In the DTA experiments supercooling was prevented using ice formation germs. Different researchers used AgI, which is a very effective ice nucleation germ (Meier [110], Bager [28][29]), but the disadvantage is its low initiation temperature of -4°C.

Another type of ice formation germs was used for this work: Cholesterol, melted between two glass cover sheets and then recrystallized (see section 3.2.3 Fukuta [52]). In our experiment it proved to have initiation temperatures up to -0.7 °C. Cholesterol was preferred to other substances owing to its easy commercial availability and handling. Metaldehyde, the only known substance with higher initiation point (Fukuta [53]) was not used due to its toxical properties.

Some milligrams of cholesterol were placed on the bottom face of the specimen (closest face to the heat flow meter). It was then fixed with an adhesive Al-tape, the same that prevented the specimen from moisture exchange.

Fig 100 shows typical DTA result (reference subtracted) for two different concrete specimens of the same concrete (mix 2, w/c = 0.63) with and without cholesterol. The specimens were stored under water and never dried ("virgin"). The corrected apparent heat capacity $C_{PA\ corr}$ is given in function of the temperature of the copper block $T_0$ (calorimeter temperature). The corrected values represent the crystallization heat only.
Two phase transition peaks can be distinguished in the freezing curve of the water impregnated specimen. For specimens without application of ice formation germs (without cholesterol), similar results were found by many other researchers (Dorner [112]).

A similar plot for the reference specimen (dried at 110°C, without correction) would give a straight line with no peaks, representing only the heat capacity of the specimen.

The first ice formation peak (right) is situated at significantly higher temperatures with the use of the ice formation germs.

Compared to the first peak (right) in the DSC (freezing) experiment with similar specimen at -21°C the first peak in the DTA experiment is found at much higher temperatures (= -1°C).

The application of ice formation germs (cholesterol) at one surface prevented from supercooling. A big part of the pore water in the inside of this specimen was prevented from supercooling by initiation of ice formation at the surface of the specimen. This means that the water in a big part of the pores was nucleated by the ice that was penetrating the specimen and not from germs or by homogeneous nucleation within these pores.

Without freezing germs, the tendency for high supercooling was less when the cycle was repeated various times. Some remaining prestructuring of the pore water may explain this.

In the intermediate temperature region (-5°C to -25°C) no phase transition peak can be found. However some crystallization heat, decreasing at lower temperatures, is detected. This is with and without freezing germs.

According to pore size freezing point relations this means polydisperse pore size distributions with no multimodal characteristics.

We think that phase transitions in this temperature region found by other researchers (Bager [28][29], Beddoe [30]) are supercooling peaks which do not represent real pore size distributions (see section 11.10).
A second freezing peak (left, fig 100) lays at about -40°C with and without cholesterol application. According to pore size freezing point relation this would, for spherical pores (after Brun [46]) correspond to a radius of 2 nm. Nevertheless, the water in such fine pores is unlike to freeze even at these low temperatures.

Another explanation is possible: the phase transition at -40°C could be the consequence of supercooling. It is known that bulk water cannot be supercooled to temperatures below -40°C as then homogeneous nucleation starts (Mason [51]). The freezing peak at -40°C could represent supercooled water, which freezes by homogeneous nucleation. The thawing curve may prove this, as no thawing peak at such low temperatures is found (fig 101).

The existence of supercooled water at -40°C might be found in isolated pores with no direct access to the penetrating ice, so that they can not be nucleated by this ice (see later). A similar phenomenon might be found in the mercury intrusion porosimetry (MIP) where so-called inkbottle pores only can get filled through smaller neck pores.

The comparison of the thawing curves (fig 101) shows that the applied ice formation germs do not significantly change the thawing characteristics. Their only effect is to provide freezing germs.

![Thawing curve comparison](image)

Fig. 101 Effect of cholesterol on the result of a DTA heating experiment (mix 2, w/c=0.63)

In the intermediate temperature range (-25°C - -5°C) the thawing curve shows a similar shape as the freezing curve. Continuing phase transition is found all along the thawing process.

In contradiction to results of other researchers (Bager [28],[29], Beddoe [30]) the hysteresis between freezing and thawing is very small as is shown in fig 102. Freezing and thawing curves are plotted here with reversed signs to make them comparable.

The peak in the freezing curves at about -40°C does not appear in the thawing curves. At the same time, values somewhat higher than for the freezing curves are obtained in the temperature region between -7°C and -25°C for the thawing curves. From this, the water freezing at -40°C can be interpreted as to melt over a wide temperature range between -25 °C and -7 °C (3 - 10 nm).
Near zero degrees, apparent heat capacities are lower at thawing than at freezing. This could be explained by supercooling effects at freezing.

The comparison of the results of different mix designs shows quite similar characteristics with a somewhat higher content of bigger pores for mix 2 with the higher w/c - ratio. One should remind that the design was so that the total amount of cement stone was equal.

For comparable studies other mix designs with wider variation and smaller maximal grain size should be used. This was not the objective of this principal study of the freezing mechanisms.

The freezing rate has a minor influence on the calorimetric results. Without freezing germs the probability that supercooling occurs is higher with higher freezing rate. This is not the case when ice formation germs are applied. The thawing rate also has little influence on the melting curve (fig 103).

However at high thawing rate an "overflow" above 0°C is observed. This is a sign that the temperature distribution within the specimen is not uniform. Some regions within the specimen still contain ice meanwhile others are already at temperatures above 0°C. An analog effect to supercooling of water, superheating of ice, does not exist. A lower rate of 1°C/h prevents from such effects but is very time consuming so that for all other experiments the freezing and the thawing rate was set to 5°C/h.
11.4 Influence of storage humidity

According to Kelvin equation (section 3.1), in concrete stored at constant relative humidity pores smaller than the corresponding critical radius remain water filled only. Because of the pore size - freezing point relation the phase transition in the DTA experiment therefore should be initiated at lower temperatures for lower saturation. The freezing DTA of mix 2 (w/c=0.63) in fig 104 is showing this very well.

For the storage at relative humidities higher than 90% RH a first peak appears at -1°C to -5°C. For all tested storage conditions (above 70% RH) a peak at -40°C is found (freezing), at the lowest relative humidity (70% RH) it is significantly less pronounced. Some experiments with specimen stored at 35% RH showed no phase transition at -40°C. This result demonstrates that a large amount of evaporable water within a concrete specimen is non-freezable even at -40°C. We think that most of the physically adsorbed water is non-freezable.

For the storage humidities 90% and 94% RH small phase transition peaks between -30°C and -25°C are found and the peak at -40°C is higher than for the other saturation conditions. We think that this is because of supercooling effects: Due to the relatively high degree of saturation the capillary pores contain a lot of freezable water. Nevertheless some coarser capillaries remain air-filled. A coarser air-filled capillary pore (fig 105) might separate two pores. When the ice penetrates one of these pores, the water in the other pore is not nucleated, as it is not in direct contact with the ice: it gets supercooled. At lower temperatures it may be nucleated through a smaller pore (pore size - freezing point relation) or by homogeneous nucleation (at -40°C). The effect of the connectivity of the pores is discussed in more detail in section 11.10.

In the thawing DTA graph (fig 106) all peaks below -20°C disappeared. Especially interesting are the curves for the specimen prestored at 90% RH. At freezing no phase transition above -25°C is detected and a high peak at -40°C is seen. No phase transition below -20°C is found in the thawing curve.
Neither in the freezing nor in the thawing curve the difference between virgin (never dried) and resaturated (with water from 70% RH) is very pronounced.

Different result found by other researchers (Bager [28][29]) also may be the consequence of increased supercooling in never dried specimen. In their experiments the water in the virgin specimen may be prestructured which lowers the probability to form a freezing germ of critical size. With the application of ice formation germs, as done in our experiments, possible prestructuring of water less influences the nucleation.
11.5 Resaturation with salt solutions

The effect of resaturation with salt solutions was studied in detail. Similar studies were carried out by (Beddoe [30], Xu [115]). On site this is the most common case, as weather conditions change frequently and the moisture content of concrete structures at least at the outer surface (Kaufmann [117]) is characterized by drying and resaturation.

The effect of drying and resaturation here was studied on specimens which first were stored at different relative humidities (70%, 90%, 94% and 97% RH; at 20°C) for more than 6 month (see section 11.2). These specimens then were completely immersed in a 3 mass-% salt solution during 4 days. The thawing curves for the specimens resaturated with a 3% sodium chloride solution from the different saturation degrees are given below (fig 107).

The higher the moisture content before resaturating (higher storage humidities), the more the thawing DTA curves are shifted towards higher temperatures. It seems that the salt and the pure water phase get somewhat separated in resaturation, which is best seen when resaturation is from 94% RH, where two phase transition peaks can be distinguished. This can be explained by a partly removal of preexisting humidity ("old water") when the "new" salt water is penetrating the specimen when resaturating (Kaufmann [118]).

In frost deicing salt resistance tests, the moisture history therefore can have significant influence on the results.

Some specimens previously stored at 70% relative humidity (20°C) were resaturated with sodium chloride solutions of different concentrations. The results are given in fig 108 (freezing) and fig 109 (thawing).

The freezing point of a salt solution is depressed compared to pure water. The depression is higher with higher salt content (Raoult's law). Hence it is not surprising that, in the freezing curves (fig 108), the first transition peak (right) is found at higher temperature for lower salt
content. An additional phase transition peak at freezing is found at -30°C for a salt content of 10 mass-% (fig 108).

Fig. 107 Thawing of mix 2 (w/c=0.63) stored at the indicated relative humidities and resaturated with a 3 mass-% NaCl solution

Fig. 108 Freezing of mix 3 (w/c=0.45) resaturated from 70% RH with NaCl solutions of indicated concentrations (mass-%)

In the thawing curve (fig 109) a similar peak appears (10 mass-% NaCl) at -21°C, which is the eutectic temperature of aqueous NaCl solutions (salt concentration: 30 mass-%). The difference in the temperature may be explained with supercooling effects at freezing. Some pores seem to get filled with a eutectic NaCl solution. This is already the case when resaturating the specimen with an only 10 mass-% NaCl solution. A possible explanation could be salt segregation during freezing. The "eutectic" peak (-21°C) is not symmetrical in
the thawing curve. The pore size - freezing point relation is also valid for pores filled with a eutectic salt solution so that pores of different sizes freeze at different temperatures.

The main melting peak (near -5°C) of the same specimen is even more dispersed and asymmetrical. Some phase transition signal even is found near 0°C. This could be explained by some pores being filled with a salt solution of a lower concentration. This could be explained by salt ion segregation during freezing, either.

![Graph showing thawing of mix 3 (w/c=0.45) resaturated from 70% RH with NaCl solutions of indicated concentrations (mass-%)](image)

### Fig. 109
Thawing of mix 3 (w/c=0.45) resaturated from 70% RH with NaCl solutions of indicated concentrations (mass-%)

#### 11.6 DTA results of hardened cement paste

In addition, some DTA experiments with hardened cement paste were performed. Principally the same results as for concrete specimens are found. One has to take into account, that the total porosity of the concrete specimen was about four times less than the one of the hardened cement paste specimens. The specimens of which the results are shown in fig 110 (freezing) and fig 111 (thawing) were never dried specimen (virgin). Similar results were obtained for specimens resaturated from 70% RH. In the figures the plot of a concrete specimen (mix 3, w/c=0.45) is added.

While for hardened cement pastes of water/cement ratio 0.4 and 0.5 similar pore content is found, higher pore content is found for hardened cement paste of w/c=0.8. Owing to the very high water content of this mixture, supercooling is very small. The first freezing peak assumes a more symmetric form, indicating a maximum in the pore size distribution at = -1.5 °C (calorimeter temperature).
Fig. 110  DTA freezing curves of water saturated hardened cement paste specimens

Fig. 111  DTA thawing curves of water saturated hardened cement paste specimens
11.7 Calculation of freezable water content

To calculate the freezable water content one has to take into account the fact that the specimen temperature differs from the calorimeter temperature (see fig 97) and therefore an additional heat flux is contained in the apparent heat capacity \( C_{pA} \) that has nothing to do with phase transition heat. Especially when supercooling is present, this effect is important.

In the freezing experiment, the heat flux \( j_{Q,\text{cal}} \) from the specimen towards the calorimeter (metal block) can be written as:

\[
\frac{dQ}{dt} = c'(T_{sp}(t) - T_{cal}(t)) = \frac{V}{S} \]

\[
\Rightarrow T_{sp}(t) = \frac{V}{Sc'} + T_{cal}(t) \quad \text{(compare section 11.1)}
\]

When freezing is initiated, the crystallization heat is set free and the specimen temperature \( T_{sp} \) starts deviating from the slope that it would have without phase transition (see fig 97).

At the same time the specimen is cooled by the Lauda bath. The total net heat flux \( j_{Q,\text{tot}} \) that is exchanged by the specimen (incl. crystallization heat) is:

\[
\frac{dQ_{\text{tot}}}{dt} = c_p \frac{dT_{sp}(t)}{dt}
\]

where: \( c_p \) : specific heat capacity of the specimen

The total heat flux \( j_{Q,\text{tot}} \) can be separated into a flux towards the calorimeter \( j_{Q,\text{cal}} \) and the heat flux \( j_{Q,\text{crystallization}} \) induced within the specimen from the crystallization heat. Neglecting the heat exchange through the thermal insulation we get:

\[
j_{Q,\text{tot}} = -j_{Q,\text{cal}} + j_{Q,\text{crystallization}}
\]

Without any further crystallization \( (j_{Q,\text{crystallization}} = 0) \) the specimen temperature then would fall exponentially as would \( j_{Q,\text{cal}} \) and the voltage output of the calorimeter. This can be derived solving the resulting differential equation when \( j_{Q,\text{tot}} = -j_{Q,\text{cal}} \) and applying (37) and (38). With further phase transition we get:

\[
\frac{dQ_{\text{cryst}}}{dt} = c_p \frac{dT_{sp}(t)}{dt} + \frac{V}{S} = c_p \frac{dV}{Sc'} dt + c_p \frac{dT_{cal}(t)}{dt} + \frac{V}{S} \frac{dT_{cal}(t)}{dt} = \frac{dT_{cal}(t)}{dt} = a < 0
\]

freezing rate

\[
= \frac{c_p}{Sc'} \frac{dV}{dt} + c_p \frac{dV}{Sc' dt} + \frac{V}{S} \frac{dT_{cal}(t)}{dt} = a < 0
\]

(see equation 33)

\[
= \frac{c_p}{Sc'} \frac{dV}{dt} + \frac{V}{S} \frac{dT_{cal}(t)}{dt} = a < 0
\]

crystallization heat per mass unit

\[
\Rightarrow \frac{1}{g_{ssd}} \frac{dQ_{\text{cryst}}}{dt} = \frac{ac_p}{c'} \frac{dc_{pA,\text{corr}}}{dt} + a c_{pA,\text{corr}}
\]

where: \( g_{ssd} \) : dry specimen mass [g]
A similar relation can be derived for the thawing experiment. The freezable water content \( w_f(T) \) can be derived by integration

\[
(42) \quad w_f(T) = \frac{1}{\rho_{\text{ssd}}} \int_{T=0}^{T} \frac{1}{W_a(T)} \, dt
\]

The values for the freezable water content are given in Table 6. They were derived from DTA data with a freezing/thawing rate of 5°C/h.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Adiabatic</th>
<th>Freezing</th>
<th>Thawing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-2</td>
<td>-5</td>
<td>-10</td>
</tr>
<tr>
<td>Concrete</td>
<td>1.1</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td>mix 2 (w/c=0.63)</td>
<td>0.9</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>mix 3 (w/c=0.45)</td>
<td>0.7</td>
<td>1.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The values are similar to those derived from expansion measurements (Table 5 section 7.5). The amount of freezeable water is in the order of the degree of saturation of the capillary pores. Gel water hardly freezes at temperatures below -50°C.

The amount of freezeable water of hardened cement paste is comparable with the amount of freezeable water in the cement matrix of concrete.

### 11.8 Calculation of pore size distribution

Using theoretical pore size freezing/melting relations a pore size distribution can be calculated from calorimetric data. The variation of specific heat of water and of ice with temperature is not taken into account.

The hysteresis between freezing and thawing in the calorimetric experiment was found to be small when supercooling at freezing is not important. As the hydraulic radius of the liquid-ice interface influences significantly the freezing and the melting point of a pore solution (see section 3.2.2), the difference between the hydraulic radius of the liquid-ice interface for freezing and for thawing is thought to be small. For the calculation we therefore assign an equilibrium ice front with a spherical liquid-ice interface, being independent of the pore shape. However the calculation also may be done for other liquid-ice interfaces.

After Brun [46], in the case of a spherical liquid-ice interface, both solidification (freezing) and fusion (thawing) give the same values for the apparent heat and the pore size freezing/melting point relation.

As the thawing curves are more precise and not influenced by supercooling, it is preferred to use the thawing curve for the calculation.
Spherical liquid-ice interface => solidification = fusion

\( W = -5.56 \times 10^{-2} \Delta T^2 - 7.43 \Delta T - 332 \) \([\text{J/g}]\) app.solidification/fusion energy

\( R_p = -64.67/\Delta T + 0.57 \) \([\text{nm}]\) pore radius

\[ dV_{\text{pore}} = \frac{dQ_{\text{cris}}}{W_p} \]

where: \( V_{\text{pore}} \) : pore volume

\[ dQ_{\text{cris}} = \frac{dQ_{\text{cris}}}{dt} = \frac{1}{a} d(\Delta T) \]

From equation (44) we get by derivation: \( dR_p = \frac{64.67}{(\Delta T)^2} d(\Delta T) \)

Together with equation (45) we get for the differential pore volume:

\[ dR_p = \frac{64.67}{(\Delta T)^2} d(\Delta T) \]

The relation is strongly dependent on \( \Delta T^2 \) so that the small values measured at low temperatures are of big importance. A logarithmic pore size distribution is preferred.

By derivation of \( \log R_p \) (with \( R_p \) given by equation 44) we get:

\[ d(\log R_p) = \frac{1}{B - \frac{A}{\Delta T}} d(\Delta T) \]

\[ A = 64.67 \]

\[ B = 0.57 \]

\[ = \frac{A}{\Delta T - B(\Delta T)^2} \]

Together with equation (45) we get:

\[ dV_{\text{pore}} = \frac{dQ_{\text{cris}}}{dt} = \frac{1}{64.67 Wa} \left( 64.67 \Delta T - 0.57 (\Delta T)^2 \right) \]

The pore size distribution was calculated for resaturated concrete specimens from thawing DTA - data with a thawing rate of 1°C/h. The results are given in fig 112.

A maximum of the pore radius \( R_p \) in the pore size distribution is found around 30 nm. This agrees well with the results from mercury intrusion porosimetry (MIP) data (see chapter 10). According to pore size - freezing point relation this corresponds to a freezing point of -2 °C. The same freezing point depression would be observed in a 3% salt solution.
Fig. 112 Pore size distribution calculated from thawing DTA-data

11.9 Comparison of calorimetry (DTA) and mercury intrusion porosimetry (MIP)

The DTA method has the big advantage that no special preconditioning like drying of the specimens is necessary, a simple and well controllable storage under water is sufficient. The specimen can be observed in a non-disturbed condition.

The difficulties on theoretical assumptions, especially on pore shape are similar in the MIP and the DTA method. The effect of inkbottle pores is important for MIP and for freezing DTA measurement. The inkbottle pores are interpreted as to belong to a smaller diameter. In the freezing DTA measurement some heterogeneous nucleation (freezing germs are present) in the inkbottle may prevent from supercooling so that such an inkbottle would not be interpreted as to belong to the size of its neck. The subestimation of pore size therefore may be somewhat less in the DTA method (freezing).

On melting, supercooling phenomena are not present in DTA. The ice in the pores melts according to the pore size. The pore size is therefore estimated correctly. The difficulty here is that the specimen has to be frozen before melting curve can be determined. This may lead to damages in the pore system when the degree of saturation is too high.

Additionally, the presence of pore solutions with unknown solute content may be a problem for the interpretation of freezing DTA data.

A pore can only be detected by means of calorimetric methods when it is water filled. The sensitivity for DTA method is high in a mean pore size range of some nanometers to some hundreds of nanometers. Bigger pores or microcracks are detected much easier with the MIP method. The effect of repeated frost cycling was therefore studied with the MIP method only. The specimen dimension (MRI: d=15, h=30 mm; DTA: d=10, h=18 mm) was more favorable in MIP to detect small differences.
11.10 Discussion

Our calorimetric test results differ from the results of other researchers (Bager [28][29], Beddoe [30]) in two points:

First, only a small hysteresis between freezing and thawing was found in our DTA experiments.

Second, no phase transition peak was found in an intermediate temperature region between -15 and -25°C. Meier [110] and Dorner [112] did not find a phase transition peak in this temperature region also.

These differences should be explained by the different specimens, specimen dimension (Bager [28][29] cylinders Ø 14.6 mm, l=65 mm; Beddoe [30] cubes l= 1-2 mm), apparatus (Bager [28][29]: Calvet micro-calorimeter (DTA), Beddoe [30]: Perkin-Elmer (DSC)) or other experimental details.

The hysteresis effects frequently were explained by a difference between pore size-freezing point and pore size-melting point relations owing to pore geometry. A shape factor was introduced (Brun [46], Beddoe [30]).

Using a model with cylindrical pores, Setzer explained the big hysteresis between freezing and thawing they found with a different liquid-ice interface curvature (or hydraulic radius) between freezing and thawing. As shown in fig 113 he assumes nucleation from a freezing germ of critical size (spherical ice embryo) that has a smaller hydraulic radius than the (final) ice body when it melts (Setzer [33]). In his model nucleation is from a freezing germ of critical size and not from an equilibrium ice front.

The phase transitions in the intermediate temperature region were attributed by Beddoe to ice formation in "meso-pores". Their diameters were calculated (Beddoe [30]) from a pore size - freezing point relation.

![Fig. 113 Difference of hydraulic radius between freezing (spherical ice germ) and thawing (cylindrical ice body) (Setzer [33])](image)

These concepts cannot explain the observed differences in the calorimetric measurements.

An explanation for these differences can be given as follows.

When the freezing point T₀ is reached, without supercooling, ice is first formed at the concrete surface. Let us now assume that no spontaneous ice nucleation within the concrete specimen occurs (no spherical freezing germ) but that nucleation is by direct contact with the penetrating ice only (percolation). The existence of such an ice front was found by Bager [28][29] and was confirmed in our calorimetric tests. Scherer [141] calculates the nucleation rate in a pore and concludes that ice nucleation within a porous material is not very probable so that nucleation rather is initiated by percolation of an ice front.

The equilibrium ice front can continue to penetrate the concrete at lower temperatures only. Let us call R₁ is the pore radius with freezing point of its pore water being T₁ according to the pore size - freezing point relation. At a temperature T₁ < T₀ all pores which are connected to the surface by a larger radius than R₁ (all neck entrances are larger than R₁) are allowed to freeze (fig 114). The existing ice at the surface guarantees the nucleation so that in these pores no supercooling occurs. At a lower temperature T₂ all pore water of the pores which are connected to the surface by pores with necks larger than R₂ will freeze and so on.
As we see, some pore space, although containing very big pores may not freeze because the ice front cannot penetrate them, as all pores which would connect them to the ice front have necks which are too small. Big "regions" therefore may supercool and freeze at much lower temperatures than they would if they were connected by bigger pores.

When they finally get connected at a lower temperature (or nucleated) their pore water would freeze together forming a freezing peak which could be interpreted as freezing of pore water of smaller pores. The effect is similar as in mercury intrusion porosimetry (MIP).

The probability for the existence of such regions containing supercooled water increases when big pores have small entrances only and it increases with the distance from the surface.

Interfaces of aggregates (in concrete) or fine cracks (may be introduced by drying) change the situation drastically although their influence to the total porosity may be small. They can be considered as bigger pores forming a network of connected pores that freeze at temperatures near the freezing point of water. For example, vacuum evaporation at modest temperature of 50°C of hardened cement paste can lead to a fine network of microcracks. This was observed both with a scanning electron microscope (SEM) and a confocal microscope. The probability of supercooling of large regions even at large distance from surface hence is strongly reduced.

The supercooling of whole pore regions can lead to a big hysteresis between freezing and thawing. Large amount of pore space may freeze at lower temperatures than it would according to the pore size freezing point relation. However, the pore ice thaws exactly at the melting temperature according to pore size melting point relation as no superheating is possible (Fagerlund [32]).

The assumption that no nucleation in pores with no direct contact with the ice front occurs is supported by experiments of Bigg [48] who measured big supercooling of small water drops and by our DSC measurements where, without ice nuclei application, no freezing until -20°C was found. It is also supported by the demonstrated positive effect of ice formation germs.

![Diagram showing connectivity of pores in hardened cement paste](image-url)

Fig. 114 Connectivity of pores in hardened cement paste
Bager and Sellevold [28][29] reported a second freezing peak at about -20°C. They used cylindrical specimens where one surface was nucleated by freezing germs. The probability of supercooling of large amount of pore water increases with increasing length of the specimen. The specimen used in our experiment were much shorter (l=10 mm) compared to the specimen used by Bager (l= 65mm) and were mainly concrete specimens with a connecting network consisting of the porous cement-aggregate interfaces.

Without local supercooling, the hydraulic radius in our model would be almost the same for freezing and for thawing. The liquid-ice interface is assumed to be spherical for both freezing and thawing so that only a small hysteresis results.

11.11 Conclusions

1. Strong supercooling may affect the calorimetric results especially when very small specimens are measured. The consequence is wrong interpretation of calorimetric data. Supercooling therefore must be excluded so that only the freezing point depression due to pore size or soluble salts (metal hydroxide) can influence the phase transition of the pore solution. It can be reduced by the application of ice formation germs (ice nuclei). Cholesterol prepared in a mica sandwich technique proved to be very powerful ice nuclei with activation temperature near 0°C.

2. Correct specimen (not calorimeter) temperature measurement is very important to obtain reliable calorimetric data.

3. The ice is penetrating the specimen as an ice front when ice formation is activated on one side only.

4. The influence of freezing/thawing rate on the phase transition is small.

5. At freezing of water impregnated specimens (no vacuum), two main phase transitions of pore water can be distinguished. The first, the most important, is found near 0°C representing large amount of freezable water in coarser capillary pores. Ionic solutions probably present in the pores showed no freezing point depression effect. A second phase transition is found at about -40°C and can be attributed to homogeneous ice formation as it does not appear on thawing. Only continuous phase transition, without further peaks, is found in the intermediate temperature regions (-5°C to -25°C).

6. No significant difference for the amount of freezable water between never dried specimen (virgin) and resaturated specimen is found.

7. Only small hysteresis between freezing and thawing of pore water is found.

8. The total amount of freezable water depends strongly of the degree of saturation of the specimen. Freezing/thawing of only partial saturated specimen starts at lower temperature. The amount of freezable water at lower temperatures remains almost unchanged. Somewhat increased freezing at -40°C for medium storage conditions can be attributed to increased probability of supercooling owing to interruption of the connectivity of the water filled pores.

The amount of freezable water is in the order of the degree of saturation of the capillary pores. Gel water hardly freezes at temperatures below -50°C.

9. Resaturation with salt solutions shows partly removal of prestorage moisture by the penetrating salt solution so that a pure water and a salt phase transition can be distinguished. The effect is more important at higher prestorage humidities.

10. Resaturation with salt solutions of higher concentrations (5-10 mass-%) show partial eutectic (30 mass-%) freezing and thawing.
11. Phase transition in hardened cement paste is as in concrete. The amount of freezable water of hardened cement paste is comparable with the amount of freezable water in the cement matrix of concrete.

12. Pore size distribution is calculated from calorimetric data (thawing curve) assuming spherical liquid-ice interface. Continuous pore size distribution with a maximum at a pore radius of about 30 nm is found in concrete specimens.
CHAPTER 12 ULTRASOUND METHODS

Non-destructive ultrasonic method is used in two different ways to study the freezing mechanisms in concrete.

On the one hand, the signal attenuation or a loss of ultrasound velocity due to the inner frost damage (crack formation) can be measured (Setzer [119], Kalinski [120], Erhard [121]). On the other hand, the significant increase of the ultrasound velocity of water when ice is formed allows a direct detection of ice formation (Pimenov [122], Belanger [123]).

12.1 Characterization of the inner frost damage

Some experiments to study the influence of subsequent frost cycles have been performed on mortar specimens (max. grain size: 4 mm). The attenuation of ultrasonic longitudinal waves (p-waves) was studied by means of Spühler's three-coefficient ultrasound spectroscopy (Spühler [124]). The method is based on the following description of wave attenuation:

\[ A_1 = A_0 G_t \exp \left( Q_r + Q_s f + Q_d f^d \right) d \]

where:
- \( A_0 \): amplitude position 0
- \( A_1 \): amplitude position 1
- \( G_t \): geometrical factor
- \( Q_r \): coefficient of reflection
- \( Q_a \): coefficient of absorption
- \( Q_s \): coefficient of scattering
- \( f \): frequency [MHz]
- \( d \): distance of transmission

The equation considers the three main processes of ultrasonic wave attenuation in a material: Reflection of confining surfaces, absorption and scattering due to different impedance (\( Z = \text{density} \times \text{velocity} \)). The material constants \( Q_r, Q_a, Q_s \) are determined by analysis of the received signal of broadband p-waves. Additionally, p-wave velocity was measured as the velocity of ultrasound is influenced significantly by inner damage, which enlarges the shortest path for an ultrasonic pulse. Transducer and receiver were arranged in a transmission line (fig 115).

![Fig. 115 Arrangement of transducer and receiver](image)

The mortars of different w/c-values (0.25/0.5/0.75) were studied before and after 9 and 34 frost cycles. The mortars with the w/c-ratio 0.75 showed already after 9 cycles significant decrease of the pulse velocity and the coefficients. But the reduction was only in some regions. Depending of the positioning of the transducer and the receiver, larger reduction or even no change of the values was observed. This effect was larger with increased number of frost cycles and was then also observed on mortars with w/c-ratio of 0.5.
It therefore was not possible to determine quantitative values for the coefficients and the pulse velocity. The damage is assumed to be very irregular and possibly oriented (see chapter 9).

12.2 Study of ice formation by ultrasonic pulse transit time

12.2.1 Method and apparatus

In the scope of this work an ultrasonic method was mainly used to study the ice formation. The ultrasonic method has the advantage of direct non-destructive determination of ice formation in large specimen and on-site.

In order to determine the velocity of an ultrasonic pulse passing a material, the transit time of a longitudinal pulse between two measurement positions was detected. The ultrasonic pulses were generated by an electro-acoustical transducer that was fixed to the concrete surface with acrylic glue (HBM X-60, thickness<0.1mm), that permitted very good contact.

The pulses were received and converted into electrical signal by a second transducer (receiver). For the experiments a PUNDIT of CNS-Electronics was used. Transducer and receiver consist both of a piezoelectric Pb-Zr-Ti ceramic that is placed in a protective steel cover and works at a frequency of 50 kHz. The wave length was about 10 cm which is much more than the size of the biggest aggregates (3cm) so that scattering effects mostly can be neglected.

The input signal to the transducer is shown in fig 116.

![Graph](image)

**Fig 116** Input signal (negative rectangular pulse, beginning at t=0) to the transducer

The output signal produced by the receiver in the case of a dry concrete specimen at 20°C is plotted in fig 117a). The measured pulse transit time as given by the PUNDIT was 14.5 µs. The input signal was triggered at a level indicated by the arrows. About 15 µs after the activation of the trigger a negative impulse was produced by the receiver.
The output signal in the case of a wet specimen at -20°C (frozen) is given in fig 117b). The measured pulse transit time as given by the PUNDIT was 12.5 µs. The output signal in the case of a frozen specimen looks, apart from some smaller intensity quite similar as the one obtained with a dry specimen at 20°C. The first pulse arrives about 3 µs earlier than in the case of a dry specimen at 20°C than in the case of a frozen specimen. This corresponds well to the difference in the measured transit time as given by the PUNDIT.

Fig 117  Output signal produced by the receiver  
\[\text{a) dry at 20°C  \quad \text{b) wet at } -20^\circ\text{C}\]

The velocity \( v \) of ultrasonic pulses traveling in a solid material depends on the density and the elastic properties of that material. It can be shown that in the isotropic case the longitudinal pulse velocity \( v \) is:

\[
(51) \quad v = \sqrt{\frac{E(1-v)}{\rho(1+v)(1-2v)}}
\]

where:
- \( E \) : dynamic modulus of elasticity
- \( \rho \) : density
- \( v \) : Poisson ratio
Therefore it is possible to derive the dynamic modulus of elasticity from pulse transit time measurement. The value for the dynamic modulus is somewhat higher than for the static modulus of elasticity.

The pulse velocity of a porous specimen is significantly increased when its pore water freezes. This is due to the very different longitudinal wave velocities of 1485 m/s in water (20°C/1 atm) and of 3828 m/s in ice Ih (0°C/1 atm) and conforms to Hill's modification theorem (Hill [125], Huet [126]). Hence, when a water filled pore freezes, the transit time to pass this pore decreases drastically. This fact can be made use of to determine the moment of phase transition of water held in the pores. Further, it allows the calculation of the freezable water content. Assuming that the mean total transit time of a pulse to pass through a porous material is the sum of the transit times to pass through each of its phases (cement matrix, water, ice) (Pimenov [122]), the difference of the pulse transit time before and after phase transition can be calculated to be:

\[
(52) \quad t_u - t_f = V_i \left(\frac{1}{c_W} - \frac{1}{c_i}\right) 
\]

where:
- \(t_u/f\) : unfrozen/frozen transit time
- \(c_W\) : sound velocity in water
- \(c_i\) : sound velocity in ice
- \(V_i\) : amount of frozen pore water

The above assumption does not take scattering and refraction processes into account, which may depend on pore size and ultrasound frequency. Nevertheless the given equation allows a rough estimation of freezable water content in function of temperature and, using pore size freezing point relation, of pore size distribution.

12.2.2 Results with thick plates (50mm)

Principal behavior of pulse velocity in concrete at low temperatures and the influence of water content was studied on concrete of mix 2 (w/c = 0.63). Transducer and receiver were arranged here in a transmission line (fig 115). This arrangement was chosen to measure a bigger concrete volume. The freezing and the thawing rate for the air temperature in the climatic chamber was set to 10°C/h in all pulse transit time experiments.

The result for three specimens of concrete stored at a) 70% RH b) 90% RH c) under water (resaturated from 70%RH, without frost medium) is given in fig 118. The temperature was measured at the center of the 200x200x50 mm² plate.

The moisture content has big influence on the pulse velocity below 0°C. A phase transition near the freezing point of water is observed. Further lowering of the temperature increases the pulse velocity. Smooth phase transition similar to the one observed with the calorimetric method is found.

In the three cases the freezing and the thawing curve are quite similar without important hysteresis effects.

This can be explained as follows. The change of the pulse velocity is the result of the sum of all phase transitions in the whole volume between the transducer and the receiver. The measurement of the temperature was fixed to one point at the center of the specimen. The temperature gradient in the specimen \((T_{\text{center}} - T_{\text{surface}} \approx 1 - 2 \, \degree C)\) therefore may shift the velocity curve in the freezing range towards higher temperatures and on melting towards lower temperatures which may make small hysteresis effects disappear. Additionally, the hysteresis of freezing and melting of water held in bigger pores, which are supposed to have more important influence on the ultrasound velocity, is thought to be small.

Similar results (freezing) were found in dynamic modulus of elasticity measurements by Sellevold [127].
The freezable water content was calculated from specimen c) (mix 2, w/c=0.63) and is compared in table 7 with the result from calorimetric data. It has to be mentioned that the minimal temperature in the ultrasound experiment was only -28°C whereas it was -45°C in calorimetric test. The phase transition at -40°C may not be included in the thawing data of the pulse transit time test. The results for the freezable water content are quite similar (table 7).

Table 7  
Comparison of freezable water content [$10^{-3}$g/g dry] calculated from calorimetry and ultrasonic pulse transit time (mix 2, w/c = 0.63)

Owing to a lack of exact theoretical description of ultrasonic pulse velocity in multiphase systems like concrete and the resulting difficulty in calculation of freezable water content, no further calculations was performed.
Ultrasonic pulse transit time experiments were performed to observe the moment of ice formation in the outermost concrete layer (1 to 10mm). Many different arrangements of the receiver and the transducer are possible (Kaufmann [116]). To study the phase transition in frost-deicing salt resistance test an arrangement as given in fig 119 was chosen.

![Test arrangement](image)

Fig. 119  Test arrangement

Receiver and transducer were fixed (with acrylic glue) at an edge of a concrete plate (150x150x10mm³). The plates were covered by an insulation on their bottom side. An aluminum tape on their side allowed the application of a frost medium on the top of the specimen. To prevent frost medium loss by evaporation a thin polyethylene foil covered the whole apparatus. The pulse transit time was continuously registered by means of a datalogger.

These experiments were performed on thin plates (150x150x10mm³). The observed volume therefore was much smaller. The temperature measurement was improved, as the temperature distribution in the specimen was more uniform. In order to determine the influence of the upper frost medium layer, a test with a dry (70% RH) concrete plate, insulated by an impermeable aluminum tape against humidity uptake was performed. It showed that the change in the pulse velocity due to the phase transition of the frost medium layer was only 0.7 m/s/K. This owes to the velocity in the frozen frost medium layer being at most 3828 m/s, which is much slower than in concrete. As only the fastest pulse is measured the contribution of the ice layer is negligible.

The temperature was measured on the surface of the concrete within the frost medium \( (T_{\text{top}}) \). Temperature profile tests showed that this temperature agreed very well with the temperature in the outermost concrete layer (Studer [128], fig 120).

The pulse velocity was calculated from the transit time assuming the pulse to pass from the center of the transducer to one edge of the receiver which gives results of pulse velocity nearest to the ones obtained with the direct transmission method. The diameter of the transducer and the receiver heads was 50 mm. Their distance (edge to center) was 90 mm. The experiments were performed on thin concrete plates (150x150x10 mm³). To avoid perturbation from crack formation, the frost resistant concrete with a higher air void content was studied (mix 3, w/c=0.45) first. The differences in the pulse velocities at positive temperatures must be attributed to material scattering, as the considered volume was very small.

The ice formation was studied on specimens with various impregnation (prestorage) and frost media.
12.2.3.2 Pure water as impregnation and as frost medium

In fig 121 the result with frost medium water (prestorage: water 7d) is given in terms of time. The pulse velocity increases slowly and continuously when the water starts freezing. In the outermost concrete layer some ice is already formed before all the upper water is frozen. When phase transition in the water layer is completed and the temperature falls again, the ultrasound velocity begins to increase rapidly while a more significant amount of ice is being formed. The relative change in ultrasound velocity is around 8%.

The situation is quite different in the case of strong supercooling (-4°C) shown in fig 122, with sudden phase transition in the frost medium layer. Supercooling is obtained by a thinner frost medium layer, which yields a smaller probability for the activation of freezing germs. The same concrete specimen as without supercooling was used.

In terms of time, the ultrasonic pulse velocity in the outermost concrete layer changes quickly when freezing is initiated. A large amount of ice is formed within the concrete at this moment. The pulse velocity then remains almost unchanged until the temperature falls again, indicating that further ice is formed in smaller pores at lower temperatures.

On the subsequent frost cycle some additional water was added and no supercooling occurred. The pulse velocity increases gradually as in fig 121 again.

The thawing details are similar for both situations (fig 123a,b). The pulse velocity decreases continuously with increasing temperature.
Fig. 121  Pulse velocity and surface temperature of a plate 150x150x10 mm³ (mix 3, w/c=0.45, prestorage water) with frost medium water (1ˢᵗ cycle) detail at freezing

Fig. 122  Pulse velocity and surface temperature of a plate 150x150x10 mm³ (mix 3, w/c=0.45, prestorage water) with frost medium water (2ⁿᵈ cycle) detail at freezing with strong supercooling
Fig. 123a)b) Pulse velocity and surface temperature of a plate 150x150x10 mm$^3$ (mix 3, w/c=0.45, prestorage water) with frost medium water (2$^{nd}$ cycle), thawing after a) no supercooling
b) supercooling
Plotting the measured pulse velocity against the plate (top) temperature (fig 124) give similar results as with thick plates studied in section 12.2.2 (fig 118). Only a small hysteresis between freezing and thawing is observed, mainly between -5°C and -15°C. At lower temperatures the pulse velocity increases linearly with only 2.5 m/s°K.

12.2.3.3 Pure water as impregnation and salt (NaCl) solution as frost medium

On another specimen (mix 3, prestored under pure water for 7d) a 3 mass-% NaCl solution was applied as frost medium layer (fig 125). A first big increase of the pulse velocity is observed when the salt solution starts freezing. The situation looks similar as in the case with a supercooling of the frost medium. This suggests that a large amount of ice is formed suddenly in the outermost concrete layer. The initiation peak might be even steeper but the pulse transit time is measured in a bigger concrete thickness. The slowness of penetration of the ice front therefore may have softened the velocity increase in the pulse transit time experiment.

Again, when the temperature falls further, additional ice formation occurs.

At thawing (fig 126) a more continuous phase transition is observed. Freezing and thawing with a salt solution as frost medium layer (impregnation with pure water) show some hysteresis. The differences between freezing and thawing can be explained with local supercooling of the pore water at freezing. The pore water is supposed not to freeze before enough freezing germs from the freezing frost medium layer are provided.
With a higher concentration of salt in the frost medium (impregnation with pure water) the pulse velocity increases drastically when freezing is initiated (fig 127). Like in the other cases
the pulse velocity then increases gradually to reach a maximum at about \(-15^\circ C\). At lower frost medium temperatures it remains constant.

The small initial temperature peak observed when freezing is initiated (figs 125/127) might be a consequence of the rapid freezing of locally supercooled water, also.

![Diagram](image)

**Fig. 127** Pulse velocity and surface temperature of a plate 150x150x10 mm\(^3\) (mix 3, w/c=0.45, prestorage water) with frost medium 10% NaCl solution (1st cycle) detail at freezing

**12.2.3.4 Salt solution as impregnation and as frost medium**

When the frost medium and the storage liquid both consist of a 3\% NaCl solution (fig 128) the initial sharp increase of the pulse velocity does not disappear but is much less pronounced.

The rapid initial freezing, probably at the outermost surface layer \((< 1\, \text{mm})\) in contact with the frost medium, can be explained by ion segregation effects. When the salt solution freezes, salt ions are not incorporated into the ice lattice in a first step. Freezing experiments with salt solutions showed very low salt concentration in the first ice layers which were formed when freezing started (Tilby [56]). The salt ions segregate and the pore solution therefore freezes as it would be supercooled pure water. The pore solution freezes at higher temperatures (near 0\(^\circ\)C) than its freezing point according to pore size freezing point relation for a salt solution would be.

Similar initiation peaks, sometimes more pronounced, also were found for other concrete specimens with a 3\% NaCl solution as impregnation and as frost medium layer.

In non-frost resistant specimens these peaks partly disappeared with increasing number of the frost cycle. As the transit time of the shortest path was measured, this may be due to crack formation in the outermost surface layer, which would lower the pulse velocity in the surface region. Therefore the fastest pulse would search its way in a somewhat deeper concrete level, where the segregation effects are no longer important.
Fig. 128 Pulse velocity and surface temperature of a plate 150x150x10 mm³ (mix 3, w/c=0.45, prestorage 3% NaCl solution) with frost medium 3% NaCl solution (1st cycle) detail at freezing

12.3 **Conclusions from ultrasonic methods**

1. The inner frost damage was studied by means of Spühler's three-coefficient ultrasound spectroscopy. With increasing number of frost cycles the wave attenuation increased. The change of the amplitude was strongly dependent on the measurement position. Additionally a reduction of ultrasonic pulse velocity with increasing number of frost cycles was observed. The reduction was only in some regions. This leads to the conclusion that the inner frost damage is irregular and possibly oriented.

2. Ice formation in the outermost concrete layer was studied by means of pulse transit time measurement. The application to thin plates (10mm thickness) and a simultaneous application of a frost medium layer allowed a direct qualitative analysis of temperature dependent rate of ice formation.

3. Ice formation in concrete starts when freezing in the frost medium layer is initiated. In the case of water without supercooling this is at 0°C. The increase of the ultrasound velocity can be either very fast or slow, depending on supercooling, impregnation liquid and frost medium.

<table>
<thead>
<tr>
<th>Impregnation (prestorage)</th>
<th>frost medium</th>
<th>ultrasound velocity (at freezing initiation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>water without supercooling</td>
<td>smooth increase</td>
</tr>
<tr>
<td></td>
<td>water with supercooling</td>
<td>very steep increase</td>
</tr>
<tr>
<td>water</td>
<td>3% salt</td>
<td>steep increase</td>
</tr>
<tr>
<td></td>
<td>10% salt</td>
<td>steep increase</td>
</tr>
<tr>
<td></td>
<td>3% salt</td>
<td>steep but small increase</td>
</tr>
</tbody>
</table>
With supercooling of the frost medium layer, high initial ice formation rate in the concrete occurs. The application of a salt solution as frost medium layer leads also to fast initial ice formation. This may be due to salt ion segregation. In each case progressive ice formation with decreasing temperature follows, reaching a maximum at about -15°C.

4. The freezable water content is calculated from ultrasonic pulse velocity. Similar values as from calorimetric data are obtained.

5. Only minor hysteresis between freezing and thawing of pore water is found.
CHAPTER 13  ACOUSTIC EMISSION

13.1 Method

In order to characterize the deterioration of concrete in freeze thaw cycles, the acoustic emission technique (AE) was used. Damage events cause acoustic emission which is detected by AE-sensors (Don Jeong [130]).

The sensors (2 or 4) were place below thin (10 mm thickness) concrete plates. The sensors were piezoelectrics (5 mm crystal, 10mm casting; Dunegan Engineering model SE 150-M) with 150 kHz nominal resonance frequency. The crystals are in a commercial casing with a ceramic wear plate adhered to the crystal. A vacuum grease served as couplant between the wear and the concrete. The force delivered by a rubber band attaches the sensors. External excitation was used to affirm good coupling (Nordstrom [131]).

The threshold was set to 40 dB.

A frost medium layer (≈ 3 mm) could be applied on the top surface of the specimens (fig 129). The specimen was then placed in a climatic chamber (air driven) in a way that the sensors were hold by the rubber band only. The freezing and the thawing rate in the surrounding air was kept constant at 10°C/h. The temperature of the air and on the top concrete surface (in the frost medium) was continuously registered by means of a data logger.

![Test arrangement in acoustic emission measurement](image)

**Fig. 129**  Test arrangement in acoustic emission measurement

13.2 Results

13.2.1 General remarks

Acoustic emission generally is supposed to have its origin in damage or failure of a material part. In our experiment, some additional acoustic emission could either be generated by the freezing of the frost medium, the pore solution, the cement matrix or the aggregate stones. Additional sources can be the freezing of condensed water in or around the sensor, the vibrations of the specimen or the sensor and thermal contraction of the sensor. Thus it is very difficult to assign an AE event to a specific source in freezing and thawing experiments.

Special attention was taken on the acoustic emission from the frost medium layer. In an additional test, AE of pure water that was held in a plastic canister was studied (fig 131). Significant AE from pure water (56x56x10 mm$^3$ and 56x56x20 mm$^3$) during phase transition was reported by Shimada and Sakai [132]. They found AE to increase with freezing rate...
(>6°C/h) and amount of water for melting AE, whereas the influence upon freezing AE was not clear. These researchers did not study the influence of supercooling.

In our experiments with pure water the number of acoustic emission during thawing was important, with high amplitude (fig 131a). The AE was uniformly distributed in time with a sharp initiation. Similar result was found for frost resistant concrete and cement paste specimen (w/c < 0.26) with water as frost medium layer.

During freezing, the AE amplitudes were smaller than 60 dB (fig 131b). Even significant supercooling of the frost medium (5°C) did not result in higher amplitudes or intensity at freezing. Almost no AE was found at freezing initiation and only few AE just after the temperature freezing plateau.

Both experiments on the frost medium canister lead to the conclusion that the acoustic emission technique can be applied to concrete specimens only during the freezing phase. During the thawing phase the noise from the frost medium layer would hide the signals coming from the specimen.

Regardless of above remarks, acoustic emission measurement proved to be a useful tool to study crack formation in concrete due to frost and frost deicing salt solicitation.

Different damage in the concrete specimen results in different acoustic emission signal. Microcracks, macro cracks, rupture events and point defects are possible (table 8). Microscopical damage may not be found in AE measurement as easy as big macroscopical damage. Especially freezing of pore water at low temperatures and thawing of pore water might preferably cause microstructural defects that may not be detected in AE experiment.

<table>
<thead>
<tr>
<th>In frost test</th>
<th>Point defect</th>
<th>microcrack</th>
<th>macrocrack or boundary crack</th>
<th>rupture event</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE signal</td>
<td>Pore</td>
<td>fracture process zone</td>
<td>interface larger cracks</td>
<td>stone ejection</td>
</tr>
<tr>
<td>Amplitude</td>
<td>Diffuse</td>
<td>diffuse</td>
<td>local (clustered)</td>
<td>local (clustered)</td>
</tr>
<tr>
<td>Orientation</td>
<td>None</td>
<td>small</td>
<td>significant</td>
<td>failure path</td>
</tr>
</tbody>
</table>

Table 8 Damage and emission events

![Different types of AE signal (schematic)](image-url)

Fig. 130 Different types of AE signal (schematic)
AE of a water container and air temperature versus time
a) freezing, b) thawing.
The abcissa of the arrow shows the time at which the phase change begins as detected by the temperature plateau.
13.2.2 Results

The effect of supercooling was studied on a concrete specimen of mix 2 (w/c = 0.63) with pure water as impregnation (1 week under water) and as frost medium.

In the first frost cycle no supercooling takes place and no acoustic emission is found when the freezing of the frost medium layer begins (point A, fig 132). With further freezing of the frost medium layer more AE events with higher amplitude are observed (B-C). When the frost medium is completely frozen and the temperature falls again (C-D) more AE with high amplitudes is found. The amplitudes reach 100dB which is much higher than the 75dB observed during the melting of a water filled container. It was observed that the temperature at the edges of the specimens lowered earlier than at the center because of only thin insulation. This may explain the somewhat earlier AE (around C) than might be expected.

AE diminishes when a temperature of about -6°C in the frost medium is reached. This agrees well with the expansion measurement.

The situation is different when the frost medium is allowed to supercool some degrees which is the case in the second frost cycle (fig 133) with the same specimen (3°C supercooling). Important AE signal is detected at about freezing initiation, some AE exactly at this point (A') and more AE somewhat later (A'-B') with higher amplitude and intensity. AE signal from frost medium mostly can be excluded as shown above. Rapid ice formation hence leads to significant damage in the concrete specimen at freezing initiation and somewhat later, perhaps due to relaxation of cement matrix or increased load by further freezing of pore water and crack opening.

In AE experiments with smaller supercooling (<1°C) much lower amplitude at freezing initiation (< 52 dB) was found.

Further AE is found with further freezing when the temperature falls again (C'-D'). As in the case without supercooling, AE stops below -6°C.

At thawing (fig 134) a lot of AE with high amplitude is found, mostly due to melting of the frost medium. Acoustic emission starts at temperatures (-5°C) below melting point. First low amplitudes were detected. In tests with other, frost resistant specimens, where the maximal temperature was chosen so that the frost medium layer did not melt, no AE was found at thawing. Therefore some of the signal below melting point may be attributed to concrete damage at thawing although it is very difficult to distinguish between frost medium melting effects and acoustic emission owing to concrete damage formation.

The AE signal in the case of a salt solution (5 mass-% NaCl) as frost medium is shown in (fig 135).

While during the first frost cycle few AE signal was detected only, a lot of AE with higher amplitude is found during the fifth frost cycle. Most of the AE is found at freezing initiation (point A). Further AE is found when temperature continuous falling.

The observed AE is similar to the one that was found in the case of supercooling. Some supercooling, which was difficult to prevent, certainly give some contribution but most of the AE signal is due to the fast initial freezing of the salt solution.

This confirms the results of the expansion experiments, where in the case of a salt solution as frost medium a strong instantaneous expansion was found. This expansion increased with increasing number of the frost cycle. The AE signal also increases significantly with increasing number of the frost cycle. We can conclude that strong expansion causes damage and hence results in the emission of AE signals.
Fig. 132 AE emission and frost medium temperature versus time
mix 2 (w/c=0.63, frost medium water)
1\textsuperscript{st} frost cycle, freezing without supercooling

Fig. 133 AE emission and frost medium temperature versus time
mix 2 (w/c=0.63, frost medium water)
2\textsuperscript{nd} frost cycle, freezing with supercooling
13.3 Conclusions from acoustic emission

1. Acoustic emission measurement during the freezing period, with simultaneous application of a frost medium layer, revealed that the observed expansions cause measurable damage in concrete and cement paste.

2. With supercooling of the frost medium layer important AE is measured at the freezing initiation. Without supercooling this is not found.

3. With a salt solution as frost medium layer, the AE at freezing initiation increases and gets important with increasing number of the frost cycle.

4. For freezing it is possible to attribute emission signal to damage events only. For melting, the noise produced by the melting of ice of the frost medium layer does not permit to study the damage formation.

Fig. 134 AE emission and frost medium temperature versus time
mix 2 (w/c=0.63, frost medium water)
1st frost cycle, thawing
Fig. 135  AE emission and frost medium temperature versus time
mix 1 (w/c=0.5, frost medium 5% NaCl solution)
a) 1\textsuperscript{st} frost cycle b) 5\textsuperscript{th} frost cycle
Part IV

MODELLING AND GENERAL CONCLUSIONS
CHAPTER 14  QUALITATIVE MODEL FOR FROST DAMAGE

14.1  Scope

The results from the analytical experiments allow the development of a qualitative damage model. As experimentally no principal differences between laboratory (fast weathering tests) and on-site behavior was found, this model is formulated in general form. Some parameters such as freezing rate or saturation condition influences the frost resistance, but not the fundamental processes that lead to the damage.

The different damage mechanisms that can lead to a frost damage are already known and most of them were described in chapter 4. The experiments performed in this work demonstrate that not a single damage mechanism is responsible for the observed deterioration of concrete under frost deicing salt attack. A combination of different main mechanisms is most probable.

The proposed model concentrates on the case of a homogeneously saturated porous material (with an isotropic salt distribution) that is subjected to freeze/thaw cycles.

14.2  Freezing and thawing of pore solution

The model is based on the idea of a penetrating ice front (see section 11.10 fig 114).

The damage formation due to the phase transition can be separated into five main phases: freezing initiation, ice front penetration, liquid redistribution phase, thawing phase and refilling phase.

14.2.1  Freezing initiation

Freezing of water is initiated through freezing germs like ice, snow or ice nuclei.

Without sufficient freezing germs, supercooling can occur. Two main cases are possible:

1. supercooling in a liquid covering the porous material
2. supercooling of the pore solution

The first case is important in standard frost deicing salt resistance test with the application of a frost medium layer.

The second case is possible in non-connected pore space, owing to small neck entrances. It is also possible when the porous material is covered by an outer salt solution. If the freezing point of the outer salt solution is lower than the freezing point of the pore solution (= 0°C) and the ice formation within the porous material is not initiated until it is initiated in the covering salt solution, the pore solution gets supercooled.

Another effect similar to supercooling is important in the presence of deicing salts: ion segregation by freezing. When the porous material is saturated with a salt solution, freezing is not initiated until the freezing point of the salt solution is reached. At freezing, ion segregation in an outermost layer occurs, so that the liquid that freezes actually has a lower salt concentration with a higher freezing/melting point. Hence the liquid in the outermost concrete layer freezes like if it would be supercooled compared to the surrounding salt solution.

Supercooling or ion segregation lead to high ice formation rates. This is because of a large amount of pore solution that freezes at the same time, owing to pore size distribution and pore size freezing point relation. Additionally, growth velocities of ice crystals are increased (Pruppacher [59]).

High hydraulic pressures in the pore results.
Supercooling due to ice nucleation and ion segregation is mainly a concrete surface effect and hence is most important in the case of surface scaling. It may also be important for the inner concrete when big zones of non-connected pore space exist. This is the case for high performance concrete for example.

While supercooling on-site is not very probable (chap. 2.2), salt segregation by freezing is possible.

14.2.2 Ice front penetration

Once ice formation is initiated and the temperature keeps falling, the pore solution continues freezing according to pore size freezing point relation. In the presence of deicing salts, the salt concentration in the pores also influences the freezing points (Raoult's law).

As an ice front penetrates the material (fig 114) pressure rises in the unfrozen water, owing to the 9% volume increase of the water upon phase transition.

Hydrostatic pressure is produced when the ice front penetrates a closed pore space without exits, or with low permeability exits. Examples are water filled cracks and porous aggregates. A closed container model is applicable in these cases (Fagerlund [62]).

Hydraulic pressure is built up, when the velocity of the penetrating ice front and the degree of saturation is big enough relatively to the remaining permeability of the porous medium (Powers [4][66]). The water permeability of a partly frozen specimen is much lower than in the thawed state.

From the experiments in chapter 6 it seems that, without supercooling, hydraulic pressure is not important in the case of concrete. It may be important when the actual degree of saturation is much above the critical degree of saturation. This is for example the case in hardened cement pastes stored under water.

The existence of a progressive expansion in the second freezing phase (part II) supports a model where the permeability is big enough to allow a first sufficient transport of the excess water preventing considerable concrete expansions. Permeability decreases rapidly when the water in the bigger pores freezes. The amount of freezable water then may be big enough to produce hydraulic pressure. Nevertheless, owing to the very low permeability, a closed container model may be sufficient to describe the situation.

14.2.3 Liquid redistribution

When ice is formed the equilibrium of the pore solution is disturbed. Owing to the lower chemical potential of the frozen pore solution, unfrozen pore solution (in finer pores or supercooled due to insufficient connectivity) is redistributed. The pore solution migrates to the ice in the bigger pores, in microcracks or even at the entrances of the air inclusions. This may lead to shrinkage of the cement matrix (Setzer [140]).

As the ice contracts thermally when the temperature falls further, empty pore space is formed which can be refilled by migrating water. The migrated pore water then freezes.

Would this process go on, ice lenses would grow continuously (Lindmark [133]), but the experiments presented in section 7.4 do not support this mechanism.

In the presence of salt solutions, osmosis may also contribute to redistribution. Due to ion segregation, the borders of bigger pores where the main part of the pore water is already frozen, may contain higher concentrated salt solutions which attracts unfrozen pore water.
14.2.4 Thawing

When the temperature rises again, pore solution starts melting. Melting first begins in the finer pores, according to pore size melting point relation. Further redistribution of pore liquid is possible. At the same time, the pore ice expands thermally. This expansion is larger than the one of the cement paste, owing to the larger thermal expansion coefficient of ice and as a consequence of the redistribution of pore solution. Tensile stresses result, which depend on the difference between freezing/melting temperature and minimum temperature of the frost cycle (Grübl [79]).

14.2.5 Resaturation

The development of tensile stresses may result in additional microcrack formation, opening and growth, which opens new empty pore space. When the pore solution is completely thawed, additional liquid water from the outside may penetrate into the concrete. The microcracks that have opened are resaturated. Also pore water, that moved to air pores during the redistribution phase and now partly fills them, is replaced. Therefore the water content in the material increases. Hence, resaturation is very important for progressive material deterioration.

14.3 Effect of cycle repetition

During the first frost cycles, initial microcracks are formed by the mechanism described above. When the cycles are repeated, the initial cracks that once are formed are refilled with liquid, which increases the local degree of saturation. Initial cracks grow in further frost cycles by the same mechanisms that lead to the initial crack formation as well as by the locally increased expansion owing to the higher degree of saturation.

The crack can be treated like a big water filled pore, which behaves at freezing like a closed container. The thermal contraction of ice, together with the liquid redistribution from smaller pores, cause further crack propagation at temperature reincrease. Scaling and inner crack formation are the consequence of the same mechanisms. Nevertheless big differences between the amount of removed material at the surface (scaling) and the degree of inner crack formation can be observed in frost deicing salt resistance tests. As supercooling and ion segregation are mostly related to the surface, small variations in the process of freezing initiation may cause big differences in the results.

14.4 Influence of aggregate stones

The presence of aggregate stones may influence the frost resistance in two different ways:

i) increased porosity and coarser pores of the cement–aggregate interface
ii) porous aggregate

When the ice penetration front reaches the porous cement – aggregate interface or a porous aggregate, the ice formation of water held in these pores is initiated immediately, owing to the larger pore diameter and hence the higher freezing point of water held in these pores. This pore water freezes like water held in a closed container. The resulting compression stress can cause crack formation (see fig 136). The volumetric dilatation of the cement paste matrix (freezing and thawing) and the withstanding aggregates support this process. The appearance of scaling would be more probable the higher the content of porous aggregates and larger the expansion of the cement paste are.
The effect of the cycle repetition is described above.

![Diagram](image-url)

**Volumetric dilatation of cement matrix**

**Ice penetration front**

**Crack growth**

**Volumetric dilatation of water**

freezing in coarser pores at the aggregate-cement matrix interface and within porous aggregates

**Fig. 136** Schematic crack growth mechanism at the cement – aggregate interface

### 14.5 Influence of salt concentration

The concentration of the deicing salt can have positive and negative consequences for frost deterioration in this model.

For freezing initiation (phase 1), low salt concentrations lower the effect of salt segregation as the virtual degree of supercooling (difference between freezing point of salt solution and the freezing point of pure water) is small. High salt concentration increase this difference, but the freezing process may be more continuous.

The probability for supercooling may be diminished by a high ion content. If only the surface water is highly concentrated and the pore solution is at low salt concentration (for example on-site after intense rainfall and the following application of deicers when the temperature falls) a big supercooling of the pore water may result.

For the ice front penetration (phase 2), a lower salt content means lower degree of saturation. The freezing initiation phase and the ice front penetration phase are well separated in time (see instantaneous and progressive expansion chap. 6.4). The ice front additionally may penetrate slower as only a few pores, the biggest ones, may freeze at the same time. The maximum of pore size distribution is at about 30-50 nm which corresponds to a freezing point of -1 to -2 °C. For higher salt concentration the freezing initiation phase and the ice front penetration phase are superimposed.

A consequence of ion segregation is that a eutectic salt concentration may be reached. A eutectic NaCl solution does not freeze above -20°C, so that the freezable water content is lowered. Replacing the deicing solution during the thawing phase by water can prevent this (Lindmark [133]). The amount of scaled material then depends only slightly of the salt concentration.
For the redistribution of pore water (phase 3), a higher salt content is favorable due to osmosis. At the same time the difference between the freezing and melting point and the minimal temperature decreases with an increasing salt content so that the effect of redistribution decreases.

The thawing phase (phase 4) also is influenced by a high salt concentration owing to the difference between minimal temperature and freezing/melting point of the salt solution. Smaller temperature differences for higher salt concentration signifies a smaller thermal expansion difference between cement matrix and pore ice and hence lower stress intensity.

In the resaturation phase a higher salt concentration is favorable to increase the degree of saturation because of osmosis and the lower vapor pressure of the salt solution.

The sum of all the mentioned effects results in a pessimum for frost resistance at a NaCl-concentration of 3-5 mass-%, as observed experimentally.

14.6 Comparison of on-site behavior and laboratory testing

As mentioned above, no principal differences between the damage mechanisms on-site and in fast accelerated weathering laboratory tests is found. Nevertheless some differences are obvious.

Supercooling on-site is not very probable, while it may be important in laboratory tests. Supercooling in laboratory may be caused by big freezing rates or well-controlled temperature cycling (only small temperature differences to set point) and by the application of frostmedia that do not contain possible ice formation germs.

The slower freezing rate on-site (-0.5°C/h) compared to the laboratory tests (-20°C/h influences the ice front penetration phase (phase 2) resulting in slower ice formation rates.

The higher minimal temperatures on-site (-5°C, for one cycle within 24h) compared to the minimal temperature in laboratory tests (-15 to -20°C) also influence the second phase, as the ice in the smaller pores does not freeze on-site. The redistribution phase and the thawing phase (phase 3 and 4) also are influenced by the smaller difference between freezing point and minimal temperature that is found on-site.
CHAPTER 15 CONCLUSIONS

15.1 General conclusions

The phase transition of pore solution of cementitious materials in an open system where the surface is exposed to water or a sodium chloride solution has been studied applying specially designed experimental methods. Many of these methods are used for the first time to the problem of frost damage and allow to study ice formation including supercooling and to a certain extent other effects like salt ion segregation.

Ice formation in the studied system can be separated into two main phases: An instantaneous nucleation part and a progressive ice penetration (percolation) part.

Further it is demonstrated that big hysteresis effects between freezing and thawing can be avoided through special ice formation germs (ice nuclei). This result obtained in calorimetric tests is also confirmed by ultrasonic pulse transit time experiments.

The consequence of ice formation, the formation and growth of damage is characterized by means of MIP (mercury intrusion) and microscopical analysis. Comparing acoustic emission with expansion results closes the link between non-thermal expansion and crack formation.

In special designed experiments no indication for a progressive growth of ice lenses is found.

On-site solicitation and damage was studied and compared to laboratory tests. No indication for a different behavior is found.

A qualitative sequential model is proposed to explain the main experimental findings. The model distinguishes between five different phases:

1. Freezing initiation
2. Ice front penetration
3. Liquid redistribution
4. Thawing
5. Resaturation

Each phase is important and contributes to the frost deicing salt deterioration. The different effects of the deicing salt are discussed. The separation into five different steps allows an improved analysis of the interaction of different isolated damage mechanisms that have been proposed earlier by other researchers.

The advantage of this sequential model is that it does not need to differentiate between on-site and laboratory damage mechanisms, although the solicitation may be somewhat different.

As the model is based on the experimental results and because one aim of this thesis was to provide the experimental basis for a numerical simulation (Thesis F.Besson), some of the most important experimental findings as given in the different chapters are recapitulated below.

15.2 Experimental Findings

1. Freezing and thawing in natural frost cycles are very slow compared to typical temperature change rates in laboratory tests. Typical values on-site for the freezing rate on the concrete surface are in the order of 0.5°C/h. The thawing rate is due to solar irradiation somewhat higher, reaching 1.5°C/h. The temperature distribution in the outer 5 cm of the concrete is very flat. The mean temperature difference between surface and at the depth of 5 cm is less than 1°C.
2. The minimum temperature for a complete frost cycle (within 24h) under natural condition is higher than -5°C.

3. The relative humidity during winter is very high, reaching almost 100% on frost days. The concrete hence is highly presaturated.

4. On-site, freezing is initiated when the temperature falls below 0°C. Sufficient ice nuclei and white frost prevent on-site from supercooling.

5. In laboratory tests, supercooling of the frost medium as well as in isolated pores can occur. Supercooling leads to high ice formation rates and permanent damage at freezing.

6. In the case of thick concrete specimens (200x200x50 mm³) significant deviations from thermal contraction behavior is only found with completely (under vacuum) saturated specimen. It is not found for specimens that are previously stored under water for one week. Important depart from normal thermal contraction behavior of not completely saturated specimen was found with a simultaneous frost medium layer application on thin specimens (150x150x10 mm³) measured parallel to the frost medium interface. It was also observed perpendicular to the frost medium interface on thicker specimens.

7. The expansion is a volume effect. Similar expansion is observed perpendicular and parallel to the frost medium interface.

8. Without supercooling, freezing of pore water starts near 0°C even in the presence of high ion content in the pore solution of normal concrete. The pore water freezes continuously according to the size of the pore in which it is held. The ice penetrates the specimen as an ice front.

9. Significant bending of thin concrete plates is observed. This is interpreted as being the result of a freezing gradient owing to the penetration of an equilibrium ice front.

10. The possibility of the simultaneous application of a frost medium layer was crucial for the study of resaturation effects. It also allowed a separation of freezing initiation and ice front penetration.

11. Concrete deterioration through frost deicing salt attack in the presence of a liquid frost medium layer is progressive. Expansion at phase transition, permanent residual expansion (damage) and ultrasonic pulse transit time increase with increasing number of the frost cycle. Temperature cycling below the freezing point of the frost medium does not cause additional damage. Water migration from unfrozen frost medium layer is necessary to cause progressive deterioration of concrete. Water uptake and increase of the degree of saturation is important.

12. The application of a salt solution as frost medium layer leads to fast initial ice formation. Segregation of salt ions is possible and leads to high ice formation rates.

13. No experimental significance for progressive ice lens growth was found. No expansion is observed when holding the specimens constant below freezing point. In the expansion experiments even some relaxation as expected for hydraulic pressure is found when interrupting the temperature cycle below 0°C.
Test arrangements where the specimen are cooled on one side and thawed on the other (with water) and constant 0°C interface within the concrete, show no significant expansion that would be typical for progressive ice lens formation.

14. Supercooling must be prevented in freezing experiments where pore size distributions or material properties like the amount of freezable water are derived, as it may lead to misinterpretation. It can be reduced by the application of ice formation germs (ice nuclei). Cholesterol prepared in a mica sandwich technique proved to be a very powerful ice nuclei with activation temperature near -0.7°C. Big supercooling also is prevented by a big volume of the frost medium layer owing to higher probability for ice nucleation.

15. The freezable water content can be calculated from calorimetric, pulse transit time and expansion data. Similar results are obtained.

16. No significant difference for the amounts of freezable water between never dried specimen (virgin) and resaturated specimen is found.

17. Freezing/melting of only partly saturated specimen starts at lower temperature. The amount of freezable water at low temperatures remains almost unchanged. The total amount of freezable water is in the order of the degree of saturation of the capillary pores. Gel water hardly freezes at temperatures below -50°C.

18. Only small hysteresis between freezing and thawing of pore water is found. Bigger hysteresis in expansion experiments can be attributed to permanent damage formation.

19. Resaturation with salt solutions shows partial replacement of the prestorage moisture through the penetrating salt solution. The effect is more important at higher prestorage humidities.

20. Resaturation with salt solutions (NaCl) of higher concentrations (5-10 mass-%) show partial eutectic (30 mass-%) freezing and melting, indicating salt ion segregation.

21. Phase transition in hardened cement paste is like in concrete. The amount of freezable water of hardened cement paste is comparable with the amount of freezable water in the cement matrix of concrete.

22. Pore size distribution can be calculated from calorimetric data. Continuous pore size distribution with a maximum at a pore radius of about 30 nm is found. The calculated results, although somewhat shifted towards finer pores, are similar as obtained by mercury intrusion porosimetry.

23. Beside the damage of concrete by scaling, inner cracks parallel to the frost medium surface are found after frost deicing salt attack. The crack path follows the interface between the cement paste and the aggregate. A depth of 8 mm is typical for concrete. The crack pattern preferably goes through the air pores or porous aggregates.

Specimens that are exposed to natural conditions on-site show similar crack pattern, already after one year of exposure.

24. For hardened cement paste, cracks parallel to surface with equal distance (1-2 mm) from each other are observed after frost deicing salt attack. Additionally, a texture similar to cement particle distribution in fresh cement paste is observed.
15.3 Need for further Research

All the above findings are strictly only valid for the cement type and concrete mixes used in this work. However the experimental methods and the qualitative model also can be applied to any other mix designs and other porous materials. Only physical aspects have been studied which seems to be reasonable for ordinary Portland cement concrete. Chemically aspects may be important for other cement types.

The experimental limitations in the expansion experiments caused by bending of the specimens should be studied in further detail. Measurement of deformation (expansion of the top and of the bottom side) could be useful to quantify volume expansion and to calculate the acting forces. Studies of the influence of freezing rate and minimal temperature in expansion experiments on thin plates would be possible and certainly very useful.

Salt segregation during phase transition in capillaries should be studied experimentally.

The connectivity of the pore space has to be characterized. Not the total amount of pores of a certain size, but their mean length and their connection to the surface and the smallest neck radius should be determined.

The influence of temperature and partly frozen pore water has to be studied. As a material property the permeability of partly frozen specimen should be derived. This would allow estimating, from amount of freezable water, the pressures that can be built up in function of time and temperature.

Owing to the complexity of the problem, a numerical simulation would be useful. Special attention should be put on crack formation and growth. First interesting results have been obtained at EPFL (Besson [134]) in connection with the present study.
References


name: Josef Peter Kaufmann-Sarmiento

date of birth: 1964-08-20

place of birth: Knutwil /LU

denomination: RC

family: married with Constanza Kaufmann-Sarmiento, 1 son (Patrick)

formation:
1971-76 primary school Knutwil /LU
1976-83 grammar school Sursee/LU
1983-89 ETH Zürich
   completion as dipl. phys. ETH (Master of Physics)
   main domains : optics and meterology
   diplom work : magneto-optics

professional activities:
1989 scientific assistant at ABB research center Dättwil
1990 south america (1year, tourist)
1991-93 scientific assistant EMPA Dübendorf section
   Concrete/Binder:
   - water transport (MRI- and X-ray tomography measurements)
   - particle size distribution (laser particle sizer)
1993 ICRC (int. committee of red cross)-delegate in Colombia
since 1994 newly at EMPA Dübendorf section Concrete/Binder
   - frost deicing salt resistance
   (common project with EPFL)

languages:
German
   good English, Spanish and French knowledge
   some Portuguese knowledge

Publications (selection)


Appendix A: Expansion
Fig. A-1 Expansion versus time of mix 1 (w/c=0.5) with frost medium water (impregnation: 1 week in pure water)

Fig. A-2 Expansion versus temperature of mix 1 (w/c=0.5) with frost medium water (impregnation: 1 week in pure water)
Fig. A-3  Expansion versus time of mix 1 (w/c=0.5) with frost medium 3% salt solution (pure water impregnation) (3rd frost cycle was not measured)

Fig. A-4  Expansion versus temperature of mix 1 (w/c=0.5) with frost medium 3% salt solution (pure water impregnation)
Appendix B: Calorimetry
Fig. B-1  Freezing curves of mix 3 (w/c=0.45) prestored at the indicated relative humidities

Fig. B-2  Thawing curves of mix 3 (w/c=0.45) prestored at the indicated relative humidities
Fig. B-3  Freezing of mix 2 (w/c=0.63) resaturated from 70% RH with NaCl solutions of indicated concentrations (mass-%)

Fig. B-4  Thawing of mix 2 (w/c=0.63) resaturated from 70% RH with NaCl solutions of indicated concentrations (mass-%)
<table>
<thead>
<tr>
<th>Listing of the official «EMPA Reports»</th>
<th>arranged according to the report numbers</th>
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<tbody>
<tr>
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<tr>
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<tr>
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<td></td>
</tr>
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</tbody>
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<tr>
<th>Page</th>
<th>Author/Title</th>
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<td>Seite</td>
<td>Autor</td>
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<td>230</td>
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<td>244</td>
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