The characterisation, improvement and modelling aspects of
Frost Salt Scaling of Cement-Based Materials
with a High Slag Content
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SUMMARY

Blast furnace slag cement concrete is used extensively in a number of countries. In comparison with OPC, it is particularly well known for its excellent performance in marine environments. One disadvantage of slag cement is its vulnerability to scaling under the combined load of freezing-thawing and de-icing salts. The current investigation was triggered by positive observations regarding certain grinding agents used in slag cement production to improve frost salt scaling resistance. The investigation was aimed at explaining the cause of this improvement, at finding alternative methods to improve scaling resistance and at developing a model that would be suitable for the simulation of frost salt scaling behaviour.

The investigation conclusions are essentially confined to high slag cement, particularly type CEM III 42,5/B which has a 67% granulated slag content. The w/c ratio of the paste, mortar and concrete specimens is generally maintained at 0,45.

Carbonation, known as the critical parameter in frost salt scaling, constituted the key area of interest. From previous investigations it is known that carbonation increases porosity and coarsens the pore system in slag cement paste while it actually does the reverse in OPC paste. In the light of literature a new hypothesis has been suggested that the transition zones, which are the weakest points in normal-performance cement-based materials, critically determine frost salt scaling resistance. These zones are even more indicative in the case of slag cement pastes because of the significant amount of transition zones that can be weakened by carbonation unlike with low-slag cement or OPC pastes.

In the present investigation it was observed that carbonation causes significant slag cement paste shrinkage. It was especially the transition zones between non-reacted slag particles and hydration products that were found to be affected. Consequently this process leads to the paste having a coarser pore structure thus making it prone to greater water uptake when compared to non-carbonated slag cement paste or OPC paste. The new hypothesis was supported by findings emerging from the ESEM study. It was observed that frost salt scaling attack generates cracks in the microstructure which adhere to slag-matrix interfacial zones. This was confirmed by nanoindentation tests which demonstrated that carbonation creates a significant number of weak zones in the slag cement paste. In the case of OPC paste the picture that emerged was quite different.

Natural air carbonation influences the mineral characteristics of cement pastes. The XRD study revealed that both slag cement paste and OPC paste possess various types of carbonate minerals, namely: calcite, aragonite and vaterite. However, accelerated carbonation creates overwhelmingly stable calcite phases in both types of cement pastes which are subsequently transformed from metastable carbonates. This observation draws attention to the role played by Ca(OH)$_2$ in the good scaling resistance of OPC or low-slag cement systems. A curing regime, especially curing in lime water, appears to be favourable for slag cement materials. However, when compared to the effect of carbonation, the influence that the curing water quality has on scaling resistance is minimal. The contribution made by prolonged water curing to scaling resistance could have been greater but, as it was, the curing periods were limited to 5 weeks in the interests of remaining realistic and practical.

The main goal of the project was to investigate the improvements in frost salt scaling resistance instigated by chemical grinding agents on the basis of the various positive results gained from the preliminary tests. The intention was to study the effects that the chemicals had on the cement paste
microstructure in order to understand frost salt scaling resistance in slag cement concrete and so as to contribute to structural improvements in that area.

A microstructural comparative study was carried out on slag cement pastes that contain alkanolamines/hydrocarboxylates (the best performing ones) and diethylene glycol–based (the worst performing example) grinding agents. The most notable difference was in the pore structure of the paste samples. Alkanolamines/hydrocarboxylates-based grinding agents were found to produce smaller pore sizes when compared to the ones containing diethylene glycol. This is consequently likely to give rise to higher carbonation resistance, lower water uptake and, eventually, to higher frost salt scaling resistance. However, the improvement achieved by alkanolamines / hydrocarboxylates is not sufficient to enhance the scaling resistance of the slag cement materials investigated in similar detail to OPC pastes.

Another technique that was investigated was sodium monofluorophosphate (Na-MFP) surface treatment. Remarkable improvements in frost salt scaling resistance were achieved by applying a 10% Na-MFP solution to the surface of the carbonated slag cement paste and concrete. The scaling resistance improved by about 95% after 7 freeze-thawing cycles. Evidence was found pertaining to the reaction between Na-MFP and metastable carbonates in the carbonated slag pastes. The application appears to significantly increase the tensile strength of the carbonated slag cement paste which is extremely favourable in terms of scaling resistance.

The study finally resulted in the development of a new integrated model. The model mainly takes into account the glue-spall theory and the hypothesis developed in this thesis and it runs on the Delft Lattice Model platform. The model successfully demonstrates the experimental observations and the crack patterns created by the scaling action.

The glue-spall theory suggests that cement-based material surface scaling derives from external ice layer cracking due to further cooling. Cooling consequently generates tensile stress due to the shrinkage of ice and causes cracking when the stress exceeds the tensile strength of the ice. This theory can explain many phenomena including the pessimum effect. On the basis of this theory, the new integrated model proved to be capable of simulating two important experimental observations. Under identical conditions the model can predict higher surface scaling at a 3% salt concentration level in relation to higher and lower values. The effect of ice layer thickness is furthermore found to be crucial with respect to frost salt scaling. Under identical material and environmental conditions the thicker external ice layer creates more damage than thinner ice layers. This observation was also successfully demonstrated with the new integrated model.

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**SAMENVATTING**

Beton gemaakt met hoogovencement wordt in een groot aantal landen op uitgebreide schaal toegepast. Met name vanwege de betere prestaties in marine milieu in vergelijking met beton met Portland cement. Een nadeel van beton met hoogovencement is echter haar kwetsbaarheid tegen vorst-dooizoutaantasting, hetgeen resulteert in een grotere oppervlakte afschilfering dan bij toepassing van Portland cement. Deze promotiestudie is geëntameerd nadat is gebleken dat verschillende maalhulpmiddelen, toegepast tijdens het malen van de grondstoffen van hoogovencement, de vorst-dooi schade van slakcementbeton positief kunnen beïnvloeden. De intentie van het onderzoek is de oorzaak van de verbetering te verklaren, na te gaan of ook bij vorst-dooizoutschade hetzelfde verschijnsel op zou kunnen treden, alternatieve oppervlaktebehandelingen te onderzoeken en nieuwe modellen over vorst-dooi(schade) te ontwikkelen.

De conclusies van het onderzoek zijn vooral beperkt tot de toepassing van hoogovenslakcement, in het bijzonder CEM III/B 42,5 met 65% gegranuleerde hoogovenslak. De watercementfactor van de onderzochte cementpasta’s, mortels en beton is in het algemeen vastgelegd op 0,45.

De carbonatatie van beton is een belangrijk fenomeen en blijkt de kritieke parameter te zijn in geval van vorst-dooi(schade). Vanuit de literatuur is bekend dat carbonatatie een toename veroorzaakt van de porositeit en een vergroting van het poriënsysteem in pasta’s met hoogovencement, terwijl dit bij Portland cement het tegenovergestelde is. Uitgaande van de literatuurgegevens is de hypothese gesteld dat het de overgangszone (interfacial transition zone (ITZ)) zijn die de zwakste schakel vormen en dat zij daarmee een kritieke wijze de vorst-dooizoutschade bepalen in beton. Bij beton met hoogovenslak zijn deze overgangszones zelfs nog meer bepalend voor het gedrag omdat er, naast de hechtingszones tussen het toeslagmateriaal en het cementsteen, een significante hoeveelheid extra ITZ bestaat vanwege de slak-cement-interactie. Deze extra “interfaces” kunnen door carbonatatie aanzienlijk verzwakken, een fenomeen dat bij Portland cement beton of bij beton met een laag slakgehalte niet dan wel minder optreedt.

In dit onderzoek is geobserveerd dat carbonatatie een belangrijke krimp van de slak-cementsteen veroorzaakt. Vooral de overgangszone tussen de niet gereageerde slakdeeltjes en de hydratatieproducten bleek te zijn beïnvloed door carbonatatie. Het resultaat van dit proces is een cementsteenstructuur met grovere poriën waardoor de cementsteen meer water kan absorberen dan bij niet gecarbonateerde cementsteen of bij cementsteen van Portland cement. De bovengenoemde hypothese wordt ondersteund door de resultaten van elektronenmicroscopisch onderzoek (ESEM-onderzoek). Er is gevonden dat door vorst-dooizoutaantasting scheuren worden gegenereerd in de microstructuur die de slak-matrix interfaces volgen. Bij nano-indentatiemetingen is geconstateerd dat carbonatatie een significante hoeveelheid zwakkere zones introduceert in slak-cementpasta’s waarbij dit bij pasta’s met Portland cement niet het geval was.

Natuurlijke niet geforceerde carbonatatie beïnvloedt de mineralogische karakteristieken van cementpasta’s. Röntgenologisch onderzoek bracht aan het licht dat zowel verharde slakcementpasta’s als Portland cementpasta’s de carbonaattypen calciet, aragoniet en vateriet bevatten. Echter, geforceerde (versnelde) carbonatatie veroorzaakt de grotendeels (hoewel niet complete) omzetting naar de zeer stabiele calcietfase uit de overige metastabiele carbonaatfases in beide cementtypen. Deze observatie geeft het belang aan van de rol van de grotere concentratie van Ca(OH)₂ in de gunstiger prestatie van Portland cement beton bij carbonatatie.
De wijze van nabehandel, in het bijzonder opslag in kalkwater, blijkt gunstig te zijn voor slakcement gebonden materialen. Echter, vergeleken met het significante effect van carbonatatie, blijkt de invloed van de samenstelling (demi-water, leidingwater, kalkwater) van het water dat gebruikt wordt voor de nabehandeling gering te zijn. Het ligt in de verwachting dat een langduriger opslag onder water een verbeterde vorst-dooizoutweerstand zal bewerkstelligen, maar de verhardingsperioden werden beperkt tot vijf weken om een meer realistisch beeld te verkrijgen.

Een van de doelstellingen van het project was om de verbetering van vorst-dooizoutbestandheid door bepaalde maalhulpmiddelen te onderzoeken in verband met positieve resultaten van voorafgaande studies. De bedoeling was om de invloed van deze chemicaliën op de microstructuur van cementpasta's te onderzoeken om meer inzicht te verwerven in -en bij te dragen aan- de structurele verbetering van de vorst-dooizoutweerstand van slak-cementbeton.

Hiertoe is een vergelijkend microstructureel onderzoek uitgevoerd op pasta's van slakcementen die gemalen waren met alkanolamines/hydroxycarboxylaten maalhulpmiddelen (de beter presterende cement) en diethyleen glycol maalhulpmiddelen (de minder goed presterende cement). Uit het onderzoek bleek dat het alkanolamine/hydroxycarboxylaat maalhulpmiddel een kleiner poriënsysteem genereert dan diethyleenglycol. Als gevolg hiervan zal cement gemalen met het alkanolamine/hydroxycarboxylaatmiddel een enigszins betere carbonatatieweerstand, lagere waterabsorptie en eventueel een betere vorstdooizoutweerstand vertonen. Bij het uitgevoerde vorstdooizoutonderzoek bleek echter dat de vorst-dooizoutweerstand van dit cement niet zodanig was dat het vergeleken kon worden met het prestatienniveau van Portland cement.

Een andere onderzochte techniek om tot verbeterde vorstdooizoutweerstand te komen is die van de oppervlaktebehandeling. In dit geval is gebruik gemaakt van natriummonofluorofosfaat. Een opmerkelijke verbetering van de vorstdooizoutweerstand werd bereikt bij de toepassing van een 10%-Na-MFP oplossing op het oppervlak van gecarbonatere cementpasta, mortel en beton. De verbetering bedroeg 95% na zeven vorst-dooicycli. Uit het onderzoek bleek dat er een reactie heeft plaats gevonden tussen Na-MFP en de resterende metastabiele carbonaten in de gecarbonatere slakcement pasta's. De oppervlaktebehandeling blijkt de treksterkte van gecarbonatere slakcement pasta significant te verbeteren en dit is van groot belang voor de weerstand tegen afshilferen bij vorst-dooizoutaantasting.

Een nevendoel van het onderzoek was om te komen tot de ontwikkeling van een nieuw geïntegreerd model voor afshilferen van het betonoppervlak. Het ontwikkelde model maakt gebruik van de "glue-spall" theorie en de in dit proefschrift ontwikkelde hypothese en werkt verder met het Deltse Lattice Model platform. Het model is succesvol in de simulatie van de experimentele observaties van de scheurpatronen gegenereerd door de afshilfermechanismen.

De glue-spall theorie gaat uit van het idee dat afshilfering van het materiaaloppervlak gegeven wordt door het scheuren van de externe ijslaag bij doorgaande afkoeling omdat op een gegeven ogenblik de opgebouwde trekspanning de sterkte van de zout-ijs combinatie zal overschrijden. De theorie kan veel fenomenen verklaren inclusief het pessimum effect. In het kader van deze theorie bleek het nieuwe model in staat te zijn om twee belangrijke experimentele observaties te simuleren. Onder identieke condities kan het model de grotere mate van afshilfering bij zoutconcentraties van 3% voorspellen vergeleken met de geringere scaling bij lagere en hogere zoutconcentraties. Bovendien voorspelde het model het additionele effect van de dikte van de ijslaag die van cruciaal belang blijkt te zijn bij vorst-dooizoutschade. Met identieke materiaal- en milieuncondities zal een dikkere ijslaag een grotere schade geven dan een dunnere ijslaag. Deze voorspelling van het model is via observaties gecontroleerd en bewezen.

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CDF

ASTM C672-92

SS 13 72 44, 3rd edition, Procedure A

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Set of equations

Solving the equations

# References
LIST OF ABBREVIATIONS

O PC  Ordinary Portland Cement
ITZ  Interfacial Transition Zone
w/c  water to cement ratio
C₂S  dicalcium-silicate
C₃S  tricalcium-silicate
C₃A  tricalcium-aluminate
C₄AF  tetracalcium-aluminaferrite
AFT  ettringite
AFm  monosulphate
CDF  Capillary suction of Deicing solution and Freeze thaw test
CIF  Capillary suction, Internal damage and Freeze thaw test
EN  European Standard
ASTM  American Society for Testing and Materials
MIP  Mercury Intrusion Porosimetry
XRD  X-Ray Diffraction
ESEM  Environmental Scanning Electron Microscope
EDX  Energy Dispersive X-ray
BSE  BackScattered Electron
GSE  Gaseous State Electron
C-S-H  Calcium Silicate Hydrate
M-S-H  Magnesium Silicate Hydrate
CH  Calcium Hydroxide
Na-MFP  Sodium Monofluorophosphate
QI  Quality Improver
DEG  Diethylene glycol
CPD  Critical Pore Diameter
Chapter 1

INTRODUCTION

1.1 BACKGROUND

Blast furnace slag is a by-product of blast furnace iron manufacturing. When molten slag is rapidly quenched it forms granules, which have (latent) hydraulic properties. When the granulated slag is activated it reacts to form cementitious products. Because of its cementitious properties slag is used as a constituent in cement or as a concrete admixture. To enhance reactivity the slag is ground to cement fineness (Pietersen 1993; Bijen 1998).

The utilization of slag in cementitious materials dates back to the 1800's. Modern slag cements started being produced at the beginning of the previous century and - because of its excellent technical properties and the way it positively affected cement production costs - slag soon found a wide range of applications. In Western European countries slag cements claim an important share of the cement market. The Dutch cement and concrete market is well known for the fact that a relatively high proportion of its cement uses ground granulated slag. In the Netherlands slag cement occupies more than 50% of the market share.

Slag cement has important advantages. In comparison to other current cements it is environmentally friendly. Energy and raw material consumption is particularly low. In general, slag cement has comparable properties to ordinary portland cement (OPC). Nevertheless, there are some essential differences. Slag cement tends to be more resistant to sulphate attack, much more resistant to aggressive material penetration such as from chloride-ion compounds, but it also reveals slower strength development at a young age, lower resistance to carbonation and lower frost salt scaling resistance.

The latter issue forms the subject of this thesis. In comparison with OPC concrete, slag cement concrete displays faster surface deterioration in freezing-thawing and de-icing salt loading, thus resulting in the disappearance of the concrete or mortar skin.

In decision-making processes, slag cement is often not chosen in conjunction with its relatively low resistance to frost salt attack when compared to OPC. This plays an important part in countries where frost salt deterioration is an issue. In the Netherlands, slag cement is not used in road construction work because of the de-icing salts factor. Improvement in this behaviour could stimulate the application of this cement, thus in turn helping the cement industry to reinforce national commitment to the Kyoto agreement because when slag is utilized as a replacement to OPC, CO$_2$ emission levels are automatically lowered.
This project was initiated by ENCI B.V., the first Dutch cement manufacturer and by Delft University of Technology’s section of Material Science and Sustainable Construction within the faculty of Civil Engineering and Geosciences. The project was a direct result of positive test result observations concerning frost performance in slag cement concrete specimens that contain certain chemical grinding agents.

1.2 AIM OF THE STUDY

The principal aim of the project was to investigate why the frost salt scaling resistance of slag cement concrete is improved by applying grinding agents of the type previously investigated within the Dutch cement industry. It is predicted that the insight obtained could contribute to the structural improvement of frost salt scaling resistance in slag cement concrete.

One research question related to the effect that the grinding agents have upon the microstructure of cement paste and concrete, because it is known that microstructure is of utmost importance to frost scaling resistance and that trace amounts of grinding agents would not be likely to modify the chemical composition of the hydrating cement. Another question related to how the scaling process could be modelled on the basis of this microstructure so that behaviour under frost salt attack becomes predictable. Finally, alternative ways of improving the frost salt scaling resistance, other than by using grinding agents, were also taken into account.

1.3 THE THESIS CONSTRAINTS

The current thesis mainly discusses the experimental findings on the frost salt scaling of CEM III/B 42.5 N HSR LH cement-based materials containing approximately 67% of granulated slag and ob-
tained from the ENCI B.V. cement factory. The findings presented in the present thesis should therefore only be considered in relation to the materials and methods used in this study.

The present investigation is linked to laboratory investigation. Precisely how representative laboratory investigation is in terms of everyday practice remains debatable. Curing conditions are, for instance, different in practice from in the laboratory. In this study, the aim was to take a rather realistic approach by using 1 week wet curing and to subsequently dry/carbonate the specimens for 3 weeks prior to introducing freezing-thawing exposure. The whole notion derived from the fact that in real life construction practice, the concrete elements receive water curing for not more than a couple of days. However, a contra-argument could be raised by claiming that slag cement systems rich in slag reveal inadequate hydration when water curing is incomplete. This dilemma compelled the thesis author to conduct the experiments on the basis of case A and case B comparisons instead of on the basis of definite quantitative conclusions. The reader is therefore invited to bear in mind that the results of this thesis may be representative of broader material behaviour under the environmental conditions presented here.

Only the factory interground cements, CEM III/B 42,5 N HSR LH (EN 196), rich in slag (> 67%) fall within the scope of this research study. Unless otherwise indicated, the reader should therefore think of these cements whenever the term “slag cement” is used.

1.4 THE THESIS LAY-OUT

The thesis comprises nine chapters. The considerations fall into four basic sections: the literature overview, material characterization, how scaling resistance can be improved and the different numerical modelling aspects.

The second chapter is reserved for the literature survey. There previously conducted research on the frost salt scaling concept is considered, together with the theories behind the problem and just how all of that connects with slag cement-based materials.

In the third chapter carbonation, the most important single parameter affecting the frost salt resistance of slag cement concrete, is separately investigated. The effect of carbonation on the microstructure and frost salt scaling resistance of the slag cement matrix is discussed.

In Chapter 4 some of the important curing parameters affecting frost salt scaling resistance are studied and an attempt is made to explain the relationship between the effects of those parameters and frost salt scaling.

Chapters 5 and 6 deal with the conceived improvement techniques. In the former chapter, the effects of grinding agents on the microstructure and frost salt scaling resistance of slag cement paste and concrete are discussed. In Chapter 6 the effect of an alternative method, known as sodium-monofluorophosphate surface treatment, on the microstructure and frost salt scaling resistance of carbonated slag cement paste and concrete is discussed.

In Chapter 7 a new integrated model for the frost salt scaling mechanism is introduced. The model uses the Delft Lattice Model as a tool and it simulates frost salt scaling in cementitious materials in accordance with the hypothesis developed by the thesis author and on the basis of Valenza and Scherer’s theory.

Chapter 8 presents two parameter studies with the new model.

The thesis ends with Chapter 9 which contains the conclusions and the recommendations.
A visualization of this thesis is given in Figure 1.2.

Figure 1.2 Visualization of the thesis.
Chapter 2

LITERATURE STUDY

2.1 TECHNICAL BACKGROUND

It is generally accepted that there are two deleterious and different mechanisms of frost attack on concrete; internal cracking, and surface scaling. This fact was first characterized by Powers in 1945, and in the 1960s the phenomenon of scaling became pronounced (Powers 1945; Verbeck 1957; Hansen 1963; Powers 1965; Snyder 1965). However, the distinction between surface scaling and internal cracking was not systematically made until relatively recently. Internal cracking leads to expansion cracking and loss of mechanical properties and, ultimately to complete destruction of concrete. However, surface scaling is characterized by a loss of mass on the concrete surface. This process gradually advances from the surface and exposes the coarse aggregate. It affects surface related properties such as the skid resistance on roads and the protection of the reinforcement by the concrete cover against corrosion, but not necessarily the mechanical properties.

Surface scaling of concrete is the result of the joint action of cycled freezing-thawing and de-icing salt loading. The areas of concrete showing the greatest deterioration are usually horizontal, near ground level under relatively wet conditions, and subjected to repeated freezing and thawing in the presence of de-icing salts. Although considerable amount of fundamental research has been conducted, a review of the literature indicates that there is little information on the actual conditions existing within the scaled concrete surfaces and the disruptive action of microclimatic changes occurring during freezing-thawing cycles (Moukwa 1988).

In the assessment of the frost salt scaling resistance of concretes made of cements containing granulated slag, a number of questions are still unanswered. The reports on the frost salt scaling resistance of granulated slag cement concretes appear to point in both directions. In many laboratory studies, the replacement of cement by slag has been found to reduce the frost salt scaling resistance of concrete (Marchand 1994). However, in real environmental conditions, several good service records have been reported even for the concrete structures containing very high slag content (Bijen 1998; Lang 2002).

Over the years, several attempts have been made to explain the frost salt scaling deterioration of concrete. However neither of these theories developed appear to explain the observed phenomena fully.
2.2 Frost damage mechanisms

Internal cracking and disruption are typical deteriorations that can be observed when concrete is subjected in the laboratory to rapid freezing and thawing cycles. If, during such tests, concrete freezes in water, surface scaling can occur in addition to internal cracking, but if concrete freezes in air (and is not adequately protected by sufficient closely spaced air voids), a very typical map cracking can be observed (Pigeon 1995).

There is no definite answer so far whether the basic mechanisms of internal cracking are also responsible for scaling. However, it is known that those basic mechanisms (hydraulic, osmotic etc.) are at least up to a certain extent responsible for scaling, since the investigation results have shown that air entrainment helps to protect concrete from scaling.

In this section the previously proposed mechanisms on frost and frost salt scaling damages are summarised.

2.2.1 Mechanism(s) of plain frost damage

Some of the degradation mechanisms are considered common in plain frost attack and frost salt attack. Therefore, the plain frost damage mechanisms are presented initially.

The basic mechanism of frost deterioration is generally explained with the term closed container mechanism. The idea beneath this fact is the specific volume of ice is larger than that of water and thus, if a sealed container is fully filled with water, ice formation causes large internal pressure. Since the specific volume of ice is roughly 9% higher than that of water, pressures will generate if 91.7% of the container is filled with water.

According to Powers, although concrete often contains sufficient air, even after long periods of storage under water, it would still not be frost resistant. The major cause of disintegration is not the ice pressure itself, since this would consequently not need to develop, but rather the hydraulic pressures that would arise during ice formation when water was expelled from the pore in which freezing takes place. This hypothesis has since been called as hydraulic pressure hypothesis (Powers 1965).

Microscopic ice lens growth theory has been proposed by Powers and Helmuth in 1953. The theory has been further developed by Setzer (Setzer 2002). According to this theory, if the temperature of the paste is above 0°C, water in the capillary pores can be considered to be in thermodynamic equilibrium with water in gel pores. If the temperature decreases sufficiently below 0°C, ice lens begins to form in a number of capillary pores. This means the breaking of the equilibrium because ice has lower free energy than that of liquid water. The liquid water in the gel pores acquires a potential energy that forces it towards the capillary pores where ice lens started to form. When this water reaches the capillary pores, it freezes and the ice crystals grow up. This ice body generates pressure against the walls of paste and if the pressure becomes too big permanent damage occurs because the pores cannot expand significantly. This is where the air entrainment takes action against the expansion due to freezing. The entrained air bubbles, should they contain water, act either as alternative sites for ice growth. They then compete for water with the ice within the large pore. During freezing, the pore water is attracted to these alternative sites due to the lower chemical potential of the ice within the entrained air bubble. This has the effect of reducing the growth in the large pore and, thus, of reducing swelling (Schulson 1998).

However this theory assumed the liquid in the pores as pure water and did not consider the dissolved chemicals. Later, Powers and Helmuth modified their hypothesis and this modified version is known as osmotic pressure theory. Different soluble substances, e.g. alkalis and chlorides, will
lower the freezing point. This means that at a temperature, where a cavity filled with pure water would freeze solid, the same cavity with solution would only be partly frozen. The outcome would be a cavity with pure ice in equilibrium with a solution with an increased concentration of the soluble substance, so the concentration would differ from the concentration of smaller voids, where ice formation has not occurred. This produces an osmotic pressure forcing water in smaller voids to diffuse into the larger cavity and thereby supply water for further ice formation. The osmotic pressure may not be regarded as an independent mechanism, but as a strengthening of the microscopic ice lens growth theory (Hasholt 2002).

Fagerlund contributed to the question by introducing the degree of saturation concept. The degree of saturation $S$ is defined as the ratio of the weight of evaporable water (including the gel water) within the material at the time of freezing divided by the weight of evaporable water at complete saturation from the oven-dry (at 50ºC) state to a state of constant weight under vacuum. From a series of experiments performed on non-air entrained concrete specimens of w/c ratios 0.4 to 0.5, Fagerlund concluded that the critical degree of saturation $S_c$ is about 0.80 (Schulson 1998)(Figure 2.1).

![Figure 2.1 Decrease in Dynamic Young’s modulus (normalized) vs. degree of saturation for concrete under freezing thawing loading measured in five different laboratories (from Schulson (1998)).](image)

Another theory is the thaw theory. According to this model, damage is assumed to occur not during freezing but during thawing (Bijen 2003). When water in the large pores is frozen, it attracts water from adjacent smaller pores both as fluid as well as in vapour form. The smaller pores are more or less freeze-dried by the ice in the larger pores. Consequently the ice in the larger pores will grow. This is similar as the process of ice lens growth. Then subsequently the temperature will rise. The ice will expand and because the thermal expansion coefficient of ice is 5 times larger than that of concrete it will exert forces. It can be calculated that tensile forces will be introduced which can be
expressed as $0.36 \times T$ (N/mm$^2$). This means that at a temperature of 15ºC the tensile strength of concrete will be exceeded (Figure 2.2).

Figure 2.2 Frozen water in large pores (left) and expansion of ice in pores during warming-up (right).

### 2.2.2 Mechanism(s) of frost salt scaling

Several mechanisms have been proposed by the researchers, so far. While some of these mechanisms have common points in certain aspects, there are other mechanisms proposed to give a different explanation to the frost salt scaling phenomenon. In this section, some important examples with regard to previously proposed mechanisms are presented.

**Powers (1965)**

One of the first hypotheses to explain the frost salt scaling mechanism came from Powers. He proposed that the deleterious effect is because of combined effect of hydraulic and osmotic pressures. Salt content would attract more water into the pores and consequently the hydraulic pressure is generated when ice becomes relatively bigger. Powers states that de-icing salts will spread much faster in the capillary pores than in gel pores and that the salt concentration gradients thereby formed between gel pores and capillary pores would promote this mechanism.

However, this mechanism is found dubious. Lindmark (1999) explained the reasons as follows. After freezing has begun in a salt solution, the chemical potential of the salt solution will be equal to that of ice. Thus, at a given temperature, the combined ice and salt solution mixture would have no more intense ability to attract water than would a pure ice body at the same temperature. Lindmark thought that it was the outer salt solution that caused the frost salt scaling.

**Hansen (1963)**

Another contribution to frost salt attack issue is the dilation pressure due to salt crystal growth. Once the solution in the larger pores reaches a supersaturated state (either by evaporation or
freezing of water), salt crystallization starts and salt molecules are drawn from smaller pores into large ones (Ghafoori 1997).

**Snyder (Snyder 1965)**

Snyder claimed that scaling appears when there was a steep salt gradient beneath the concrete surface. He concluded that the development of a concentration gradient through the depth of the concrete was the primary cause of scaling. The ultimate effect of the concentration gradient probably is to produce excessive thermal and hydraulic pressures through its effect on the freezing point of the liquid phase within the concrete.

According to this theory the de-icing salts have a number of effects that influence the deterioration rate. Bijen summarized these effects as follows (Bijen 2003):

- Salts penetrate the pores and increase the average water content of the pores due to hygroscopic character of the salts.
- The salts do lower the freezing point. The freezing point will decrease linearly with the salt concentration in the pore water. As shown in Figure 2.3, this can lead to situations where there is a thin unfrozen layer sandwiched between two frozen layers. The unfrozen layer will freeze when the temperature drops further. However, there is then no space left for the freezing water to be transported out when the ice expands. This explains the well-known scaling off of concrete surfaces that are subject to frost salt scaling deterioration.
- The difference in vapour pressure between ice and water decreases at increasing salt concentrations in the water. The freeze-drying of smaller pores by ice in the larger pores will diminish.
- Moreover the surfaces where de-icing salts are used are generally horizontal and often wet and therefore more prone to damage.

![Figure 2.3 Frozen layer with intermediate unfrozen layer leading to scaling.](image)

**Harnic, Meier and Rosli (Harnic 1980)**

Explanations on the mechanisms of frost salt scaling deterioration of concrete have been offered by Harnic et al as well. According to these researchers, water molecules in the air have a higher ten-
tenancy to condense into a salt solution than into water. The hygroscopic property of salts, along with the newly melted ice on the surface, increases the degree of saturation of concrete and further enhances the detrimental effects of hydraulic and osmotic pressures. Besides, thermal shock resulting from the dry application of de-icing agents is harmful to concrete. The heat required to melt snow and ice is extracted mostly from concrete. Subsequently, through temperature gradients, internal tensile stresses of short duration can develop, exceeding the tensile strength of concrete (Ghafoori 1997).

Harnic et al. have suggested that a sudden drop in the temperature during the process of melting ice by means of de-icing salts can cause internal stresses in the concrete. Their attempt to confirm the theory from field measurements did not meet with complete success (Lindmark 1999).

Binbin (1988)

Binbin concluded that CaCl₂ reacts with calcium aluminate phase of the cement and contributes to the deterioration of concrete when freezing in CaCl₂ solution. According to him this reaction does not take place at room temperature but in freezing environment. He also observed that NaCl solution is much more harmful than CaCl₂. He assumed that the effect of NaCl is the combination of effect of NaO H and CaCl₂. CaCl₂ may react apart from the formation of Friedel’s salt, further with lime, forming calcium oxychloride as a result of the chloride-lime reaction. On the other hand, the formation of NaO H as a result of the fixation of Cl⁻ increases the alkalinity of pore solution, which in turn attacks active aggregates (if any). Apparently this chemical explanation is not directly related to the frost salt scaling mechanism but rather mainly on the decrease of resistance of material against the frost salt attack.

Stark and Ludwig (1997)

Stark and Ludwig also proposed a chemical degradation mechanism for frost salt attack. They gave a chemical explanation to frost salt scaling of slag cement concrete in case of carbonation. According to them, metastable carbonates, namely aragonite and vaterite are responsible for the lower resistance of carbonated slag cement concrete. These researchers claim that combined effect of frost and salt transforms these metastable carbonates to a very poor crystal structure and leads to a less resistance against frost salt scaling. However authors do not explain the connection between carbonate mineral transformation and frost salt scaling.

According to Stark and Ludwig, there is some indication that the stabilization of the metastable forms of calcium carbonate in cements rich in granulated slag may be affected by the magnesium oxide in the slag (Stark 1997). It is known that Mg-ions cause a reduction in activation energy and an increase in the rate of transformation from metastable aragonite to stable calcite (Stepkowska 2003).

The amount of free MgO in cements is kept to a minimum due to the demand for soundness. MgO may hydroxylate to brucite Mg(OH)₂, but is stable in a pore solution at low pH. The MgO content in slag cements may rise to 12-14% and enrichment of Mg-ions is observed at specified sites such as inner and skeleton hydration products of slag binder. The exact forms of hydration or hydroxilated products at Mg rich sites are still unclear (Matala 1995). Pietersen reported that compared to the unhydrated slag, the slag interior is enriched with MgO with factor three, and it also contains less SiO₂ and CaO (Pietersen 1993). The analysis of the inner edge of the slag contains significantly less silicium and aluminium, slightly increased MgO and an approximately similar CaO compared to the unhydrated slag. According to these authors the outer edge has an increased CaO content while having a similar MgO content. The MgO concentration gradually decreases from outer edge of the slag toward the matrix.
Valenza and Scherer (2004)

The authors propose a theory based on “glue-spall” mechanism. According to this theory de-icing salts are entrapped subsequent to freezing and create weak pockets inside the frozen ice layer. Depending on the salt concentration, the cracking of the ice/brine layer generates frost salt scaling. They proposed a theoretical explanation for the greater damage of pessimum salt concentration under frost. The principle idea is that following the ice formation on top of the concrete surface, ice starts to shrink due to further cooling. The shrinkage of ice exerts tensile stresses because of the thermal expansion coefficient difference ($4 \times 10^{-5}$) between ice and concrete which results into three consequences depending on the solute concentration of the freezing liquid. These are;

Weak salt concentration (0.1%): Due to the ice formation, the exerted tensile stress cannot exceed the tensile strength of ice, so no cracking occurs.

Pessimum salt concentration (1-3%): Due to the ice formation, the exerted tensile stress exceeds the tensile strength of ice and breaks the ice, which triggers surface scaling (see Figure 2.4).

Strong salt concentration (10-20%): In this case the ice layer is too soft to exert enough stress to the underlying cementitious material, hence no scaling occurs.

![Figure 2.4 Schematic description of frost salt scaling mechanism according to glue-spall theory.](image)

Although the authors give answers to the many critical questions concerning frost salt scaling, there are still points, which this theory cannot account for, such as beneficial effect of air entrainment. According to their theory the air voids should affect the scaling inversely, which is the opposite of the experimental results. They gave as a possible explanation to that as air entrainment reduces the bleeding and increases the strength of top layer.

Another contrary finding to this theory is encountered throughout the present PhD project. Valenza and Scherer claimed that frost salt scaling can only occur when there is an external salt solution. However, the thesis author has experienced that the scaling can occur on top of a CDF testing specimen (see Appendix A) when the mortar has very high level of water uptake (Figure 2.5).
2.3 INTERNAL FACTORS OF FROST SALT SCALING

2.3.1 Cement and microstructure

Between the various types, classes and brands of cements, certain differences on the frost salt scaling resistance of concrete have been observed. Those cements appear to be different in pore system and tensile strength of the hardened paste. It has been found, for instance, that the use of finer cements can improve the frost salt scaling resistance probably because of increased rate of hydration which provides presumably higher tensile strength (Marchand 1994).

Laboratory test results reported by Fagerlund indicate that the use of low alkali/low $C_3A$ cements reduces the amount of frost salt scaling and the spread between individual specimens (Fagerlund 1986). However, Stark et al. proposed the opposite that higher $C_3A$ content may lead to more AFm formation which may transform into AFT under frost salt attack and reduce the scaling resistance (Stark 1997).

The microstructure of concrete plays a significant role in the lifetime prediction and investigation of damage mechanisms in frost (salt) attack (Wowra 2002). With respect to this phenomenon, pore size distribution is of paramount importance. The pore size distribution of slag cement concrete is substantially finer than that of OPc concrete. The percentage of gel pores is higher and the capillary pores are lower (Bijen 1996).

Slag in cement has a major effect on increasing the density, on decreasing the thickness of interfacial transition zone and on reducing porosity. This may decrease the degree of permeability and the risk of frost damage for low-air-content concrete.

In early stage of carbonation, the pore size distribution of OPc paste usually exhibits mostly pores with lower radii while carbonation of concrete rich in slag generally presents a distribution with sig-
significantly larger pore sizes. The main cause for these observations is the difference of calcium hydroxide content of the cement. Slag cement contains significantly less calcium hydroxide compared to OPC.

Under certain conditions, further carbonation leads in both cases to the formation of porous silicate hydrates due to decalcification of the C-S-H. This effect will occur for high slag content concrete earlier than for OPC, because it contains less lime of the hydrated cement, which will be depleted faster (Bijen 1998; Wowra 2002).

2.3.2 Mixture characteristics

As could be expected, most field and laboratory data show that, for normal strength concrete, the frost salt scaling resistance increases as the water to cementitious material ratio decreases (Marchand 1994). This seems natural since an increased w/c ratio will lead to a larger capillary porosity and a larger permeability thus to an increased amount of freezable water at each and every temperature. Because of this dependence on capillary porosity, it’s been hypothesized that concrete of very low w/c ratio might be immune to frost salt attack even without air entrainment (Lindmark 1999). This opinion even influenced the national concrete standards like in the Dutch standard, where it is not compulsory to use air-entraining agents when a concrete mixture has w/c ratio lower than 0.45.

However we should be more cautious before concluding that simply reducing the w/c ratio would reduce the frost salt scaling. There are number of researchers who put forward that it is not entirely possible to impede ice formation by decreasing the w/c ratio. For example, Zuber et al used low temperature calorimetry to show that even concrete with w/c ratio of 0.25 contains freezable water at temperature well over -20°C (Zuber 2000).

Nevertheless in general, it appears that using lower w/c ratio is favourable with respect to frost salt scaling resistance. However, one should keep in mind that there are some other parameters, which influence the frost salt scaling resistance of concrete along with w/c ratio so the situation should be approached broadly.

For all concrete mixtures, workability is an important property, since it determines the ease with which they can be properly placed and consolidated. Very few test results reported on the topic indicate that normal strength concretes with very high slumps tend to have a reduced scaling resistance. However, according to Marchand, there is no information in the literature for high slump concretes with very low w/c ratio having high superplasticizer contents (Marchand 1994).

2.3.3 Curing sensitivity

Although the reasons for this are not always well understood, the type of curing can have a very significant influence on the scaling resistance. Many authors have reported in recent years that concretes cured with a membrane forming curing compound have a better scaling resistance than similar water cured concretes (Marchand 1994).

Curing outdoor with wet burlap covered with polyethylene is the best curing method overall with respect to scaling resistance. Curing with the curing compound appeared to have protected the concrete surfaces against scaling, primarily in the very early stages of the test. According to Afrani and Rogers, if good resistance to frost salt scaling is required, wet burlap is the best curing technique (Afrani 1994).
Marchand and Sellevold reported that the frost salt scaling resistance of concrete was significantly reduced when specimens were subjected to a predrying treatment at 40°C and 0% R.H. and then resaturated with water prior to testing. This effect was associated with the coarsening of the pore structure. They also found that predrying at 40°C and 110°C and prolonged predrying at 20°C decreases the frost salt scaling resistance of OPC, class F and class C fly ash concretes (Marchand 1995).

Slag cement concrete appears to be more susceptible to curing than any OPC concrete with the same workability. When cement is replaced by slag (or fly ash) the permeability is affected more negatively by carbonation. Consequently replacement of cement by equal mass percentages of slag will generally make concrete more vulnerable to degradation by de-icing salts. When the concrete is designed with an identical strength development, the differences in frost salt scaling resistance between OPC and concrete with slag cement concrete will be smaller. This is in fact observed for concrete slag cement, which, during the first cycles, shows behaviour similar to the concrete with OPC. The differences between concrete with slag cement and OPC concrete would be expected to be smaller when curing is prolonged (Wiebenga 1985; CUR 1992).

### 2.3.4 Effect of finishing

Surface finishing operations can influence the properties of the surface layers, and thus the scaling resistance. Overworking, in particular, can increase the value of the air void spacing factor. Moulded surfaces, as opposed to towelled surfaces, are also often exposed to freezing in the presence of de-icing salts (Marchand 1994). Johnston observed a very significant difference between the scaling resistance of the top surface of a fly ash concrete specimen and that of the moulded bottom surface of the same specimen (Johnston 1994). This is likely to be due to bleeding of the top surface concrete leading to different air void characteristics and w/c ratio.

The test results indicate that the higher porosity of the surface layers relative to the bulk tends to markedly reduce the frost salt scaling durability of wood towelled laboratory specimens during the first freezing and thawing cycles (Pigeon 1996).

Research is required to understand the mechanism of the formation of this layer, particularly since it could be influenced very significantly by the conditions existing during bleeding (Pigeon 1996).

### 2.3.5 Mineral additions

Mineral additions can influence the frost resistance of hardened concrete by affecting the functioning of air entraining agents, by altering the stability of entrained air, by changing the rate of strength development, by affecting the pore structure of hardened cement paste and, in the case of de-icing salts, by reducing the chloride permeability of the concrete. Ageing of concrete containing additions may also result in a different pore structure than ageing of OPC concrete (Virtanen 1990).

Earlier tests made with additions give no clear answers as to whether these materials are beneficial or harmful to the frost resistance and frost salt scaling resistance of concrete. It seems that negative results in many cases have been due to extreme amounts of additions used in concrete. It could seem possible, considering results presented in literature, to limit the amounts of ground slag, fly ash and silica to maximums of 50%, 25% and 10% of the total binder content, respectively. It seems also that the use of slag or silica in such limited amounts could give a positive influence to frost-resistance of concrete, while fly ash does not have any greater advantages to offer (Virtanen 1990).
A drawback of fly ash is its (in)sensitivity to air entrainment. As the foam index tests reasonably indicate, the negative influence of fly ash is because of the adsorption of air entraining agents by the coal particles (Fraaij 1990).

Although it is clearly possible to obtain good engineering properties with concrete containing fly ash, numerous laboratory studies have indicated that the incorporation of these supplementary cementing materials is generally harmful to the scaling resistance of concrete (Pigeon 1996).

Wiebenga from TNO-IBBC have also investigated the effects of fly ash on frost salt scaling resistance. The specimens were frozen to -17°C and subsequently thawed by application of sodium chloride salts in a quantity of 550 gr/m². Initially the replacement of cement by fly ash results in more loss of mass, especially for portland blast furnace slag cement (CEM III). After more cycles the differences between the concrete with fly ashes and the reference concrete become smaller. However, after 25 cycles the concretes with fly ash still show more loss of mass than the reference concretes (Wiebenga 1985).

However, in practice, frost salt resistance performance of fly ash concrete seems to be significantly opposing. According to Thomas (Thomas 1997), there is clearly a lack of consistency between the performance of fly ash concrete under accelerated laboratory and field conditions. A number of field placements containing fly ash are continuing to provide good service in severe conditions. These contradictory results are partially due to inadequacies in the test method itself. However many studies demonstrate satisfactory performance for 30% fly ash concrete with w/c ratio below 0,45 and good air entrainment (Wiebenga 1985).

In the Netherlands, fly ash concrete application is considered as a good practice and fly ash concrete has been serving in road constructions with satisfactory performance against frost salt attack for many years.

Initially slag cement concrete appears to scale faster than OPC concrete. However, it is reported that after some time the scaling rate becomes lower than for OPC (Bijen 1998). Heavy initial scaling of blast furnace cement concretes with a granulated slag content > 55% is due to the fact that the frost salt scaling resistance of the carbonated surface layer is lower than that of the core concrete. With lower granulated slag contents no increased initial scaling is observed. It is suggested that the high rate of scaling of the carbonated surface zone is related to recrystallization of calcium carbonates (Stark 1997).

In the Dutch climate conditions, concretes with a w/c ratio less than 0,45 are considered to be resistant, regardless of the cement type. Actually for road structures mostly OPC concrete or Portland fly ash cement concrete is used to avoid an early high rate of surface scaling (Bijen 1998).

Nevertheless, properly produced slag cement concretes with a lower content of granulated slag < 45% have a good frost salt scaling resistance and without air-entrainment they are often better than the respective OPC concretes (Stark 1997).

Virtanen reported that problems with frost resistance were encountered when excessive amounts of external pozzolan additions were used in laboratory tests. According to him, the amount of ground granulated slag, pulverized coal fly ash and silica addition should be limited in frost-resistant concrete to 50%, 25% and 10% by weight of total binder content, respectively (Virtanen 1990). Moreover, some agencies limit the amount of slag in an OPC concrete mix to 25-30% of the total cement weight (Hogan 1990; Sippel 2005).

To understand the different frost salt scaling resistance of slag and OPC concretes, it is important to know in which stage of freezing the differences occur. Whereas in tests for frost resistance under water the scaling of both slag and OPC concrete is linear, heavy initial scaling is observed in tests
for the frost salt resistance of concrete containing cements rich in granulated slag (slag content $\geq$ 60%) in 3% NaCl solution (Figure 2.6).

![Figure 2.6 Typical scaling performances of OPC concrete and slag cement concrete (BFC) with $\equiv$ 60% (m/m) slag content cement with and without air-entraining agents (a.e.a.) under frost salt attack (CDF Test) (Stark 1997).](image-url)

On the other hand, there are also contrary findings on the performance of slag cement concrete against frost salt scaling. According to Marchand et al., field observations and laboratory tests carried out on cored specimen showed that slag cement concretes had a better frost salt scaling resistance with respect to OPC concrete. Moreover, Fagerlund, in his comprehensive report, draws the following conclusion:

“The salt scaling resistance is very much increased with increasing slag content. The concretes made with cement type D (65% slag) have a high degree of salt scaling resistance even without additional air-entrainment, while the concretes with portland cement (type A) and with cement containing 15% slag (type B) fail completely already after few cycles. The reason for the superior behaviour of the cement with high slag content is probably the very low diffusivity of chloride ions in such concretes (Fagerlund 1982).” As a note, specimens were moist cured for 7 months.

The salt scaling resistance is very much reduced with increased air content. Note, the concretes with OPC have inferior durability even with 6.2% air. This was unexpected with regard to the high quality air-entraining admixture used, the low spacing factors and the excellent durability in pure-water freezing (Fagerlund 1982).

However, Fagerlund no longer agrees with the above-mentioned conclusion due to his doubts about the quality of this experimental study (Fagerlund 2002). The work of Fagerlund shows once again that the laboratory test results should be interpreted carefully.
2.3.6 Air entrainment

It has been widely agreed since late 1940s that the usage of air entraining agents improves the resistance of concrete against plain frost attack. However, it is still not fully agreed if those chemical admixtures are useful in improving the frost salt scaling resistance of concrete, as well. Nevertheless, by far, most of the researchers claim that it is the most significant measure to improve the frost salt scaling durability of concrete and is well put forward this experimentally (Stark 1997).

To obtain the required fresh air content, the amount of air entraining agents in slag cement concretes rich in granulated slag has to be much greater than in OPC concretes. For certain amount of air entraining agent, pozzolanic cement concrete possess less air than the one with OPC. But even a sufficient content of air voids in the hardened concrete does often not lead to an improvement of the frost salt scaling resistance of concretes rich in granulated slag. Only few authors achieved results that the frost salt scaling resistance of slag cement concrete might be improved by air entrainment in the same way as that of Portland cement concrete (Stark 1997).

In the opinion of some authors the low effectiveness of air entraining agents in slag cement concretes rich in granulated slag is of secondary importance, as blast furnace cements are able to develop a very dense microstructure and so a high frost salt resistance may be developed even without air entraining agents. On the other hand, it was found in several studies that the use of systems rich in granulated slag without air entraining agents reduced the frost salt scaling resistance in comparison to Portland cement (Stark 1997).

However, experience shows that concrete may be protected against damage due to frost salt attack by an appropriate air void system. If the system of artificial air voids in the concrete is adequate the "natural" porosity in the range of gel and capillary pores is of minor importance in the frost salt scaling resistance of the concrete (Stark 1997).

In order to produce a resistant concrete, air entrainment is prescribed in most countries. Since, air entrainment is not usually done in the Netherlands, experience is rather limited. In comparison with OPC concrete there are no particular problems with respect to the control of air entrainment and the homogeneity of the air bubbles in the slag concrete (Bijen 1998). It may be concluded that neither the relatively high total amount of scaling compared to OPC concretes nor the heavy initial scaling of the slag cement concretes (with more than 55% slag) may be attributed only to an insufficient air void system (Stark 1997).

Air void structure

The most important parameter with regard to general frost resistance is the air void structure. Many researchers believe that this is also valid for the frost salt scaling. Several parameters determine the general air void profile of a concrete structure. Air content, spacing factor and specific surface are the important parameters which are considered as the key parameters according to the national standards e.g. ASTM 457 (ASTM 2006).

Total air void content can be estimated by means of point counting or traverse line methods. There are alternative methods like scanning the flat concrete surface by high-resolution flatbed scanner. However this does not yield high accuracy due to the restrictions arising concerning the optical resolution of the scanners.

Power’s spacing factor is considered as an important parameter especially for plain frost attack. It is defined as the largest half distance between air voids. This theory was developed as an extension of the hydraulic theory (Powers 1965). Powers defined the spacing factor as follows:
$$L = \frac{P}{S \cdot A}$$  
for $p/A < 4.33$  

and

$$L = \frac{3(1.4(p/A + 1)^{1/3} - 1)}{S}$$  
for $p/A \geq 4.33$

where;

$L$: is the spacing factor (mm)
$A$: is the total air volume (percentage of total volume)
$S$: is the specific surface (mm$^{-1}$)
$p$: is the paste content (percentage of total volume)

Apparently more research is needed on the effect of air void parameters on frost salt scaling resistance. In Figure 2.7, frost salt performances of 60 Canadian concrete structures are presented (Fournier 1987). However the authors did not determine the type of cements used.

Generally the deterioration due to scaling simply increases with an increase of the spacing factor. An important consequence of this is that an adequate air entrained concrete performs much better than no air entrainment. Certain tests have also indicated that excessive air entrainment can reduce the scaling resistance, probably because of the reduction of the tensile strength of the paste and of the easier saturation of the surface layers (Marchand 1994). However, since entrained air bubbles are also water repellent, the explanation of easier saturation with high-entrained air content is doubtful.

![Figure 2.7 Effect of air void characteristics on the frost salt scaling (Fournier 1987).](image)

However, many other researchers are on the contrary side. Janssen and Snyder investigated the effect of air void parameters on concrete specimens with different contents of fly ash and slag (Janssen 1993). The specimens had water to binder ratio of 0.45. Having tested according to
ASTM 666, the authors could not find any correlation between the frost salt scaling and air void parameters. The results of Setzer also revealed similar results to Janssen and Snyder’s as can be seen in Figure 2.8 and Figure 2.9 (Setzer 1997).

![Figure 2.8](image1.png)

**Figure 2.8** Scaling performance of the concrete specimens having various spacing factor values. According to CDF test (Setzer 1997).

![Figure 2.9](image2.png)

**Figure 2.9** Scaling performances of the concrete specimens having various amounts of artificially entrained air voids below 300 μm. According to CDF test (Setzer 1997).

### 2.3.7 Carbonation

Carbonation of slag concrete is more rapid than of OPC concrete (Bijen 1989; Stark 1997). Carbonation also results in a coarser pore structure of slag cement paste, while the opposite is true for OPC paste (Matala 1995). This phenomenon could explain the observed relative low frost salt scaling resistance of slag cement concrete.

In the current thesis a separate chapter (Chapter 3) is devoted to the relationship between carbonation and frost salt scaling behaviour of slag cement systems. In that chapter, both the literature
about the relationship between carbonation, microstructure and frost scaling resistance, and experimental investigation within the framework of this dissertation are being discussed.

### 2.3.8 Sealants

The scaling rate of concrete can be decreased by applying sealants. The use of silane-, siloxane- and silicone resin impregnation materials might help to slow down scaling action to some extent (Vasikari 1983).

The epoxy-based sealants are effective in preventing scaling only if the application of the sealant is done on dry surface conditions (Vasikari 1983).

### 2.3.9 Polymers

Using polymer dispersion as an addition to polymer-cement-concrete can increase the frost salt scaling resistance of concrete. Su found good frost salt scaling resistance performances of the mixtures with 11,2% and 22% (m/m) polymer. The author also pointed out that the increase in resistance is due to strong decrease in water absorption during frost test because of the hydrophobic nature of the polymers, especially at increasing contents (Su 1995).

All concretes with various compositions and various kinds of polymers show a positive resistance against frost salt attack compared to conventional concretes (Bordeleau 1992; Ohama 1995; Zajc 1995).

The results also show that a conventional concrete with good air void spacing factor and a low w/c ratio can be almost as resistant to frost salt scaling as latex modified concrete (Bordeleau 1992).

### 2.3.10 Fibers

Cantin and Pigeon concluded that the use of macro steel fibers does not affect the frost salt scaling resistance of concrete. Scaling can occur over the fibers that are near the surface, but this has no significant overall influence on the total amount of scaling damage (Cantin 1996).

### 2.4 EXTERNAL FACTORS OF FROST SALT SCALING

#### 2.4.1 Minimum freezing temperature

The influence of the minimum temperature reached during frost cycles on the extent of damage increases at lower temperatures. Studer reported that due to change from -18°C to -16°C the amount of scaled material was reduced by 38-52% as compared with only 4-22% reduction due to the change from -13°C to -11°C. According to him, extrapolation of test results to the behaviour of concrete under natural frost cycling, where minimum temperatures mostly are above -5°C, seems therefore to be more reliable with moderate (-10°C) than with low minimum temperatures (-20°C) (Studer 1993). Lindmark also observed similar effect of minimum temperature on OPC concrete
specimens. According to him, while it seems clear that -7°C causes only slight scaling, the difference between -14°C and -22°C is ambiguous (Lindmark 1999).

2.4.2 De-icing salts

The size of the global de-icing chemical market was approximately $3.5 billion in 1996 according to a federal aviation administration report. Chloride-based products, in particular sodium and calcium chlorides, have dominated the de-icer market which, in the US alone, amounts to more than one-third of the US$1.5 billion expenditure associated with winter maintenance (Santagata 2000).

There are mainly two groups of de-icer solutions; chloride and acetate solutions.

Calcium chloride de-icing salts especially affect those concretes containing reactive dolomite aggregates by enhancing de-dolomitisation reactions that release magnesium to form brucite and magnesium silicate hydrate (M-S-H). Calcium chloride affects the cement paste of both durable and non-durable concrete. The paste markedly discolors.

Magnesium chloride produces distinctive alteration rims at the margins of reactive dolomite aggregate. Magnesium chloride also produces significant concrete crumbling because of widespread replacement of C-S-H by non-cementitious M-S-H resulting from reactions between Mg²⁺ and the C-S-H cement phase. According to Lee et al., no reaction rims are observed in durable concrete by the use of sodium chloride. Brucite in the cement paste appears to be stable in NaCl-treated concrete. However in all chloride solutions, paste deteriorations can be observed due to decalcification.

On the other hand, according to Ohama and Kim, over five decades of field service experience and extensive laboratory testing have shown that properly air entrained concrete has excellent resistance to surface scaling due to freezing and thawing and the use of common de-icing chemicals. Service records and laboratory tests have also shown that scaling is primarily a physical action. However, ammonium nitrate and ammonium sulfate fertilizers have been sold as deicers. These materials in the presence of water react chemically with all forms of concrete and cause objectionable disintegration, even at room temperature. Their use must be strictly prohibited (Ohama 1995).

2.5 Chemical aspects

Generally, little attention is paid to chemical-mineralogical processes under frost and frost salt attack. A few papers, which have been published on this subject, are based on the assumption that chemical new formations due to frost or frost salt attack occur mainly with calcium sulpoaluminate hydrates.

The comparison between the specimens, which were frozen under water, and those, which were not frozen, showed that monosulphate and ettringite behaved quite differently under the specific humidity and temperature conditions of a frost attack. While ettringite proved to be very stable, part of the monosulphate was transformed to ettringite during freezing.

The results of the investigations led to the conclusion that the sulphate required became available by the partial decomposition of the monosulphate due to carbonation. The gypsum, formed in this process, may then form ettringite with the non-carbonated monosulphate (Stark 1995).
Considering the phase transformations observed, it has to be assumed that an influence on the frost and frost salt scaling resistance of the concrete is only to be expected when monosulphate (AFm) is transformed to ettringite (AFt), which results in an increase in volume.

It was stated that in the cement with a low C₃A content, more AFm was transformed to AFt under frost attack. Under frost salt attack, however, more trisulphate was formed in the cement rich in C₃A (Stark 1995).

According to Stark and Ludwig, since the influence of physical factors are more significant than chemical factors, it is possible to produce concretes with a very high frost and frost salt scaling resistance, independent of the clinker composition (Stark 1995).

The results of their study clearly show that the amount of scaling decreased (bend of scaling curve) at the moment when the scaling process changed from the carbonated to the non-carbonated material.

Binbin also investigated the chemical attack of de-icing substances on cementitious materials (Binbin 1988). He extended the research beyond the salts such as NaCl and CaCl₂ and studied the materials like urea and alcohol. His study is the most comprehensive study on the chemical aspects of frost salt scaling.

On the basis of his visual inspection, the aggressive nature of the deicing agents is in the following order:

For inorganic agents:
NaOH > KOH > NaCl > KCl > CaCl₂

For organic agents:
Urea > acetone > ethyl alcohol > methyl alcohol

Above-mentioned observations make it likely that physical action cannot be considered as the only notion with respect to frost salt scaling resistance.

Binbin explains the details of chemical interaction between hydration products and various deicing agents under freezing conditions. In the current thesis, only the influence of NaCl is investigated since it causes the combined attack of NaOH and CaCl₂.

### 2.5.1 The influence of NaCl

Binbin found NaCl much more detrimental than CaCl₂. This is in agreement with the findings of Verbeck and Kriegel (Verbeck 1957) and, Browne and Cady (Browne 1976). He stressed that under freezing conditions NaCl attack is a combined action of NaOH and CaCl₂.

He presented that the attack of chlorides is mainly effective on monosulphate (AFm) phase of the cement paste. He experienced this after 7 days in freezing environment at -10°C where AFm phase completely disappeared causing possibly a decrease in the tensile strength. It was also reported that C₃AH₁₆ disappeared as well.

Binbin concluded that the attack of chlorides on AFm and calcium aluminate hydrate will lead (by changing the crystal structure) to the modification of the microstructure of cement stone, thereby contributing to the damage of concrete under frost action.

This conclusion might also be important for slag cement concrete. AFm is one of the hydration products in slag cement paste (Glasser 1989) which might be affected by frost salt attack and it
can further increase the frost salt scaling degradation. However the relationship between the calcium sulpho-alumina hydrates and frost salt scaling durability is still doubtful.

![AFm crystals from a slag cement paste](image)

Figure 2.10 Two typically cracked AFm crystals (middle and upper left) from a slag cement paste with w/c 0.45.

## 2.6 Test methods

The most important characteristic property of a test method is that it classifies different materials in the same way that exposure in the field would do. The test method must absolutely not allow concretes of inferior quality to be used, but at the same time must not be too restrictive.

Speaking of frost salt scaling, one of the essential features of a test method is to be able to consider the true climatic conditions. The test method should also be representative for different types of concrete compared with behaviour under practical conditions. Unfortunately, current test methods are generally verified for the practical representativeness of OPC concrete and not for other concrete types such as slag cement concrete. Obviously, the type of concrete plays a central role in frost salt scaling since it affects permeability, amount of ice formed at a given temperature and the rate of penetration of de-icing agents.

Another problem is that all standard tests do allow the concrete to become wetter and wetter after each cycle, while in practice the concrete would hardly reach a degree of saturation as much as it is seen in the laboratory tests.

However, from reproducibility and widespread acceptance points of view, CDF, SS 13 72 44 and ASTM C672 methods can be considered successful. In the following section, brief information is given about these standard frost salt scaling test methods. The specifications of the test methods are given in Appendix A.
2.6.1 CDF – (Capillary suction of De-icing solution and Freeze thaw test)

CDF is relatively new compared to the other methods being used in the world. However recent investigations have shown that this method has a very good repeatability and reproducibility (Siebel 1997). CDF method is becoming more popular especially in Europe.

Preparation and test procedure are relatively simple and the temperature cycle can be maintained very accurately. However the method is severely criticized by Lang due to its underestimating the performance of slowly hardened cements such as slag cement. According to him, it is necessary to change the storage conditions in the CDF test or to find different acceptance criteria for different kinds of cement in correlation to their performance in practice (Lang 2002). Such criticism leads the concrete technology community to question the representativeness of CDF test as well as the other methods for practice.

2.6.2 ASTM C672-92: Standard test method for scaling resistance of concrete surfaces exposed to de-icing chemicals

According to Pigeon and Pleau, the ASTM C672 test method is particularly meaningful, considering that surface scaling now represents the most common form of deterioration due to frost action. Furthermore, the conditioning of the concrete specimens and characteristics of the freezing and thawing cycles are more similar to natural exposure conditions. However the visual rating is influenced by operator’s subjectivity (Pigeon 1995).

In recent years, many investigators have used the mass of scaled-off particles as an index of surface scaling, although this practice has not been adopted as a standard. An adequate scaling resistance is considered in case that the scaled-off particles are less than 1 kg/m² after 50 cycles (Pigeon 1995).

Laroche et al. has also concluded that from the results of the laboratory tests that were performed on both field and laboratory concretes, it can be understood that frost salt scaling test procedures such as that described in ASTM 672 are not too severe and allow to distinguish with a fair degree of reliability between those concretes which are scaling resistant and those which are not (Laroche 1997).

2.6.3 SS 13 72 44, 3rd edition, Procedure A

The Boras method is quite similar to the ASTM C 672 test method, but it has many advantages. First, the freezing front progresses vertically from the top to the bottom of the specimen, which is more representative of real field conditions. The method also provides a better assessment of the surface deterioration because this assessment is based on a quantitative measurement rather than qualitative criteria described in ASTM C 672 method (Pigeon 1995).

Petersson has reported that (in a research on salt scaling resistance of Swedish bridges) there is a good correlation between the pre-testing results and the results from the continuous testing. The pre-testing therefore seems to be useful for predicting the scaling properties for the concrete used at the building site (Petersson 1997).

This method is considered to be the most suitable testing method among the Nordic countries (Kukko 1997).
2.7 **Vision for the PhD Research**

There are many theories attempting to explain frost salt scaling phenomenon. However, none of those allows predicting the behaviour of concrete in practice fully. The mechanisms are still discussed mainly on the basis of plain frost attack theories. Although there are several hypotheses trying to explain the frost salt scaling mechanisms, complete experimental support remains absent. Without a thorough description of frost salt scaling action, any theoretical or experimental study should be considered valid for the specific testing conditions.

As can be understood from the literature, there is a general consensus that concrete rich in slag shows relatively poor resistance against frost salt attack in comparison with OPC concrete. The majority of the test results corroborates this fact though there a small amount of publication indicating contrary.

It seems that the carbonation is the dominant factor in the modification of frost salt scaling of slag cement systems. Another important point is the slag content of the cement. Results of many investigations revealed that in general the higher the slag content the lower the scaling resistance of concrete (Bilodeau 1997; Stark 1997). Furthermore, carbonation increases the pore size and consequently increases the water uptake rate of cement based materials rich in slag. Chemical factors also seem to be critical in case of carbonation. There is evidence that the metastable carbonate minerals (aragonite and vaterite) might be responsible for the scaling of slag cement concrete.

In the interpretation of experimental results, problem with lack of correlation between laboratory and practice for slag cement concrete should be taken into account. In fact only full-scale practice tests are reliable. Within the scope of this four-year investigation, it was not possible to perform such a full-scale test because time was too short. To compensate this drawback partly a thorough investigation into effects on the microstructure and the freezing behaviour is carried out.

Unfortunately, to the knowledge of the thesis author, no thorough explanation has been presented what lies beneath the lower performance of concretes bearing high amounts of granulated slag. The conflicting results clearly emphasize the need of more research to clarify the influence of slag on the frost salt scaling resistance of concrete. The use of slag cement in the production of concrete elements exposed to de-icing salts should also be considered with caution.
Chapter 3

EFFECT OF CARBONATION ON SLAG CEMENT PASTE

MICROSTRUCTURE

3.1 INTRODUCTION

Slag cement and OPC concretes perform differently when subjected to carbonation. While carbonation leads to a slight densification of the microstructure in OPC concrete, the microstructure of slag cement concrete becomes coarser. The percentage of capillary pores increases, while in case of OPC it decreases. As discussed in Chapter 2 this change in microstructure is regarded essential with respect to the scaling resistance.

The main aim of this chapter is to characterize carbonated high-slag cement paste and to discuss its relationship with frost salt scaling from various points of view such as the micro-morphology, the pore structure and the micro-mechanical features. First, the carbonation mechanism as known from literature will be discussed. Subsequently a new hypothesis concerning frost salt scaling will be introduced. Finally, the results of the experimental investigation into the effect of carbonation on the slag cement paste microstructure will be presented. The investigation covers environmental scanning electron microscopy (ESEM), mercury intrusion porosimetry (MIP), X-ray diffraction and nanoindentation studies.

3.2 CARBONATION MECHANISM

There are mainly two different reactions related to carbonation in cement pastes. These are:

\[ CH + \bar{C} \rightarrow C\bar{C} + H \]  \hspace{1cm} \text{(volume expansion)} \hspace{1cm} \text{eq. 3.1}

and

\[ C - S - H + \bar{C} \rightarrow C\bar{C} + S - H + H \]  \hspace{1cm} \text{(volume reduction)} \hspace{1cm} \text{eq. 3.2}
As can be understood, the resulting volume change of the matrix depends on the amount of calcium hydroxide (or portlandite) and C-S-H. The high slag cements possess only a few percentage of calcium hydroxide, while in case of hydrated portland cement the portlandite content can be as high as 25\% (m/m). Consequently carbonation (shrinkage) of the slag cement paste leads to a reduction in the solid volume, while in OPC paste an increase occurs.

The carbonation of calcium hydroxide mainly leads to the formation of calcite with high specific volume while carbonation of C-S-H produces aragonite formation with lower specific volume. It should be noted that aragonite has a density of 2.927 g/cm\(^3\), while calcite has 2.711 g/cm\(^3\) (Wowra 2002).

In reality, there are many lime containing phases in hydrated cement, which all can be carbonated. These reactions (including the principal ones) can be divided into three groups; Carbonation of unhydrated phases, hydroxylated phases and hydrated phases. The following reactions are summarized from the work of Matala (Matala 1995).

**Unhydrated phases:**

\[ C_3S + (3-x)\overline{C} + yH \rightarrow C_xSH_y + (3-x)\overline{C} \]  
\[ C_2S + (2-x)\overline{C} + yH \rightarrow C_xSH_y + (2-x)\overline{C} \]  
\[ C_A + \overline{C} + CH + 11H \rightarrow C_xA(C\overline{C})H_{12} \]

**Hydroxylated phases:**

\[ CH + \overline{C} \rightarrow C\overline{C} + H \]  
\[ MH + \overline{C} \rightarrow M\overline{C} + H \]  
\[ 2(Na,K)H + \overline{C} \rightarrow (Na,K)_2\overline{C} + H \]

**Hydrated phases**

\[ C_xS_yH_z + x\overline{C} \rightarrow xC\overline{C} + S_yH_{z-w} + wH \]  
\[ C_AxH_z + x\overline{C} \rightarrow xC\overline{C} + A_xH_{z-w} + wH \]
Young paste is especially vulnerable for carbonation, because the permeability is high, so the hydrated cement will carbonate fast. Compared to OPC paste, slag cement paste is more vulnerable to carbonation during hydration because it hydrates slower. This vulnerability is maybe exaggerated because of the above-discussed increase in permeability for the carbonated slag cement. Therefore, in order to reduce the carbonation effects and products, slag cement should be cured as good as possible.

### 3.2.1 Carbonation shrinkage

One of the most important consequences of carbonation in slag cement paste is the carbonation shrinkage. The carbonation reaction of hydrated cement paste causes loss of structural water and consequently the shrinkage of the matrix (see eq. 3.2).

Numerous investigations have been carried out on carbonation shrinkage however few focused specifically on the carbonation shrinkage of slag cement paste. Verbeck pioneered the research on carbonation shrinkage of cement paste and reported that OPC mortar (w/c 0.54) prisms show 0.08%, 0.09%, 0.10% and 0.11% shrinkage after 120 days of carbonation at 1%, 5%, 25%, and 100% CO$_2$, respectively (Verbeck 1958). Pihlajavaara concluded that the carbonation shrinkage may be as high as 50% of the drying shrinkage (Pihlajavaara 1976). However, according to Matala, the extent to which the carbonation shrinkage affects the pore structure is unknown (Matala 1995). He concluded that because of the heterogeneous body of the cement gel, estimation of carbonation shrinkage of the nanometric scale cement gel would be inaccurate based on volumetric calculations of the loss in gel water. Groves et al (Groves 1991) reported that the carbonation of calcium hydroxide is initially more rapid than that of C-S-H gel. However, the situation reverses because of the formation of layers of carbonates on the calcium hydroxide crystal surfaces. Hence, lack of calcium hydroxide in slag cement paste should increase the rate of C-S-H carbonation further.

Carbonation shrinkage affects the frost salt scaling resistance critically especially in slag cement paste. Two essential causes could be considered regarding the inferior frost salt scaling resistance of the carbonated slag cement concretes. One cause is that in contrast to OPC concrete, the carbonation of slag cement concrete rich in ground granulated slag leads to a coarser microstructure and an increase in capillary pore space because of the dominance of reaction described in eq. 3.2.

Another cause was suggested by Stark and Ludwig which is rather poorly supported experimentally. They claimed that carbonation of hydrated cement paste bearing more than 55% granulated slag produces considerable amount of metastable carbonates as well as stable calcite. The instability of these carbonate phases under frost salt attack results in a lower frost salt scaling resistance (Stark 1997).

Carbonation shrinkage leads to lower frost salt scaling resistance of the carbonated surface layer than that of the concrete core. In order to achieve a better frost salt resistance it is therefore necessary to minimize the carbonation. In addition to well-known methods such as using low w/c ratio and proper curing, draining formwork materials are also particularly suitable (Stark 1997). The importance of carbonation in slag cement concrete surface is presented in Figure 3.1. It is clearly seen that the surface scaling can rather aggressively advance until the carbonation front is completely removed.

According to Bijen, it can generally be stated that for a certain strength and air content the resistance of concrete with granulated slag in scaling tests is initially lower, but at higher numbers of cycles the difference compared to OPC is small or the granulated slag performs even better (Bijen
An explanation for this is that the frost salt scaling resistance of non-carbonated slag cement concrete should have higher than that of non-carbonated OPC concrete. As soon as the scaled off frontier reached the non-carbonated slag cement concrete the mass scaling dramatically slows down as can be seen in typical frost salt scaling versus freezing-thawing cycles graphs (see Figure 2.6). That explains an initially high scaling rate and later on a lower scaling rate. However, it is unfortunate that in practice maintaining a slag cement concrete structure non-carbonated is hardly possible. Hence, the initially higher scaling rate is a reason not to apply slag cement for top surfaces of the roads in the Netherlands (EU 1997).

![Graph showing relationship between depth of initial scaling and depth of carbonation of slag cement concretes with and without air entrainment agent (Stark 1997).](image)

**Figure 3.1** Relationship between depth of initial scaling and depth of carbonation of slag cement concretes with and without air entrainment agent (Stark 1997).

### 3.3 A NEW HYPOTHESIS

Until now, frost salt scaling performance difference between OPC and slag cement systems could not be entirely explained. Several laboratory test results showed that slag systems have significantly less frost salt scaling resistance in case of severe surface carbonation (see also Chapter 4).

In the light of literature, a new hypothesis is proposed in this thesis concerning the lower frost salt scaling performance of (high) slag cement systems. The hypothesis draws attention especially to the weakest link of all cementitious materials, the interfacial transition zone. In this thesis, this zone is defined as the transition border between aggregate and cement paste in concrete/mortar while it is the zone between outer hydration products and unreacted clinker/slag particles in a cement paste. Due to carbonation, especially in high slag cement pastes, this zone becomes wider and weaker. It leads to an increased liquid transport rate, to create larger pockets for freezing and eventually to a lower tensile strength of the microstructure which is susceptible to scaling. According to this hy-
pothesis, the interfacial transition zone critically determines the frost salt scaling resistance of cement-based materials.

The hypothesis suggests that the reason why low-slag content cement or OPC pastes suffers less from frost salt attack can be further explained by the interfacial zone concept. For instance, after carbonation attack, the decrease of scaling resistance in low-slag content systems can be expected much less than in the ones rich in slag when the cement fineness is comparable (Figure 3.2). This is because of the fact that the amount of slag-matrix interfacial zones in low-slag cement paste (which could be negatively affected by carbonation) is considerably less than the one rich in slag. Obviously, one should not omit the positive effect of increased clinker portion by using less slag. Increased clinker portion means increased amount of calcium hydroxide liberation which is favourable for the execution of eq. 3.1.

In case of carbonated OPC systems, minimum amount of weak interfacial zones is found because of well-integrated structures of unreacted clinkers and hydration products (Figure 3.3). Carbonation attack causes significant porosity reduction because of the dominant activity of the reaction described in eq. 3.2.

Figure 3.2 Microstructure of mortars containing cement with 25% (left) and 75% (right) slag. Figures in the lower row present the extracted clinker and unreacted slag particles from the photomicrographs. W/c = 0.45.
3.4 EFFECT ON PASTE MICROMORPHOLOGY

3.4.1 Experimental data

Materials and sample preparation

Slag cement with the slag content of 67% (CEM III/B 42,5 N HSR LH) was used from ENCI cement factory. The chemical and physical properties of the cement are given in Table 3.1. The paste mixture with w/c ratio of 0.45 was prepared and ordinary tap water was used. The mixing sequence was 2 minutes low and 2 minutes high speed mixing with a commercial HOBART mixer. Then the paste mixture was poured into a 500cc plastic bottle and vibrated for 15 seconds with a vibrating table. The bottle was rotated at a speed of 4 rotations per minute for 24 hours at the room temperature and placed in water bath until the day of sample preparation for environmental electron microscopy (ESEM) studies.

At the age of 56 days, the paste sample was cut into certain forms in order to be used in the experiments. 20×30×40 mm³ paste specimens were cut for making the polished sections. Polished sections were divided into two groups. One group was kept in the stove for 45 minutes at 35°C then immediately vacuum impregnated by low viscosity epoxy while the paste specimens were still non-carbonated. The next day specimens were grinded with no. 1200 grinding paper roll (roll#3) on the thin sectioning machine and polished with 6µm, 3µm, 1µm and 0.25µm diamond paste on a lap wheel. The second group was first ground with roll#3 then put into the carbonation chamber of 3% CO₂ at 20°C and 50±2 % relative humidity condition for 1 week.

Figure 3.3 Photomicrograph of a clinker particle consisting of C₃S and C₃A/C₄AF. Hydration border is visually strong and the clinker is integrated with the hydration products.
A DBT Diamond Roller and Grinder/86 thin sectioning machine was used for the preparation of the perfectly flat polished sections of the specimens. Low viscosity epoxy with special yellow colour epo-dye was used for distinguishing the pores and the matrix under fluorescent light of optical microscope during preparation and later for ESEM observations. Due to low atomic number of pore-filling epoxy, it does not scatter electrons and appears black under ESEM.

Table 3.1 Physical and chemical properties of CEM III/B 42,5 N HSR LH.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Physical Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>% 45.0</td>
</tr>
<tr>
<td>SO₃</td>
<td>% 3.25</td>
</tr>
<tr>
<td>SiO₂</td>
<td>% 27.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>% 12.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>% 1.27</td>
</tr>
<tr>
<td>Strength of standard mortars</td>
<td></td>
</tr>
<tr>
<td>2 days (MPa)</td>
<td>12.1</td>
</tr>
<tr>
<td>7 days (MPa)</td>
<td>32.7</td>
</tr>
<tr>
<td>28 days (MPa)</td>
<td>53.2</td>
</tr>
<tr>
<td>Blaine (m²/kg)</td>
<td>376</td>
</tr>
</tbody>
</table>

3.4.2 Results and discussion

The carbonated and non-carbonated slag cement pastes were examined by the backscattered electron mode of environmental scanning electron microscope. In Figure 3.4 and Figure 3.5 the non-carbonated paste specimens are presented. Black areas are the porosity. Unreacted slag particles can be seen as light grey areas. Unreacted clinker particles are even lighter. The transition zone between unreacted cementitious materials and reaction products are dense and mostly continuous. Especially the clinker phases are very well interconnected to the reaction products (matrix).

The situation is quite different for the carbonated slag cement paste. The carbonated slag cement paste specimens are presented in Figure 3.6 and Figure 3.7. The coarsening of the pore structure can be easily seen at 1000 times magnification. The transition zone between unreacted particles and reaction products are very wide and open. The bond strength in these zones could be assumed much weaker compared to the non-carbonated slag cement paste specimens. As can be seen in the figures, carbonation products make the system extremely open and vulnerable. Moreover, not only the pore system becomes coarser due to carbonation, but also more interconnected. This can be seen in Figure 3.8, the B/W threshold images of Figure 3.4 and Figure 3.6. The resulting porosity is up to three times of the non-carbonated paste in certain locations and leads the moisture content during frost salt attack likely to be higher. This should increase the risk of early deterioration due to frost salt attack. On the other hand, as a consequence of carbonation the tensile strength of the skin is likely to decrease significantly since the bond quality between the separate phases in the system and the total cross-sectional area diminishes. It is argued that the change in the interface between unreacted slag particles and reaction products due to carbonation plays an important role on the frost salt durability, both because of the better access of moisture and of the decrease of bond. Hence, frost salt resistance of the system is lowered.

This argument will be still valid from the chemical point of view considering the suggestion of Stark and Ludwig (Stark 1997). By the dissolution of vaterite and aragonite (which can be found ample in this transition zone), the contribution of those carbonation products to the bonding strength -if any- will be disappeared.
Figure 3.4 Photomicrograph of a 56-day old non-carbonated slag cement paste at 1000 times magnification.

Figure 3.5 Photomicrograph of a 56-day old non-carbonated slag cement paste at 2000 times magnification.
Figure 3.6 Photomicrograph of a 56-day old carbonated slag cement paste at 1000 times magnification.

Figure 3.7 Photomicrograph of a 56-day old carbonated slag cement paste at 2000 times magnification.
Another evidence, which indicates that the generally weaker structure of interfacial zone is responsible for the reduction of frost salt scaling resistance, is presented in Figure 3.9. In this figure, a drying shrinkage crack in a non-carbonated paste can be seen clearly. The crack path travels from one point to another by taking the route of the interfacial zones, which are presumably the weakest points in the system.

Figure 3.9 The path of drying shrinkage cracking passing through the interfacial zone between un-reacted slag particles and hydration products.
3.5 **Effect on Concrete Micro-morphology**

3.5.1 Experimental data

Slag cement with the slag content of 67% (CEM III/B 42.5 N HSR LH) was used from ENCI cement factory (see Table 3.1 for the properties). Concrete specimens with w/c ratio of 0.45 were prepared. The mixture properties of the concrete sample are given in Table 3.2.

<table>
<thead>
<tr>
<th>w/c</th>
<th>Cement</th>
<th>Water</th>
<th>Sand*</th>
<th>Coarse Agg*</th>
<th>SP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>350</td>
<td>159</td>
<td>951</td>
<td>915</td>
<td>1.75</td>
</tr>
</tbody>
</table>

* Commercial river sand and river gravel Dmax=16mm

b Cugla SL-01 commercial superplastisizer

After 28 days of water curing, the concrete specimens were cut into specimens in order to be used in the experiments. For backscattered electron (BSE) microscopy 20×30×40 mm³ concrete specimens were cut and polished. The BSE specimens were divided into two groups. One group was kept in the stove for 45 minutes at 35°C then immediately vacuum impregnated by low viscosity epoxy while the specimens were still non-carbonated. Vacuum process was approximately half an hour before the impregnation took place. The next day the specimens were grinded with roll#3 (no.1200 sandpaper eqv.) on the DBT Diamond Roller and Grinder/86 thin sectioning machine and polished with 6µm, 3µm, 1µm and 0.25µm diamond paste on a lap wheel. A typical polished section is shown in Figure 3.10.

The second group was first ground with roll#3 then put into the carbonation chamber of 3% CO₂ at 20°C and 50% relative humidity condition for 1 week before epoxy impregnation and polishing. Additionally, carbonated and non-epoxy impregnated specimens were also examined in order to see a better 3D-like image of the surface.

The effect of pure drying was observed on a non-epoxy impregnated polished sections put in the 0% CO₂ freeze-dryer for 9 days. Carbonated and non-carbonated broken surfaces were examined also with gaseous state electron (GSE) detector. The conditions in ESEM chamber were 21°C, 0.4 torr water pressure for BSE and 21°C, 2.5 to 3.5 torr for GSE modes.

![Figure 3.10 A typical polished section for the backscattered electron microscopy.](image-url)
3.5.2 Results and discussion

The carbonated and non-carbonated slag cement concretes were examined by BSE and GSE detector modes. In Figure 3.11 the non-carbonated specimens are presented. Black areas represent the porosity. Unreacted slag particles can be seen as light grey areas. Unreacted clinker particles are even lighter. The transition zones between unreacted materials (aggregates and unreacted slag) and reaction products are dense and mostly continuous. Especially the clinker phases are very well interconnected to the reaction products.

The carbonated slag cement concrete specimens are presented in Figure 3.12. Coarsening of the pore structure can be easily seen at 250 times of magnification. Identical to the situation in slag paste specimens the transition zones between unreacted particles and reaction products are very wide and open. However, in case of concrete, aggregate-mortar interfacial transition zone is affected by carbonation. In Figure 3.12, significant coarsening is observed in the zone of 10 to 50 μm from the coarse aggregate surface.

![Figure 3.11 BSE images of a 28-day old non-carbonated slag cement concrete. (S: unreacted slag particle, A: aggregate, C: unreacted clinker particle).](image)

The increase in interconnectivity of the pore structure due to carbonation also seems to be critical for concrete. The resulting pore structure may easily allow brine to penetrate to the vicinity of aggregate-matrix bonding location. This increases the possibility of a particular coarse aggregate to be scaled off during the frost salt attack and expose the inner surface to the further progress of damage. It is visually quite obvious that as a consequence of carbonation the tensile strength of the skin decreases significantly since the bond quality between the separate phases in the system diminishes. The observations in the current experimental study proposes that in case of severe carbonation, aggregate-matrix interfaces play an essential role in decreasing the general bonding quality and consequently in lowering the frost salt resistance of the system.

In Figure 3.13, Figure 3.14 and Figure 3.15, the same carbonated concrete microstructure is presented with BSE detector. However in this case, no epoxy impregnation was performed. By this method, a somewhat improved 3-D effect was obtained in order to observe the carbonation attack.
Figure 3.12 BSE images of a 28-day old carbonated slag cement concrete at various magnifications.

Figure 3.13 BSE photomicrograph of the carbonated concrete microstructure (without epoxy-impregnation). 1000 times magnification.
Figure 3.14 BSE photomicrograph of the carbonated concrete microstructure (without epoxy-impregnation). 2000 times magnification. (S: Unreacted slag, A: Aggregate).

Figure 3.15 BSE photomicrograph of the carbonated concrete microstructure (without epoxy-impregnation). 4000 times magnification.
In Figure 3.16 the GSE detector mode images of the carbonated and non-carbonated concrete specimens are presented. These pictures again clearly reveal that the density of the cement paste was significantly diminished by the carbonation. The interfacial zones between unreacted slag particles and hydration products are relatively weaker and wider.

![Figure 3.16 GSE microscopy images of non-carbonated (left) and carbonated (right) specimens.](image)

The concrete specimens in Figure 3.17 were prepared without epoxy impregnation. Drying cracks are visible in 2000 times magnified image (Figure 3.17 right). It is realized that the patterns of the cracks or the openings are different in “only dried” and “dried/carbonated” specimens (compare Figure 3.12 vs. Figure 3.17). As can be seen, pure drying did not have a major influence on the microstructure with regard to the interfacial zones.

![Figure 3.17 Effect of drying on the microstructure of slag cement concrete specimens (BSE images). White arrow shows the drying shrinkage cracks of an AFm formation.](image)
3.6 Effect on Pore Structure

3.6.1 Introduction

Porosity and pore size distribution are regarded as the two most important parameters with respect to freezing-thawing resistance of cementitious materials. Other parameters such as critical pore diameter and interconnectivity are also believed to be important for transport properties of the cementitious materials and eventually for freezing-thawing resistance. In this study the effect of carbonation on the pore structure of the slag systems was investigated. In order to study their porous properties, mercury intrusion porosimetry technique was used. Even though this technique does not yield highly accurate results, it is considered reliable for comparison purposes and is still one of the most commonly used experimental techniques (Diamond 2000; Ye 2003).

It is a generally accepted fact that carbonation decreases the frost salt scaling resistance of slag cement concrete drastically. Hence, it seems important to focus on the effects which influence the rate of carbonation. According to the recent researches, it is suggested that it is the pore size distribution, which controls the rate of carbonation. Results from the work of Wee et al. imply that the distribution of the pores larger than 450 Å in radius (0.09 microns in diameter) determines the rate of carbonation in the system (Wee 1999). They claim that in general the higher the portion of the small pores the higher the resistance to carbonation. Obviously in case of slag cement paste, the calcium hydroxide content is another important factor for the carbonation rate.

Many researchers have worked on the pore structure of slag cement mortar and concrete. Generally the studies were performed by mercury intrusion porosimetry. Majority of the studies conclude that slag cement systems have finer pore structure and lower total porosity with respect to OPC (Roy 1983; Roy 1986; Malek 1989; Hakkinen 1993; Sulapha 2003; Zhang 2004). Unfortunately, the effect of carbonation on the pore structure of slag cement systems has been investigated by far less number of researchers (Matala 1995; Utgenannt 2004). According to these researchers, carbonation decreases the micro-capillary (pore \(d<0.1\, \mu m\)) and leads to an increase in macro-capillary (\(0.1\mu m < d<1\mu m\)).

3.6.2 Experimental

Two types of cement pastes with w/c 0.45 were prepared in order to study the pore size characteristics in carbonated and non-carbonated conditions. The cements used were a CEM III/B 42,5 N HSR LH and a CEM I 32,5 R O PC. The chemical and physical properties of the cements are given in Table 5.8. The specimen preparation was identical to the ones in 5.5.2.

At the age of 56 days, the paste specimens were cut into small pieces (around 0.5 cm\(^3\)) in order to be used in the experiments. For each cement type, two groups were created; non-carbonated and carbonated. The non-carbonated group was put in the freeze-dryer (0% CO\(_2\) and 0% R.H.) until the specimens were completely dried. For this, approximately 1 week was needed. The carbonated specimens were put into the carbonation chamber of 3% CO\(_2\) at 20°C and 50±2 % relative humidity condition until the depth of carbonation was constant. Then the carbonated specimens were put in the freeze dryer in order to remove the remaining moisture.

The difference between the relative humidity conditions in freeze dryer (0% R.H.) and carbonation chamber (50% R.H.) was inevitable. In order to remove the moisture completely from the non-carbonated specimens without letting them carbonated a condition of 0% R.H. was needed. For the carbonated specimens, having 0% R.H. was technically as well as practically not possible since
a certain level of humidity was needed for the carbonation reactions for a long period enough to carbonate the specimens entirely.

### 3.6.3 Results

The cumulative intrusion volumes versus pore diameter and derivative intrusion volumes versus pore diameter MIP graphs are presented in Figure 3.18 and Figure 3.19. The results revealed that carbonation decreases the total intrusion porosimetry in slag cement paste and OPC paste with w/c ratio of 0.45. According to the test results, the decrease in total porosity of slag cement paste was somewhat higher than that of OPC paste.

![Figure 3.18 Effect of carbonation and cement type on cumulative intrusion volume of the pastes with w/c=0.45.](image)

In OPC paste, the first critical pore size peak could be observed around 0.7-0.8 μm and second critical pore size peak at about 0.045 μm. After the carbonation of OPC paste, a significant drop occurred in the intrusion volume of pores between 0.01-0.1 μm while a slight increase in the range of 0.1-0.5 μm. In slag cement paste, a large increase was occurred in the intrusion volume of pores bigger than 0.1 μm in diameter due to carbonation. A volume change below the pore diameter of 0.1 μm resembled to the measurements of carbonated OPC paste. This re-structuring of the porous system is quite likely to be because of the calcium hydroxide content difference between slag cement and OPC pastes. Calcium hydroxide carbonation decreases the volume of very small pores by blocking them with calcite formation. In slag cement paste the situation is mostly the carbonation of C-S-H causing significant coarsening in the system due to the lack of calcium hydroxide crystals in the hydrated slag cement paste.

These two types of cement pastes were also examined under ESEM/BSE detector. The photomicrographs of the cement pastes are shown Figure 3.20, Figure 3.21, Figure 3.22 and Figure 3.23.
Figure 3.19 Effect of carbonation and cement type on derivative volume of the pastes with w/c = 0.45.

Figure 3.20 Photomicrograph of non-carbonated 56-day old slag cement paste with w/c 0.45.
Figure 3.21 Photomicrograph of carbonated 56-day old slag cement paste with w/c 0.45.

Figure 3.22 Photomicrograph of non-carbonated 56-day old OPC paste with w/c 0.45. K: clinker, CH: portlandite, AFT: ettringite, IHP: inner hydration products.
3.6.4 Discussion

Significant differences have been observed in both pore characteristics and micromorphology of the slag cement paste and OPC paste in carbonated and non-carbonated conditions (w/c = 0.45).

The current investigation on the OPC and slag cement pastes implies that carbonation leads to decrease in total intrusion volume of both cement paste types. However, more essential information was obtained from the pore size distribution data of the cement pastes. In OPC paste major volume decrease happens in the micro-capillaries (0.01–0.1 μm). A relatively minor volume increase can be noticed in the range between 0.1 and 0.5 μm. The result is visually dense and integrated microstructure according to the ESEM observations. Probably, due to sufficient amount of calcium hydroxide in the system, carbonation reactions mainly produce higher volume calcite minerals blocking the capillaries.

However, in slag cement paste it is the volume increase in macro capillary zone (0.1-1μm), which is the most remarkable. The MIP findings regarding the coarsening of slag cement paste by carbonation is in compliance with the findings of the other researchers like Bier et al. and Matala (Bier 1987; Matala 1995).

Due to scarce amount of calcium hydroxide in especially hydrated cement paste bearing high amount of granulated slag, most of the carbonation reactions take place in the binder portion of the system. With the progress of eq. 3.2, the carbonation shrinkage in slag cement makes the cement paste more open and less strong thus more vulnerable to scaling and that carbonation proceeds faster than in OPC. It is reasonable to suggest that these observations can be explained by the reduced availability of free lime in slag cement.
3.7 EFFECT ON MINERAL STRUCTURE

3.7.1 Introduction

Effect of carbonation on the mineralogical structure of non-carbonated and carbonated slag and OPC pastes was investigated. The research goal of this experimental study was to characterize the carbonate phases in cement paste with high slag content and OPC paste and investigate the effects of accelerated carbonation and natural carbonation.

3.7.2 Experimental data

Slag cement and OPC paste specimens were prepared identical to the ones described in section 3.4.1. Two types of curing regimes were selected for the XRD-diffraction analysis. In the first curing regime the specimens were cured for 56 days under water. Thereafter, the specimens were carbonated for 3 weeks in the 3% CO\textsubscript{2} chamber. The second curing regime was exclusive for slag cement pastes and covers 2 months of water curing. After the initial water curing, the slag cement paste specimens were cut into flakes with 1-2 mm in thickness. Following the preparation, the specimens were exposed to lab air CO\textsubscript{2} concentration for 4 months.

For the XRD analysis of non-carbonated and carbonated slag cement and OPC pastes, a Philips PW3710 diffractometer with Cu tube and Ni filter was used. The 2\textdegree\theta diffraction range was from 0 to 80\degree.

3.7.3 Results and discussion

X-Ray diffractograms of the cement pastes with accelerated carbonation are presented in Figure 3.24, Figure 3.25, Figure 3.26 and Figure 3.27.

Comparison of slag cement and OPC pastes XRD data implies that there is hardly any difference in carbonation products of these two cement pastes. In both pastes, the primary carbonation product is calcite. In the second order, aragonite and vaterite can be observed. In OPC paste, calcium silicate peaks also exist in major.

Considering the results of current investigation, it is not entirely possible to confirm the findings of Stark and Ludwig while similar findings were found as Utgenannt and Matala (Matala 1995; Utgenannt 2004). Stark and Ludwig found that in carbonated OPC paste only calcite crystals were present and in slag cement paste overwhelmingly aragonite and vaterite formations (Stark 1997). They attribute this observation to the possibility of carbonation of portlandite in OPC paste and carbonation of C-S-H and/or AFm, AFt phases in slag cement paste. However, quite possibly the carbonation of C-S-H and AFm/AFt phases takes place in the OPC paste as well. In the current project since the main carbonation products in the pastes are similar, -from only chemical point of view- the frost salt scaling performances of those two cements would be expected at the same level while in reality it is not the case. However the chemical effect should not be entirely excluded since there are good indications in microscopy studies that the chemical interaction could be very important. The reason why OPC paste performs better against frost salt attack might be because of the different portions of calcium silicates, portlandite and carbonation products in these two types of pastes.
Figure 3.24 X-ray diffractogram of non-carbonated slag cement paste w/c 0.45.

Slag cement paste (non-carbonated)

$P$ : portlandite
$MA$ : $Ca_5MgAl_2Si_{16}O_{90}$
$C$ : calcite

Figure 3.25 X-ray diffractogram of accelerated carbonated slag cement paste w/c 0.45.

Slag cement paste (3% CO$_2$ carbonated)

$C$ : calcite
$V$ : vaterite
$A$ : aragonite
Figure 3.26 X-ray diffractogram of non-carbonated OPC paste w/c 0.45.

Figure 3.27 X-ray diffractogram of accelerated carbonated OPC paste w/c 0.45.
3.7.4 Effect of accelerated carbonation

The effect of accelerated carbonation was also studied in the framework of this chapter. In Figure 3.28 a comparison is presented for natural (laboratory air) carbonation versus accelerated carbonation in high CO$_2$ concentration.

Figure 3.28 XRD diffractogram comparison of 4 months in laboratory air (upper graph) and 3 weeks in 3% CO$_2$ (lower graph) carbonation of the identical slag cement pastes with w/c 0.45.

C : calcite
V : vaterite
A : aragonite
P : portlandite
From the results, it can be seen that both carbonation rates produce same carbonate phases, namely vaterite, aragonite and calcite. However, the semi quantitative analysis shows that the amount of these phases is considerably different. In lab carbonated paste sample, significant vaterite peaks are visible. It is quite interesting that even after 6 months of lab carbonation there are still some portlandite peaks available, indicating its slow carbonation rate. On the contrary, in 3% CO$_2$ carbonated paste specimens, portlandite could not be traced at all. In this sample calcite is the dominant mineral while vaterite is the secondary. It is a possibility that the metastable minerals were transformed into calcite during the accelerated carbonation as also suggested by Lang and Sylla, and Utgenannt (Lang 2001; Utgenannt 2004).

### 3.8 Effect on micro-mechanical properties

#### 3.8.1 Technical background

The electron microscopy and the mercury intrusion porosimetry results revealed that carbonation causes remarkable coarsening of the slag cement paste microstructure. The visual findings from the electron microscopy imply that there could be a significant decrease in tensile strength of the slag cement paste which should increase the vulnerability of the concrete surface against the attack of frost and de-icing salts.

A number of researchers reported the strength sensitivity of slag cement-based materials to carbonation (Manns 1968; Smolczyk 1986; Li 1998; Chi 2002). Among these researchers, only Manns and Wesche, and Chi et al. investigated the effect of carbonation on the tensile strength of slag cement-based materials. Chi et al. found that the ø10×20 cm$^3$ concrete specimens with the carbonation depth of 0.8 cm had approximately 8% higher splitting tensile strength at 28 days compared to the non-carbonated ones. However it is not entirely possible to accept these results as the effect of carbonation on splitting tensile strength because a depth of D/12 is affected by pure compressive stress which is 0.83 mm in this experimental study (Copuroglu 2001). Manns and Wesche investigated the effect of carbonation on the rupture modulus of the high-slag (82% slag m/m) cement mortars with w/c ratio of 0,50. They concluded that the higher the degree of carbonation the lower the rupture modulus of high-slag cement mortars. They also observed that rupture modulus of OPC and low-slag cement mortars were not negatively affected by the carbonation (Manns 1968).

Tensile strength of a material seems to be an essential indicator of the frost salt scaling resistance of a particular material. However, simply considering the global tensile strength of the material may not be an appropriate approach to the problem since the tensile strength depends on the strength of the weakest link in the specimen under tensile stress (see Figure 3.29). In case of frost salt scaling the picture is a bit more complex where the micro-mechanical properties of the phases in different locations determine the scaling resistance throughout the material surface (Figure 3.30). Therefore assessment of local micro-mechanical properties seems to be much more realistic than the evaluation of global tensile strength with respect to the frost salt scaling resistance of a particular material.

A technique called nano-indentation is a useful tool for measuring hardness and elastic modulus of microscopical phases of the materials. With this method, the mechanical properties can be determined directly from indentation load and displacement measurements without the need to image
the hardness impression. With high-resolution testing equipment, this facilitates the measurement of properties at the micrometer and nanometer scales (Oliver 2004).

This method was developed by Oliver and Pharr to measure the hardness and elastic modulus of a material from indentation load-displacement data obtained during one cycle of loading and unloading (Oliver 1992). The tensile strength cannot be measured directly but could be estimated by obtaining the elastic modulus of the phases. The elastic modulus can be calculated by the following formula:

$$\frac{1}{E_s} = \frac{(1 - \nu_s^2)}{E_s} + \frac{(1 - \nu_i^2)}{E_i}$$  \hspace{1cm} \text{eq. 3.11}

where, $\nu_s$ is the Poisson’s ratio of the sample, $\nu_i$ is the Poisson’s ratio of the indenter (0.07), $E_s$ is the Young’s modulus of the sample and $E_i$ is the Young’s modulus of the indenter (1141 GPa).

Figure 3.29 Schematic description of cracking of cement paste under global tensile stress.

Figure 3.30 Schematic description of the cracks induced by the cracking of external ice layer (according to glue-spall theory).
A schematic description of a typical indentation curve and impression on a cement paste are given in Figure 3.31 and Figure 3.32, respectively.

![Figure 3.31 An ideal indentation load-displacement curve showing important parameters (Oliver 1992). $P_{\text{max}}$: maximum load, $h_{\text{max}}$: maximum displacement, $S$: elastic unloading stiffness.](image)

As it was mentioned earlier, nano-indentation technique does not allow direct measurement of tensile strength. Therefore an estimation of $1/10000 \ E$ was assumed to be a reasonable approach for the tensile strength values of the cement paste phases.

![Figure 3.32 A typical nano-indentation impression on the slag cement paste.](image)
3.8.2 Experimental data

The effect of carbonation on the micro-mechanical properties of CEM III/B 42.5 N HSR LH and CEM I 32.5 R pastes with w/c ratio 0.45 were investigated. The paste mixtures were prepared identical to the ones described in section 3.4.1. After the preparation the specimens were kept at 20°C, in 95% R.H. environment for 1 year. At the end of the curing period, half of the specimens from each cement paste series were carbonated in 3% CO₂ at 20°C, in 55% R.H. chamber for 2 weeks (see Table 3.3). After the carbonation period, the specimens were grinded with grade #1200 and #4000 sand papers and polished with 6 μm, 3 μm, 1 μm and 0.25 μm polishing paste on a lapping table. Finally the specimens were soaked into the ultrasonic bath to remove the polishing paste and other particles away. The quality of the indentation surface was checked by optical microscopy.

Table 3.3 Curing regimes of the paste specimens used in the nano-indentation study.

<table>
<thead>
<tr>
<th>Paste (w/c 0.45)</th>
<th>Curing</th>
<th>Carbonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 32.5 R</td>
<td>1 year at 20°C, 95%</td>
<td>3% CO₂ at 20°C, 55% R.H.</td>
</tr>
<tr>
<td>CEM I 32.5 R</td>
<td>1 year at 20°C, 95%</td>
<td>-</td>
</tr>
<tr>
<td>CEM III/B 42.5 N HSR LH</td>
<td>1 year at 20°C, 95%</td>
<td>3% CO₂ at 20°C, 55% R.H.</td>
</tr>
<tr>
<td>CEM III/B 42.5 N HSR LH</td>
<td>1 year at 20°C, 95%</td>
<td>-</td>
</tr>
</tbody>
</table>

The nanoindentation apparatus used was Nanoindenter XP using a diamond berkovich tip (MTS Systems Corporation). The load range is 0-10 N, and the resolutions are 50 nN and 0.04 nm for load and displacement, respectively.

3.8.3 Results and discussion

The typical nano-indentation results of the non-carbonated and the carbonated slag cement pastes are presented in Figure 3.33 and Figure 3.34. In non-carbonated slag paste two distinct phases were identified. In view of the findings in the literature, mainly hydrated cement paste and possibly the unreacted slag/clinker particles were obtained.

The effect of carbonation on the microstructure of slag cement paste was also characterised by the nano-indentation results. In comparison to the non-carbonated slag cement paste a different phase was identified. This new phase had a lower elastic modulus than the lower limit for C-S-H as suggested by Constantinides and Ulm and showed similar characteristics as Ca-leached C-S-H ranging between 12.1 to 19.5 GPa.

The collective nano-indentation results of carbonated and non-carbonated slag cement pastes are presented in Figure 3.35 in the form of histogram. The results represent 18 indentations per sample. It can be clearly seen that carbonation causes significant reduction of the elasticity modulus in the 20-45 GPa zone where it corresponds to the matrix and a dramatic increase of the zones having elasticity modulus of 0-20 GPa.

The findings in the electron microscopy and mercury intrusion porosimetry investigations are supported by the results presented in this experimental study. It was observed that carbonation shrinkage significantly reduces the elastic modulus and most probably the tensile strength of the carbonated slag cement paste and this inevitably decreases the frost salt scaling resistance.
Figure 3.33 Typical load-displacement curves of 1 year-old non-carbonated slag cement paste.

Figure 3.34 Typical load-displacement curves of 1 year-old 3% CO₂ carbonated slag cement paste.
Figure 3.35 Summary of the 1 year-old slag cement paste (w/c 0.45) nano-indentation test results. NC: non-carbonated, CAR: carbonated.

Figure 3.36 Summary of the 1 year-old OPC pastes (w/c 0.45) nano-indentation test results. NC: non-carbonated, CAR: carbonated.
Nano-indentation test was also carried out on 1 year-old carbonated and non-carbonated OPC pastes (w/c = 0.45). The results are summarized in Figure 3.36. It was seen that carbonation is favourable with respect to the elastic modulus and tensile strength of OPC paste. The histogram of the nano-indentation results in Figure 3.36 shows that the OPC paste possesses 40% of the total phases in 0-20 GPa zone. This is reduced to approximately 10% after the carbonation. The carbonation led to a 100% increase of the amount of phases in the 20-45 GPa zone compared to the non-carbonated OPC paste. Overall elastic modulus and tensile strength are increased significantly and consequently a resistant microstructure is achieved by carbonation.

3.9 FROST SALT ATTACK ON THE MICROSTRUCTURE OF CARBONATED SLAG CEMENT PASTE

3.9.1 Introduction

In sections 3.3 and 3.4, it was hypothesized that one of the factors influencing the frost salt scaling resistance of carbonated slag cement pastes might be the interfacial zones in the slag cement pastes and aggregate-matrix interfacial transition zones in mortars and concrete materials. In this study, the intention was to observe the crack pattern and morphological changes in the carbonated slag cement paste due to frost salt attack. The main question was whether the weakened transition zones in carbonated slag paste is responsible for the frost salt scaling, at least up to a certain extent.

3.9.2 Experimental data

The same slag cement, a CEM III/B 42,5 N HSR LH, was used in the experimental study. The specimen preparation method was identical to slag paste specimens previously described in the current chapter. 24 hours after casting, the sample was demoulded and placed in water bath until the specimen age of 2 months. At the age of two months, the sample was cut to roughly 1-2 mm thin flakes for the carbonation and drying period of 4 months at 20°C and 50±2 % relative humidity lab conditions. At the end of the carbonation and drying period, a thin sample was put in 3% NaCl solution and exposed to 1 cycle frost salt action between -20°C and +20°C. The reason of applying only 1 cycle was the disintegration of the carbonated specimens even after two freezing thawing cycles and making impossible to observe cracks. At the end of thawing, the sample was removed from brine and put in demi water for a period of time in order to dissolve salt crystals remained on the surface of the sample.

After the conditioning, the sample was observed by large field detector of the ESEM.

3.9.3 Results and discussion

The microstructure of 4 months laboratory air carbonated slag paste can be seen in Figure 3.37, Figure 3.38, Figure 3.39 and Figure 3.40. The carbonation-drying shrinkage cracks of very thin slag paste specimens are visible. In addition, hexagonal portlandite minerals still exist even after 4 months of lab carbonation supporting the findings in the XRD analysis. Small amount of ettringite crystals were encountered as well.
In Figure 3.40 an extreme case for the widening of transition zone between an unreacted slag particle and hydration products is seen clearly. The widening is about 1-2 μm.

The condition of carbonated slag paste sample after 1 frost salt cycle attack is presented in Figure 3.41, Figure 3.42 and Figure 3.43.

In Figure 3.41 the cracks generated by the frost salt attack are shown. The crack paths follow a transition zone and pass through the hydration products to another slag/matrix interface. According to the hypothesis, the crack should propagate through the freezing thawing cycles until certain amount of mass becomes de-bonded from the main part. In case of concrete, the cracks will also follow the aggregate-matrix transition zone and aggravate the degradation. The slag-matrix transition zones apparently act as small chains to connect aggregate-matrix transition zones.

Figure 3.37 Condition of C-S-H formations in slag cement paste after 4 months of laboratory carbonation.

Figure 3.38 Portlandite formations in 4 months naturally carbonated slag cement paste.
Figure 3.39 Needle-like formations (possibly AFt) in 4 months naturally carbonated slag cement paste.

Figure 3.40 Effect of carbonation on the interface between unhydrated slag and hydration products.

Figure 3.41 Damage pattern in naturally carbonated slag cement paste created by frost salt attack. 2000 times magnification
Above-mentioned hypothesis is further supported by the following micro images. The cracks are connecting the individual slag-matrix transition zones. The pattern is of course highly dependent on the factors; i.e. degree of carbonation, amount of unreacted slag and degree of pore interconnectivity.

Figure 3.42 Damage pattern in naturally carbonated slag cement paste created by frost salt attack. 1000 times magnification.

Figure 3.43 Damage pattern in naturally carbonated slag cement paste created by frost salt attack. 1000 times magnification.
3.10 CONCLUSIONS

With the used materials and methods in this chapter, evidence has been presented that carbonation is significantly responsible for the poor frost salt scaling of cement-based materials rich in slag.

According to the observations, severe scaling of slag cement paste is likely to be caused not only by the increased porosity and easier brine uptake, but also by the debonding of the hydration products from unreacted remaining slag particles in the cement paste due to the decalcification and carbonation shrinkage. It has been found that due to carbonation along with the pore-structure coarsening, the interfacial zones between aggregate/unreacted slag particles and the hydration products widen. The nano-indentation analysis clearly revealed that carbonation decreases the elastic modulus and hardness of the C-S-H phases significantly. This would consequently lead to a poor frost salt scaling resistance because of a decrease in tensile strength.

The experimental findings were found to be supportive of the new hypothesis on the frost salt scaling.
Chapter 4

EFFECT OF CURING CONDITIONS AND Ca(OH)$_2$ ADDITION ON FROST SALT SCALING OF SLAG BASED MATERIALS

4.1 EFFECT OF CURING CONDITIONS

4.1.1 Technical background

Slag cement concrete appears to be more sensitive to curing than OPC with the same workability and w/c ratio. This is due to the lower rate of hydration and increase in permeability when carbonated, where for OPC it is the opposite. Consequently, slag cement concrete is more vulnerable to degradation by de-icing salts (Bijen 1998). It was reported that when the concrete is designed with an identical strength development at young age, the differences in frost salt scaling resistance between OPC concrete and concrete with granulated slag would be smaller. For instance, Wiebenga, showed that during the first freezing-thawing cycles the slag cement concrete shows behaviour similar to the concrete with OPC. According to him the difference would be expected to be smaller when curing is prolonged (Wiebenga 1985).

Apart from carbonation and hydration rate, the effect of the curing media is also believed to be important on frost salt scaling resistance of slag cement mortars and concrete. Stark and Ludwig studied the effect of the quality of curing water and unexpectedly found that the harder the curing water the higher the salt scaling of slag cement and OPC concretes since they expected high scaling in soft water because of the greater calcium hydroxide extraction from the cementitious system (Stark 1997).

4.1.2 Experimental data

Introduction

Frost salt scaling tests were done on mortars. Even though it seems that frost salt scaling testing on concrete specimens is more representative for the site concreting, mortar testing is technically easier and economical, however yet non-standardized. For the matter of comparison, mortars are also
believed to be suitable according to many researchers (Browne 1976; Peterson 1995; Girodet 1997).

In this study, two aspects of curing of cementitious materials are especially considered, which may have crucial effects on salt scaling resistance - carbonation and curing media.

Materials

CEM III/B 42.5 N HSR LH slag cement, which had a slag content of 68% was used in the mortar mixtures. Chemical and physical properties of the cement are given in Table 4.1.

$4 \times 4 \times 16$ cm$^3$ standard mortar bars were prepared according to EN 196-1 (EN 1994), keeping the w/c ratio in the order of 0.50 for all mortars. The mortar forms were vibrated for 40 seconds in total and filled in two layers. The air content of the fresh mortar was measured as 1.5%.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Physical</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>% 44.9</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>% 3.38</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>% 27.7</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>% 12.0</td>
</tr>
</tbody>
</table>

Curing regimes

Eleven different curing media were selected. These were:

i. 3% (by mass) NaCl solution: This extreme situation was tested to simulate seawater at 20°C during 5 week curing (Code: CL).

ii. Sealed: Specimens were immersed in tap water inside the plastic bags in order to provide minimum Ca$^{2+}$ ion leaching at 20°C for 5 weeks. Water was allowed to penetrate inside the bags (Code: Z).

iii. (Strongly) dried, no carbonation (I): After initial 6 days of water curing, specimens were kept in the desiccator under the condition of 0% R.H. and 0% CO$_2$ at 20°C during 3 weeks prior to 3% NaCl saturation period. Silica gel was used for collecting the humidity from the environment (Code: E).

iv. Dried, no carbonation (II): After initial 6 days tap water curing, the specimens were put in the desiccator for 3 weeks. Relative humidity was kept in the order of 50% by means of Mg(NO$_3$)$_2$,6H$_2$O (Magnesium Nitrate). A blend of NaOH and Ca(OH)$_2$ (Sodalime pellets with absorption cap. 28% for CO$_2$) was used to collect CO$_2$ from air and to prevent carbonation. Curing program ended with 1 week of 3% NaCl solution saturation prior to frost salt cycles. All conditions were at 20°C (Code: AA).

v. Dried, carbonated (I): After initial 6 days water curing, specimens were kept in the laboratory under the condition of 50% R.H. and 20°C, during 3 weeks prior to 3% NaCl saturation period (Code: AB).
vi. Dried, accelerated carbonated (II): After the initial 6 days water curing, the specimens were kept in the special container with 3% CO₂ under the condition of 50% R.H. and 20°C during 3 weeks prior to 3% NaCl saturation period (Code: AC).

vii. Demi water: Demineralised water was used at 20°C for 5 weeks continuous curing. The aim was to aggravate the Ca²⁺ ion leaching from the mortar specimens (Code: DW).

viii. Plain water: Tap water was used for this curing regime. In this method, cement mortars were kept in tap water at 20°C for 5 weeks and then they were exposed to freeze thaw salt cycles (Code: LW).

ix. CaSO₄ solution: Saturated CaSO₄ solution was used at 20°C for 5 weeks (Code: S).

x. Lime water: Saturated lime solution was used for curing at 20°C during 5 weeks (Code: H).

xi. 1 Molar NaOH solution: The idea of using this curing solution was to keep the curing media above pH 13 and increase the rate of slag activation. Solution was kept at 20°C for 5 weeks (Code:N).

For the carbonation series specimens (E, AA, AB, AC), initial water curing, drying period and water suction durations were kept as follows:

(Tap) water curing 6 days
Drying and carbonation period 21 days
Water suction / 3% NaCl solution saturation 7 days

Other specimens were kept in the relevant media for 5 weeks continuously. In all conditions the temperature was at 20°C.

**Frost salt scaling test**

Following the curing period, the specimens were sawn into two and subjected to freezing thawing cycles of 17±1 hrs freezing at -20±2°C and 7±1 hrs thawing at 20±2 °C. 14 cycles were completed for each series and scaled material was collected by filtration after 2, 7 and 14 cycles. The scaled mass was placed in stove at 110°C and weighed after 24 hrs drying.

![Figure 4.1 Schematic description of a mortar specimen and the freezing media (3% NaCl solution).](image-url)
Before the frost salt scaling test, lateral sides of the mortar bars were covered with two-layer isolation material, epoxy plus bituminous tape. Aim of this preparation was to fix the exposed volume and to prevent potential danger of additional scaled material falling from laterals of the specimen, which would lead to an inaccurate measurement (see Figure 4.1 and Figure 4.2).

Figure 4.2 Slag mortar specimens with mild (left) and severe (right) frost salt scaling.

Chemical analysis

The curing liquids were collected each week during the entire curing period and they were refreshed right after each collection. Chemical analysis of the curing liquids was carried out by atomic emission spectrometry (ICP AES) at the end of the curing period and just before the freezing-thawing testing.

Microstructural analysis

DBT Dimond Roller and Grinder/86 thin sectioning machine was used for the preparation of the thin sections of the carbonated specimens. Low viscosity epoxy with special yellow colour epo-dye was used for distinguishing the porosity under fluorescent light of optical microscope. Quantimet 500⁺ color image analyzer from Leica was used for image capturing and porosity measurements. Images of the specimens were taken just before the freezing-thawing cycles began.

4.1.3 Results and discussion

Compressive strength data of the specimens are given in Table 4.2. These results were measured after 5 weeks immediately before freezing-thawing cycles.
Table 4.2 Average compressive strengths of the 5-week old mortars.

<table>
<thead>
<tr>
<th>Curing Environment</th>
<th>Comp. Strength (MPa)</th>
<th>Curing Environment</th>
<th>Comp. Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL</td>
<td>62.04</td>
<td>DW</td>
<td>63.33</td>
</tr>
<tr>
<td>Z</td>
<td>63.38</td>
<td>LW</td>
<td>63.91</td>
</tr>
<tr>
<td>E</td>
<td>58.74</td>
<td>S</td>
<td>61.49</td>
</tr>
<tr>
<td>AA</td>
<td>59.65</td>
<td>H</td>
<td>62.66</td>
</tr>
<tr>
<td>AB</td>
<td>57.97</td>
<td>N</td>
<td>62.58</td>
</tr>
<tr>
<td>AC</td>
<td>51.56</td>
<td>Age of testing</td>
<td>35 days</td>
</tr>
</tbody>
</table>

Strength measurements showed that the higher the concentrations of CO₂ in air the lower the compressive strength of the slag cement mortars (see series E, AA, AB and AC with increasing CO₂ attack). The reason is most probably the increase in porosity and decrease in volume of the solid phase of the specimens due to carbonation shrinkage. Another important reason is that carbonation stops the further hydration of the cement. Thus strength development stops. The water cured specimens had higher and identical compressive strength values compared to the dried series (E: extreme drying, no carbonation).

Figure 4.3 summarizes the frost salt scaling performances of differently cured mortars.

Figure 4.3 Scaling performances of standard CEM III/B 42.5 N HSR LH cement mortars cured in different curing media.
In order to see the effect of the laboratory air CO\(_2\) concentration on frost salt scaling of slag cement mortars, a comparison should be made between dried - non-carbonated (codes E and AA) and dried - carbonated (AB and AC) specimens. Since the effect of drying is eliminated, it can be concluded that under constant relative humidity carbonation has a crucial effect on frost salt scaling of slag cement mortars. Obviously here the effect of carbonation on the hydration of slag cement and consequently on the frost salt scaling is of importance. During the carbonation, the hydration of cement stops and the reactivation is not possible when the specimen is subsequently wetted. In case of only drying, the reaction can be activated again when the cement contacts water. Thus for E and AA the reaction can continue after the drying resulting in a higher strength. Nevertheless the effect of carbonation on strength is obvious when the 28 days strength comparison is made between AA and AC.

The effect of drying can be seen by the comparison between series E (0% CO\(_2\), 0% RH) and series AA (0% CO\(_2\), 50% RH) which implies that under non-carbonated conditions, the frost salt scaling resistance of slag cement mortar decreases as the rate of drying increases. However, the effect of drying is much less significant than the effect of carbonation.

In Figure 4.4 the similarity of tendency of the scaling progresses of slag cement mortars in the present investigation and slag cement concrete taken from Stark and Ludwig are presented. (Stark 1997). According to the results, in mortar testing approximately 3 grams of scaling corresponds to 1500 gr/m\(^2\) threshold of concrete testing.

The depth of carbonation of the carbonation series was also measured by phenolphthalein spraying method. The average values for series AA, AB and AC were 0 mm, 1 mm and 5-6 mm (up to 10 mm) respectively (see Figure 4.5).

Figure 4.6 provides the micro images of the coarsening of the porosity of mortar skin due to carbonation. The differences in the paste density and interfacial transition zone are noteworthy. In Figure 4.7 the transition between carbonated and non-carbonated slag cement mortar is presented. A significant difference in paste density can be observed by the variation of fluorescent epo-dye colour intensity.

Comparing the effect of curing in Ca(OH)\(_2\) (H) with NaOH (N), it is observed that lime curing shows less scaling. Similarly a comparison can also be made between the curing regimes Ca(OH)\(_2\) (H) and demi water (DW) or tap water (LW). The lime buffer in the Ca(OH)\(_2\) saturated solution seems to be favourable with respect to a better frost salt scaling resistance. This better behaviour of the mortars cured in Ca(OH)\(_2\) solution could be the consequence of one of the following conditions; (1) prevention of Ca ion leaching from the mortar, (2) penetration of Ca ion into mortar so having more lime for slag hydration or (3) precipitation of Ca(OH)\(_2\) in the pores. Furthermore, curing in NaOH saturated water gives a better resistance compared to demi water (DW) or tap water (LW) quite possibly because of the increase of pH of the solution would increase the degree of hydration in the slag cement mortars.

The findings in this experimental study do not confirm the findings of Stark and Ludwig (Stark 1997). On the contrary, it seems that the harder curing water seems to be favourable with respect to frost salt scaling resistance of slag cement mortars because of one of the consequences presented in the previous paragraph.
Figure 4.4 (a) Effect of carbonation level on de-icing salt scaling performances of the slag cement concrete (Stark 1997). In all cases, relative humidity was 65% and slag content was > 60%. (b) Effect of carbonation level on frost salt scaling performances of the slag cement mortar. In all cases, relative humidity was 50% and slag content was 68%.
Figure 4.5 Carbonation depths of the slag cement mortar specimens. Carbonation depths are; (a) 5-6 mm (3% CO₂), (b) less than 1 mm (lab carbonation), (c) no carbonation (0% CO₂).

Figure 4.6 Microstructures of the standard slag cement mortars under fluorescent light. Effect of carbonation on the skin porosity of slag cement mortar. (a) no carbonation, calculated total porosity approx 5% in average (b) lab air, calculated total porosity 10% in average. (c) 3% CO₂, calculated total porosity approx. 20% in average.
Figure 4.7 Effect of carbonation on the paste density of slag cement mortar with w/c 0.50. Fluorescent light.

The amount of Ca\(^{+2}\) ion leaching after 5 weeks is given in Table 4.3. Values are the net amount of leached ions from the specimens.

<table>
<thead>
<tr>
<th>Series</th>
<th>DW</th>
<th>H</th>
<th>CL</th>
<th>S</th>
<th>LW</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leached Ca(^{+2}) ions (mg/l)</td>
<td>135</td>
<td>-</td>
<td>141</td>
<td>-</td>
<td>80</td>
<td>49</td>
</tr>
<tr>
<td>Scaling (14 cycles, gr.)</td>
<td>4.2</td>
<td>1.9</td>
<td>2.7</td>
<td>3.4</td>
<td>3.9</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The comparison of the average scaling of the mortar specimens cured in chloride solution (CL), tap water (LW) and demineralised water (DW) shows that there is a significant difference in the amount of scaled mass between Ca-leached (DW and LW) and non Ca-leached specimens (DW, CL, LW and N). However, the picture is more complex as we compare the results individually. Although the difference is evident between Ca\(^{+2}\) ion leached and non-leached conditions, scaling of the specimens cured in chloride water (CL) should be higher according to the general appearance of Ca leaching-scaling relationship. However, this finding supports the results of Lindmark that when the outer NaCl concentration is 3%, damage tends to decrease as the inner salt concentrations increase for the freezing temperature at -22°C (Lindmark 1999). It was also investigated to see whether the better frost salt scaling performance of the mortars cured in Ca(OH)$_2$ solution comes from alkali activation due to high pH or prevention of Ca ion leaching due to Ca ion saturated
surrounding water. Comparing the scaling results of H and N shows that Ca$^{+2}$ ion leaching is more essential for frost salt scaling resistance of the slag mortars than the activation of slag, at least for the initial 5 weeks of curing period. In case of CaSO$_4$ curing, even though the Ca$^{+2}$ ion leaching was prevented, rather high surface scaling was observed possibly due to the sulphate attack during the 5 weeks curing.

4.2 Effect of Calcium Hydroxide Addition

It was presented in the previous section of this chapter that the shortage of lime in slag cement paste is an important factor concerning its low scaling resistance. Adding lime to the slag cement mixture could be an opportunity for the resistance improvement. Therefore, the effect of calcium hydroxide on the frost salt scaling of slag cement paste and mortar was further studied by utilization of calcium hydroxide as an addition to the slag cement powder.

4.2.1 Experimental

The slag cement used in the experiments was, a CEM III/B 42.5 N HSR LH which was identical to the previous experimental study. The tests were conducted both on paste and mortar specimens. The mixture properties of the paste and mortar specimens are given in Table 4.4.

<table>
<thead>
<tr>
<th></th>
<th>Cement (gr.)</th>
<th>CH (gr.)</th>
<th>Water (gr.)</th>
<th>Sand (gr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paste plain</td>
<td>200</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Paste with CH</td>
<td>200</td>
<td>20</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Mortar plain</td>
<td>450</td>
<td>0</td>
<td>225</td>
<td>1350</td>
</tr>
<tr>
<td>Mortar with 5% CH</td>
<td>450</td>
<td>22.5</td>
<td>225</td>
<td>1350</td>
</tr>
<tr>
<td>Mortar with 10% CH</td>
<td>450</td>
<td>45</td>
<td>225</td>
<td>1350</td>
</tr>
</tbody>
</table>

The specimens were cured in water for 1 week after the de-moulding. Then they were kept under the condition of 50% R.H. and 20°C during 3 weeks prior to the 1 week 3% NaCl saturation period.

After the curing period, the specimens were exposed to 17±1 hrs freezing at -20±2°C and 7±1 hrs thawing at 20±2°C of 14 cycles. The test method for the mortar specimens was adapted from section 4.1.2. For the paste specimens, the freezing thawing cycles were also conducted in 3% NaCl solution. The scaled mass was collected and weighed after 7 and 14 cycles.

4.2.2 Results and discussion

In Figure 4.8, the frost salt scaling performances of the slag cement pastes with and without calcium hydroxide addition are given. Both of the specimens showed serious surface scaling. Calcium
hydroxide addition seems to decrease the scaling quantitatively however neither of the specimens can be considered resistant against the frost salt attack (see Figure 4.9).

The picture was not different for the slag cement mortars with and without calcium hydroxide addition. Again the addition seems to be slightly favourable but considering the amount of CH used, the improvement is negligible (Figure 4.10).

It is known that calcium hydroxide presence in a given cement system is regarded as a favourable property with respect to frost salt scaling resistance. Therefore it was expected from the slag based materials tested to demonstrate somewhat higher resistance. One of the reasons of the unsatisfactory performance could be because of the degree of efficiency of the preparation (Figure 4.11). Calcium hydroxide was mixed with cement powder during the preparation. However, in the course of cement hydration normally relatively well-distributed portlandite crystals are produced all over the volume. This might enable a uniform calcite formation and avoids agglomeration in certain locations, which would leave space for coarsening carbonation reaction of calcium-silicates (see eq. 3.2). As it was explained by Groves et al. (Groves 1991), another disadvantage is the precipitation of carbonate micro-crystals on the surface of calcium hydroxide crystal surfaces. Thus the surface of calcium hydroxide clusters are covered by secondary carbonate micro-crystals and this formation prevents the further carbonation of remaining calcium hydroxide crystals.

Figure 4.8 Effect of calcium hydroxide (CH) addition (10%) on the frost salt scaling of slag cement pastes with w/c 0.50.
Figure 4.9 Conditions of slag cement paste specimens with (right) and without (left) calcium hydroxide addition after the frost salt scaling test.

Figure 4.10 Effect of 5% and 10% of calcium hydroxide addition to slag cement mortar on frost salt scaling.
4.3 CONCLUSIONS

In this chapter the effect of curing conditions on frost salt scaling resistance of the slag cement pastes and mortars has been investigated. According to the observations, the following conclusions could be drawn:

- Carbonation is of paramount importance on frost salt scaling resistance of the standard cement mortars rich in slag. There is evidence that this is due to the restructuring of capillary pore system.
- Frost salt scaling resistance of a slag cement mortar is dependant on the curing regime and chemical composition of curing water although to a much less extent than carbonation.
- Curing in limewater up to 5 weeks appears to be favourable from frost salt scaling point of view.

Figure 4.11 Distribution of calcium hydroxide crystals in the slag cement paste bearing 10% Ca(OH)$_2$ powder. After curing 5 days in 20°C and 95% R.H.
Chapter 5

EFFECT OF GRINDING AGENTS ON FROST SALT SCALING RESISTANCE OF SLAG CEMENT CONCRETE

5.1 INTRODUCTION

Grinding agents are applied during the cement grinding process to reduce the energy required to achieve the desired cement fineness. Thanks to their surface-active and/or lubricating properties, significant improvement in general properties of cement powder can be obtained.

The investigations showed that the grinding agents show great effect on the grinding and the strength of cement pastes. They enhance the flowability, increase the fineness and improve the particle size distribution, thus reducing the mean diameter, narrowing down particle size distribution and increasing the content of fine particles. The grinding agents increase the early strength of cement mortars and accelerate the hydration of cement by increasing the crystallinity and compactness of hydration products. The grinding mechanism is that grinding agents can reduce resistance to agglomeration and improve the flowability which will intensify efficiency between particles and media. The major reason of the strength enhancement is reported to be due to improvement of the particle size distribution by the grinding agents (Jiang 2001).

The cement industry in the Netherlands proposed that by the incorporation of certain grinding additives in the cement production process, significant improvements on frost salt scaling resistance of slag cement concrete can be obtained. This research question was raised after the initial test results from the cement industry laboratories, which are summarized in the following section.

In the framework of this PhD project, frost and frost salt scaling resistance of CEM III/B 42.5 N HSR LH cement concretes with various grinding agents were evaluated. The idea was to reproduce the earlier findings of the cement industry. Furthermore, the microstructural characterisation of the cementitious materials with one of the best performing and with one of the worst performing grinding agents were carried out and a relation was tried to be established with corresponding frost salt scaling performance.
5.1.1 Earlier findings of the cement industry

During the routine laboratory tests performed by the cement industry, a significant scaling resistance was observed in one of the CEM III/B 42,5 N HSR LH cement concrete series containing alkanolamines/hydrocarboxylates based “quality improver (QI)” grinding agent. The physical properties of the three cements used in the tests can be seen in Table 5.1.

The concrete specimens had the following mixture characteristics:

\[
\begin{align*}
\text{Cement} & : 350 \text{ kg/m}^3 \\
\text{Water} & : 182 \text{ kg/m}^3 \ (w/c: 0.52) \\
\text{Sand 0/2 mm} & : 722 \text{ kg/m}^3 \\
\text{Gravel 2/8 mm} & : 271 \text{ kg/m}^3 \\
\text{Gravel 8/16 mm} & : 812 \text{ kg/m}^3
\end{align*}
\]

28-day compressive strengths of the concrete specimens were 42 MPa, 44 MPa, 51 MPa for the specimens containing QI-N, IR Q20 and QI, respectively. The freezing-thawing test was carried out according to the CIF test instead of CDF because initially the intention was to assess the plain frost resistance of the concrete specimens containing three different grinding agents. The CIF test revealed the performances of the concrete specimens as shown in Figure 5.1. During the CIF tests, the scaled off mass was collected and weighed after 14, 28, 42 and 56 cycles.

The experimental results showed that the frost salt scaling resistance of concrete specimens with QI was substantially better than the other concrete series according to CIF test where no de-icing salts are used. It is proposed that if a change in grinding agent used at very low dosage could result such a big change in frost salt resistance then knowledge of the underlying mechanism would probably make it possible to design agents that are even more effective. This assertion is raised by assuming that the similar damage mechanisms are responsible for frost and frost salt scaling because scaling performances were evaluated in a plain frost resistance tests, CIF.

![Figure 5.1 Frost scaling performances of the CEM III/B 42,5 N HSR LH cement concretes w/c 0,52 with three different grinding agents. (Test performed by the cement factory laboratories).](image-url)
Table 5.1 Specific surface and Blaine values of the cements.

<table>
<thead>
<tr>
<th>CEM III/B 42,5 ground with</th>
<th>Specific surface (m²/kg)</th>
<th>Blaine value (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QI-N</td>
<td>669</td>
<td>481</td>
</tr>
<tr>
<td>IR Q 20</td>
<td>651</td>
<td>481</td>
</tr>
<tr>
<td>QI</td>
<td>746</td>
<td>528</td>
</tr>
</tbody>
</table>

5.1.2 Cement grinding agents

Most of the grinding agents are patented by the developers and their exact chemical compositions are protected due to the commercial reasons. However, some useful information of diethylene glycol and alkanolamines/hydrocarboxylates based grinding agents is known of which their effects on slag cement pastes will be investigated throughout the chapter.

Alkanolamines/hydrocarboxylates based (QI) grinding agents

The history of this grinding agent dates back to 1930’s. It was initially proposed as a dispersing agent for cement. Later on, by the addition of triethanolamine to offset the retarding effect of the dispersant, a product called TDA™ (Tucker’s Dispersive Agent) was patented (Strohman 2002). In this thesis, this type of grinding agents is named as “quality improver, QI”.

QI chemicals are reported to show a number of advantages to the cement production such as increased early and long-term compressive strengths for production of better quality cements. A key advantage of alkanolamines/hydrocarboxylates based chemicals is that it reduces cost of cement production through reducing unit grinding costs and through partial replacement of clinker with reactive additions such as pozzolans, slag and fly ash, or with fillers such as limestone (GRACE 1996).

Quality improver chemicals have typically a pH of 8-10 and a specific gravity of about 1.20.

Diethylene glycol based (DEG) grinding agents

Diethylene glycol is a colourless, low-volatility, low-viscosity, hygroscopic liquid. Under normal conditions, diethylene glycol has no detectable odour; under high vapour concentrations, a slightly sweet odour may be detected. It is completely miscible with water and many organic liquids. The reactivity and solubility of diethylene glycol provide the basis for many applications such as grinding agent in cement production (Dow 2000).

5.2 Production of cements with various grinding agents

5.2.1 Introduction

After obtaining good frost scaling performances of slag cements grinded by QI chemical grinding agents by the cement industry laboratories, it was decided to produce unique CEM III/B 42,5 N
HSR LH cements with various grinding agents at two dosages. The unique cements were produced at ENCI IJmuiden facilities in the Netherlands.

### 5.2.2 Materials and testing

Slag cements CEM III/B 42,5 N HSR LH with 6 different grinding agents were produced. The grinding agents used in the cement production are listed in Table 5.2. In the cement production, double dosage of the grinding agents were also used as well as the manufacturer prescribed normal dosage.

<table>
<thead>
<tr>
<th>Index no.</th>
<th>Grinding agents</th>
<th>Chemistry</th>
<th>Code</th>
<th>Dosage ml/ton cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DEG</td>
<td>Diethylene glycol</td>
<td>DEG N</td>
<td>Normal 182</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>DEG D</td>
<td>Double 364</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>N/A</td>
<td>H N</td>
<td>Normal 150</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>N/A</td>
<td>H D</td>
<td>Double 300</td>
</tr>
<tr>
<td>5</td>
<td>QI-5</td>
<td>Alkanolamines/ hydrocarboxylates</td>
<td>QI-5 N</td>
<td>Normal 1300</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>QI-5 D</td>
<td>Double 2600</td>
</tr>
<tr>
<td>7</td>
<td>QI</td>
<td>&quot;</td>
<td>QI N</td>
<td>Normal 1300</td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>&quot;</td>
<td>QI D</td>
<td>Double 2600</td>
</tr>
<tr>
<td>9</td>
<td>QI-0</td>
<td>&quot;</td>
<td>QI-0 N</td>
<td>Normal 1300</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>&quot;</td>
<td>QI-0 D</td>
<td>Double 2600</td>
</tr>
<tr>
<td>11</td>
<td>QI-N</td>
<td>&quot;</td>
<td>QI-N N</td>
<td>Normal 1600</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>&quot;</td>
<td>QI-N D</td>
<td>Double 3200</td>
</tr>
</tbody>
</table>

The same raw material conveyor band was used during the entire cement production. Chemical analysis and slag content measurements of those raw materials were carried out in order to check the uniformity of the cements during the production. The following standard tests were carried out on the unique cements produced:

**Standard cement tests**

The standard cement tests performed were:
- Blaine fineness (NEN-EN 196-6:1993)
- Setting time (NEN-EN 196-3:2005 en)
- Soundness (Le Chatelier) (NEN-EN 196-3:2005 en)
- Particle size distribution (lasergranulometry)
- Cement colour (with colourmeter according to Dr. Lange)
- Circularity tests with image analysis (only on cements with DEG and QI)

Standard mortars were also prepared according to EN 197-1. Strength measurements were carried out at 2, 7 and 28 days.

**Standard concrete tests**

The following tests were performed on the concrete specimens:
- Workability (visual evaluation and slump-vibrating table measurements)
- Water demand (at the level of 120mm slump)
- Volumetric mass measurement
- Compressive strength after the ages of 2, 7 and 28 days.

**Raw material testing**

The following analyses were performed on the raw materials:
- Chemical analysis (XRF)
- Loss on ignition 750°C (slag and anhydrite)
- Loss on ignition 975°C (clinker)
- Free CaO content (clinker)
- Anhydrite content (setting regulator)

**5.2.3 Results**

The results of standard cement and concrete tests of the specimens produced with unique cements can be found in Appendix B.

**5.2.4 Remarks on the characterisation test results**

The raw materials were collected at the beginning, in the middle and at the end of the cement production process for the analysis. No significant differences were found between the specimens. The twelve cements manufactured showed apart from the grinding agents applied no significant difference in chemical composition, so the quality requirements according to EN 197-1 and EN 197-2 have been fulfilled for all unique cements.

The test results revealed that alkanolamines/hydrocarboxylates based grinding agents (QI, QI-0, QI-5, QI-N) increases the early strength of standard mortars more than the other two grinding agents, namely DEG and H (Table B1). However, 28-day compressive strengths of all specimens were found to be almost identical. The alkanolamines/hydrocarboxylates based grinding agents showed similar effect on the compressive strengths of concrete specimens as well.

It seems that there is no meaningful relationship between the chemical base of the grinding agents and the fineness of the relevant cements. The Blaine values of the cements vary from 376 m²/kg to 413 m²/kg.
Chapter 5

The circularity measurements in Appendix B show that chemically different grinding agents seem to have significantly different influence on the geometry of the cement particles (according to student-t test).

Alkanolamines/hydrocarboxylates (Q I) based grinding agent appears to produce slightly less circular particle shapes compared to DEG. The standard tests on concrete (in Appendix B) show that concrete with DEG normal dosage has a lower slump value than the one with Q I normal dosage which indicates that the workability of Q I cement is better than of DEG. This indicates that Q I has a better plasticizing effect which helps cement particles to be distributed more efficient in the system even though it generates less circularity compared to DEG.

5.3 FROST RESISTANCE OF CONCRETES WITH VARIOUS GRINDING AGENTS

5.3.1 Plain frost resistance

Introduction

Although the main research interest was to investigate the frost salt scaling performances of the unique cement concretes, it was also planned to characterize the effect of grinding agents on the internal frost resistance.

It should be noted that in the countries like the Netherlands and Belgium, plain frost damage is not considered as a frequently encountered damage like frost salt scaling.

Experimental data

In the framework of the characterisation of the unique cements, frost resistance of concretes with the unique cements was evaluated according to Belgium Standard NBN 15-231. The mix designs of the concrete specimens are presented in Table 5.3.

The concrete specimens were cured according to Belgium frost test NBN B-15-231. During freezing the environment within the chamber reached the specified -15°C ± 3°C within 1 hour. It was then maintained at -15°C ± 3°C for 15 hours. Specimens were thawed by immersion in water for 6 hours. The water temperature was maintained between 5 and 12°C. The specimens were examined and weighed before re-immersion and commencement of the next test cycle.

Elasticity modulus of the concrete specimens was measured after 14, 28, 42 and 56 freezing-thawing cycles. The measurements are summarized in Figure 5.2.

As can be seen in Figure 5.2, all specimens fulfil the requirement, which is minimum 60% of the initial elasticity modulus according to NBN 15-231. It is interesting that some of the specimens showed an increase in elasticity modulus during the freezing thawing cycles. However this increase with the exception of that of OPC is not significant, and can be attributed to the readings of the ultrasonic pulse velocity at different spots on the specimen surface. According to the current study, the slag cement concrete specimens with w/c 0.52 can be considered sufficiently resistant against frost attack regardless to the type of grinding agents used.
Table 5.3 Mix designs of concrete specimens.

<table>
<thead>
<tr>
<th>grinding agent</th>
<th>QI-0 N</th>
<th>DEG N</th>
<th>DEG D</th>
<th>QI N</th>
<th>QI D</th>
<th>H N</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/c</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>Cement (kg/m³)</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Water (kg/m³)</td>
<td>182</td>
<td>182</td>
<td>182</td>
<td>182</td>
<td>182</td>
<td>182</td>
</tr>
<tr>
<td>Fine Agg.(kg/m³)</td>
<td>785</td>
<td>785</td>
<td>785</td>
<td>785</td>
<td>785</td>
<td>785</td>
</tr>
<tr>
<td>Gravel (kg/m³)</td>
<td>1052</td>
<td>1052</td>
<td>1052</td>
<td>1052</td>
<td>1052</td>
<td>1052</td>
</tr>
<tr>
<td>air (%)</td>
<td>1.2</td>
<td>1.4</td>
<td>1</td>
<td>1.2</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td>slump (cm)</td>
<td>16</td>
<td>18</td>
<td>17.5</td>
<td>19</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>28D comp. str. (MPa)</td>
<td>40.2</td>
<td>36.4</td>
<td>43.3</td>
<td>35.4</td>
<td>36.4</td>
<td>37.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>grinding agent</th>
<th>H D</th>
<th>QI-5 N</th>
<th>QI-5 D</th>
<th>QI-N N</th>
<th>QI-N D</th>
<th>OPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/c</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>Cement (kg/m³)</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Water (kg/m³)</td>
<td>182</td>
<td>182</td>
<td>182</td>
<td>182</td>
<td>182</td>
<td>182</td>
</tr>
<tr>
<td>Fine Agg.(kg/m³)</td>
<td>785</td>
<td>785</td>
<td>785</td>
<td>785</td>
<td>785</td>
<td>785</td>
</tr>
<tr>
<td>Gravel (kg/m³)</td>
<td>1052</td>
<td>1052</td>
<td>1052</td>
<td>1052</td>
<td>1052</td>
<td>1052</td>
</tr>
<tr>
<td>air (%)</td>
<td>1.7</td>
<td>1.1</td>
<td>1.6</td>
<td>1.4</td>
<td>1.6</td>
<td>2</td>
</tr>
<tr>
<td>slump (cm)</td>
<td>16</td>
<td>17</td>
<td>16</td>
<td>20</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>28D comp. str. (MPa)</td>
<td>41.7</td>
<td>36.2</td>
<td>43.3</td>
<td>39.4</td>
<td>36.5</td>
<td>32.7</td>
</tr>
</tbody>
</table>

Figure 5.2 Plain freezing thawing performances of the new slag cement concrete specimens with w/c 0.52 (according to NBN 15-231).
5.3.2 Frost salt resistance

Materials and tests

In order to evaluate the effect of grinding agents on the frost salt scaling resistance of CEM III/B 42,5 containing concrete specimens, the current experimental study was performed. However, instead of previously used w/c ratio of 0.52 in the preliminary tests, w/c of 0.45 was investigated. The idea behind this was the fact that according to the national Dutch building codes w/c of 0.45 is the maximum allowed value for non-air entrained concrete.

The properties of the slag cements used in the scaling tests are given in Appendix B. The control specimens were prepared by the CEM I 32,5 R cement of which the chemical and physical properties are given in Table 5.4.

Table 5.4 Chemical properties of CEM I 32,5 R.

<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>PHYSICAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO, %</td>
<td>63.9</td>
</tr>
<tr>
<td>SO₃, %</td>
<td>2.68</td>
</tr>
<tr>
<td>SiO₂, %</td>
<td>20.6</td>
</tr>
<tr>
<td>Al₂O₃, %</td>
<td>5.01</td>
</tr>
<tr>
<td>Fe₂O₃, %</td>
<td>3.25</td>
</tr>
<tr>
<td>Strength of standard mortars</td>
<td>MPa</td>
</tr>
<tr>
<td>2 days</td>
<td>22.0</td>
</tr>
<tr>
<td>7 days</td>
<td>36.0</td>
</tr>
<tr>
<td>28 days</td>
<td>49.0</td>
</tr>
<tr>
<td>Blaine</td>
<td>m²/kg</td>
</tr>
<tr>
<td>285</td>
<td></td>
</tr>
</tbody>
</table>

The same mix design was used for the specimens in all tests. The mix design is presented in Table 5.5. 2gr. Na-Laurylsulphate was used as the air entraining agent (A.E.A.) per 40lt. of batch. The sieve analysis of the aggregate used in the concrete mixture is given in Table 5.6.

Table 5.5 Mix proportions of the concrete specimens for the frost salt scaling tests.

<table>
<thead>
<tr>
<th>No A.E.A.</th>
<th>kg per m³</th>
<th>With A.E.A</th>
<th>kg per m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>cement</td>
<td>344</td>
<td>cement</td>
<td>314</td>
</tr>
<tr>
<td>water</td>
<td>154</td>
<td>water</td>
<td>141</td>
</tr>
<tr>
<td>fine aggregate</td>
<td>793</td>
<td>fine aggregate</td>
<td>726</td>
</tr>
<tr>
<td>coarse aggregate</td>
<td>1051</td>
<td>coarse aggregate</td>
<td>961</td>
</tr>
<tr>
<td>A.E.A.</td>
<td>-</td>
<td>A.E.A.</td>
<td>0.045</td>
</tr>
<tr>
<td>TOTAL</td>
<td>2343</td>
<td>TOTAL</td>
<td>2143</td>
</tr>
<tr>
<td>air</td>
<td>1.50%*</td>
<td>air</td>
<td>4.00%**</td>
</tr>
<tr>
<td>Dmax</td>
<td>32mm</td>
<td>Dmax</td>
<td>32mm</td>
</tr>
<tr>
<td>w/c</td>
<td>0.45</td>
<td>wcf</td>
<td>0.45</td>
</tr>
<tr>
<td>slump</td>
<td>&lt; 5 cm</td>
<td>slump</td>
<td>&lt; 5 cm</td>
</tr>
</tbody>
</table>

*Actual fresh air content was measured as 2.5%

** Actual fresh air content was measured as 9%
Table 5.6 Sieve analysis of the aggregate used in the mix design (conforming to NEN 2560).

<table>
<thead>
<tr>
<th>Sieves (mm)</th>
<th>Coarse passing (%)</th>
<th>Fine passing (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>16</td>
<td>55.6</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>15.5</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>0.9</td>
<td>98.2</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>80.1</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>67.3</td>
</tr>
<tr>
<td>0.5</td>
<td>-</td>
<td>37</td>
</tr>
<tr>
<td>0.25</td>
<td>-</td>
<td>3.8</td>
</tr>
<tr>
<td>PAN</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Frost salt scaling tests

In order to evaluate the frost salt scaling performances of the new cements, freezing thawing regimes of three standard tests were used; CDF, Boras and ASTM C672 tests. In all tests, the slag cement grinded with QI was used since this cement showed promising results in the initial CIF tests (see 5.1.1). Since CIF is a test with normal water, the performance of this concrete had to be evaluated by standard frost salt scaling tests.

It is important to note that only the freezing-thawing cycles of the above-mentioned standard tests were used and the prescribed curing regimes were not necessarily followed. The curing regimes in all tests were kept as 1 week water curing + 3 weeks lab drying/carbonation + 1 week 3% NaCl solution saturation prior to the freezing-thawing cycles. In Scandinavian slab test, cut surfaces were tested according to the standard (see Appendix A) while cast surfaces of the concrete specimens were tested in the other two tests.

CDF test

Three slag cements and an OPC concrete mixture were tested with the CDF method. The CEM III/B 42,5 N HSR LH cements were ground with QI, QI-0 and QI-N. The OPC was the one presented in Table 5.4. The scaled mass was collected and weighed after 14 and 28 cycles. Results are given in Figure 5.3.

The OPC concrete gives clearly the most superior frost salt scaling resistance. After 28 cycles, the OPC specimens showed negligible amount of scaling. However it is noticed that after 14 cycles, the specimens with QI shows relatively better performance than the others.

The effect of air entrainment on the frost salt resistance of concrete mixtures with w/c ratio of 0.45 was also studied. Mixture characteristics of air-entrained concrete are presented in Table 5.5. The air entrainment improves the frost salt scaling resistance of OPC concrete even more to a degree of almost showing no sign of scaling. The most significant improvement is seen in the slag cement concretes. The 9% (fresh state) air entrainment decreased the total scaling almost 50% to the border of maximum scaling limit recommended in the CDF test (see Figure 5.4). This behaviour confirms the results of Stark and Ludwig (Stark 1995). However it is obvious that the frost salt scaling resistance improvement of the slag cement concrete up to the level of OPC concrete can not be achieved solely by air entrainment.
Figure 5.3 Frost salt scaling performances of 3 new cements and an OPC (CDF test).

Figure 5.4 Effect of air entrainment on frost salt scaling resistance of slag cement and OPC (CDF test).
**Scandinavian test (Boras method)**

Exactly the same mix design was used for the specimens tested by Scandinavian method for frost salt scaling performance tests. Again the QI cement concrete specimens showed the best performance while the concretes with DEG performed worst (Figure 5.5).

![Figure 5.5 Frost salt scaling performances of 5 unique cement concretes with w/c 0.45 according to Scandinavian Test/Boras Method.](image)

In Figure 5.6, the surface conditions of DEG and QI cements after the Scandinavian test are presented. The observable difference appears to be the coarse aggregate content and the mortar condition at the rim of the coarse aggregates. As presented in Figure 5.6 (left), DEG cement concrete lost a number of coarse aggregate particles as well as the mortar phase while in QI, the only observable mass loss was the mortar phase. The depths of scaling near the rim of the coarse aggregates are deeper in DEG cement concrete.

![Figure 5.6 Surface conditions of the slag cement concretes; with DEG (left) and QI (right).](image)
**ASTM C672 tests**

Additionally, the ASTM C672 testing was performed on the QI and DEG concrete specimens with w/c ratio of 0.45. The results once again showed that QI concrete presented a better performance than DEG cement concrete even though the difference was small (see Figure 5.7).

![Graph showing frost salt scaling performances of slag cement concretes with QI and DEG according to ASTM C672.](image)

Figure 5.7 Frost salt scaling performances of slag cement concretes with QI and DEG according to ASTM C672.

The air-void system characteristics of above mentioned concrete specimens with QI and DEG cements were evaluated by ASTM C457 standard test method, Procedure B. The results are given in Table 5.7.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>QI</th>
<th>DEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>air content (%)</td>
<td>8.691</td>
<td>7.314</td>
</tr>
<tr>
<td>void frequency</td>
<td>0.106</td>
<td>0.107</td>
</tr>
<tr>
<td>paste content (%)</td>
<td>20.594</td>
<td>17.571</td>
</tr>
<tr>
<td>paste air ratio</td>
<td>2.370</td>
<td>2.402</td>
</tr>
<tr>
<td>average chord length (mm)</td>
<td>0.822</td>
<td>0.683</td>
</tr>
<tr>
<td>specific surface (mm⁻¹)</td>
<td>4.865</td>
<td>5.855</td>
</tr>
<tr>
<td>spacing factor (mm)</td>
<td>0.487</td>
<td>0.410</td>
</tr>
</tbody>
</table>

Table 5.7 Air-void characteristics of concrete specimens (w/c 0.45) with QI and DEG according to ASTM C457, Procedure B.

Typical optical microscopy images of these specimens are presented in Figure 5.8. It was observed that alkanolamines/hydrocarboxylates based grinding agent (QI) produced rather spherical air voids with higher circularity than the ones in DEG specimens. The air voids in QI specimen were also similar to the ones created by air-entrainment agents. The modified point counting revealed that the specimens with QI have slightly higher total air content and spacing factor.
5.3.3 Concluding remarks

Among the unique cement concretes investigated, the one with the alkanolamines/hydrocarboxylates based grinding agent (QI) has been found to be the most resistant against frost salt attack according to the CDF, ASTM C457 and the Boras tests. The improvement was revealed after a number of freezing-thawing cycles in all tests performed. Therefore the proposition of the cement industry was confirmed.

Further investigation into the microstructural differences of slag cement based materials containing QI and DEG were carried out and the findings are presented in the following sections of the current chapter.
Although the improvement with QI is significant, the scaling resistance of concrete rich in slag with QI is not meeting the frost salt scaling resistance requirements and is inferior to OPC, CEM I.

5.4 ESEM study on DEG and QI based slag cement pastes

5.4.1 MgO distribution in cement paste

It is possible that the grinding agents may affect the liberation of MgO in the slag due to its interaction with unreacted slag particles. This may consequently contribute to the frost salt scaling resistance of the system. The details of this aspect are discussed in section 2.2.2.

Element mapping on the 28-day water cured slag cement paste specimens with DEG and QI were carried out with Philips XL-30 ESEM and an attached EDX. The analysis was performed at 250 times magnification with the beam voltage Kv 10.0, analysis resolution 256x200, data type ZAF_wt% and data range 0.00-73.42. The results are presented in Figure 5.9.

![Typical Mg distribution in the cement paste with DEG (left) and QI (right).](image)

The element mapping analysis revealed that DEG prevents the liberation of Mg more than QI (Figure 5.9). QI shows somewhat denser Mg element mapping. This may lead QI cement having more available MgO to stabilize the metastable calcium carbonates to calcite.

5.4.2 Cement paste microstructure

The quality of DEG and QI slag cement pastes were investigated with BSE detector of the ESEM. The paste specimens were cured under water for 28 days. At the age of 28 days 20×30×40 mm³ paste specimens were cut for the polished sectioning. Polished sections were divided into two groups. The first group was kept in the stove for 45 minutes at 35°C then immediately vacuum impregnated by low viscosity epoxy while the paste specimens were still non-carbonated. The next day specimens were grinded with no.1200 grinding paper and polished with 6μm, 3μm, 1μm and 0.25μm diamond paste on a lap wheel. The second group was first grinded with no. 1200 grinding paper then put into the carbonation chamber of 3% CO₂ at 20°C and 50±2 % relative humidity condition for 1 week. Finally the carbonated specimens were also epoxy impregnated and polished identical to the non carbonated specimens.

In Figure 5.10 to Figure 5.15, carbonated and non-carbonated microstructure conditions of CEM III/B 42,5 cement pastes produced with QI and DEG grinding agents are presented.
Figure 5.10 BSE images of the non-carbonated DEG (top row) and QI (bottom row) cement pastes with w/c 0.30.

Figure 5.11 BSE images of the carbonated DEG (top row) and QI (bottom row) cement pastes with w/c 0.30.
Figure 5.12. BSE images of the non-carbonated DEG (top row) and QI (bottom row) cement pastes with w/c 0.40.

Figure 5.13. BSE images of the carbonated DEG (top row) and QI (bottom row) cement pastes with w/c 0.40.
Figure 5.14 BSE images of the non-carbonated DEG (top row) and QI (bottom row) cement pastes with w/c 0.50.

Figure 5.15 BSE images of the carbonated DEG (top row) and QI (bottom row) cement pastes with w/c 0.50.
5.4.3 Remarks about ESEM observations

MgO liberation from the slag particles was seen in QI cement paste relatively more than the one with DEG. This may lead to a better stabilization of metastable carbonates in the system, which should improve the frost salt scaling resistance.

In DEG and QI, slag cement pastes with w/c ratio of 0.30, 0.40 and 0.50, carbonation creates a randomly distributed open structure. No significant/systematic morphological differences were observed between QI and DEG slag cement pastes in the ESEM study.

5.5 Effect of Grinding Agents on Pore Characteristics of Slag Cement Paste

5.5.1 Introduction

Because of having different frost salt scaling performances of the cements ground by two organic based commercial grinding agents, -diethyleneglycol (DEG) and an alkanolamines/ hydrocarboxylates based grinding agent (Q I)-, it was expected that those two cements would show different pore structure characteristics.

5.5.2 Experimental data

Two slag cements with the slag content of 67% (CEM III/B 42,5 N HSR LH), which were ground with the organic-based commercial grinding agents were used from the cement factory in the Netherlands. The company-suggested amounts of the chemicals were used in the cement production as 182 ml/ton and 1300 ml/ton for DEG and QI, respectively. The chemical and physical properties of the cements are reproduced in Table 5.8. Paste specimens with w/c ratios of 0.30, 0.40 and 0.50 were prepared. The specimens were prepared with ordinary tap water. The mixing sequence was 2 minutes low and 2 minutes high speed mixing with a commercial HOBART mixer. Then the paste mixtures were poured into the 500cc plastic bottles and vibrated for 15 seconds with a vibrating table. The bottle was rotated at a speed of 4 rotations per minute for 24 hours at the room temperature and placed in water bath until the day of sample preparation for MIP testing.

At the age of 28 days, the paste specimens were cut into small pieces (around 0.5 cm³) in order to be used in the experiments. For each cement type and w/c ratio, two groups were created; non-carbonated and carbonated. The non-carbonated group was put in the freeze-dryer (0% CO₂ and 0%RH) until the specimens were completely dry. The specimens were checked by ESEM if any damage was introduced by 0% R.H. environment and found no significant damage in the system. In order to have the specimens completely dry, 1 week to 9 days were needed depending on the w/c ratio. The carbonated specimens were put into the carbonation chamber of 3% CO₂ (by vol.) at 20°C and 50±2 % relative humidity condition until the specimens were entirely carbonated. Then the carbonated specimens were put in the freeze dryer in order to remove the remaining moisture. Carbonation front was observed by the phenolphthalein method.

Additionally, pore characteristics of w/c 0.45 slag cement concrete specimens with grinding agents QI and DEG were studied. The mix design of the concrete specimens is given in Table 5.9.
Table 5.8 Physical and chemical properties of CEM III/B 42,5 N HSR LH and CEM I 32,5 R.

<table>
<thead>
<tr>
<th></th>
<th>CEM III /B 42,5 with QI and DEG (in parentheses)</th>
<th>CEM I 32,5 R</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CHEMICAL</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>% 45.0(44.6)</td>
<td>63.9</td>
</tr>
<tr>
<td>SO₃</td>
<td>% 3.25(3.55)</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>% 27.6(27.6)</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>% 12.2(12.2)</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>% 1.27(1.19)</td>
<td></td>
</tr>
<tr>
<td><strong>PHYSICAL</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strength of standard mortars</td>
<td>2 days MPa</td>
<td>32.7(33.1)</td>
</tr>
<tr>
<td>Strength of standard mortars</td>
<td>7 days MPa</td>
<td>36.0</td>
</tr>
<tr>
<td>Blaine</td>
<td>m²/kg 376(385)</td>
<td>285</td>
</tr>
</tbody>
</table>

The 15 cm cube concrete specimens were kept under water for 1 week. The following 6 months concrete specimens were stored in the 20°C and 50±2 % R.H. lab conditions. At the end of the conditioning period, approximately 40×40×40 mm³ piece of concrete was extracted from the centre of the specimens. Coarse aggregate particles were extracted by sawing. The remaining mortar was stored in 0% CO₂ and 3% CO₂ environments prior to the MIP measurements.

Table 5.9 Mixture proportions of concrete (kg/m³).

<table>
<thead>
<tr>
<th>w/c</th>
<th>Cement</th>
<th>Water</th>
<th>Sand</th>
<th>Aggregate</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>350</td>
<td>159</td>
<td>951</td>
<td>915</td>
<td>1.75</td>
</tr>
</tbody>
</table>

* Commercial river sand and river gravel Dmax=16mm
  b Cugla SL-01 commercial superplastisizer

At the age of 28 days, the paste specimens were cut into certain forms in order to be used in the ESEM study. 20×30×40 mm³ paste specimens were cut for the polished sectioning. Polished sections were divided into two groups. One group was kept in the stove for 45 minutes at 35°C then immediately vacuum impregnated by low viscosity epoxy while the paste specimens were still non-carbonated. The next day these specimens were ground with No.1200 grinding paper roll (roll#3) on the thin sectioning machine and polished with 6 μm, 3 μm, 1 μm and 0.25 μm diamond paste on a lap wheel. The second group was first ground with roll#3 then put into the carbonation chamber of 3% CO₂ at 20°C and 50±2 % relative humidity condition for 1 week.

5.5.3 Results

The experimental data from MIP measurements of w/c 0.30, 0.40 and 0.50 slag cement pastes are presented in Figure 5.16 to Figure 5.21. In Figure 5.16 to Figure 5.18 the cumulative intrusion...
volume versus pore diameter and in Figure 5.19 to Figure 5.21 derivative intrusion volume versus pore diameter of slag cement pastes containing grinding agents QI and DEG are presented.

Figure 5.16 Cumulative volume vs. pore diameter graphs of non-carbonated (left) and carbonated (right) paste specimens with w/c 0.30.

Figure 5.17 Cumulative volume vs. pore diameter graphs of non-carbonated (left) and carbonated (right) paste specimens with w/c 0.40.

Figure 5.18 Cumulative volume vs. pore diameter graphs of non-carbonated (left) and carbonated (right) paste specimens with w/c ratio 0.50.
Figure 5.19 Derivative volume vs. pore diameter graphs of non-carbonated (left) and carbonated (right) paste specimens with w/c ratio 0.30.

Figure 5.20 Derivative volume vs. pore diameter graphs of non-carbonated (left) and carbonated (right) paste specimens with w/c ratio 0.40.

Figure 5.21 Derivative volume vs. pore diameter graphs of non-carbonated (left) and carbonated (right) paste specimens with w/c 0.50.
The MIP results for cumulative pore volume versus pore diameter of the concrete specimens with w/c 0.45 are presented in Figure 5.22. Effects of carbonation and grinding agents are presented.

Figure 5.23 shows the pore size distribution of the concrete specimens under the effects of carbonation and grinding agents.

Comparison of CEM I 32.5 R and CEM III/B 42.5 (with grinding agent QI) paste specimens w/c 0.45 is presented in Figure 5.24 and Figure 5.25.

Figure 5.22 Effects of carbonation and grinding agents on the cumulative intrusion volume of the concrete mortars w/c 0.45.

Figure 5.23 Effect of carbonation and grinding agents on the pore size distribution of the concrete mortar specimens w/c 0.45.
5.5.4 Discussion

The total porosity of the system cannot be measured accurately by measuring the total intrusion porosity as obtained in MIP. There are much finer pores existing in the system which require higher pressure than the MIP equipment can reach (~220 Mpa). Hence, the results should be evaluated only for the comparison of the pore characteristics. It should also be stressed that mercury porosimetry may destruct the pore walls which causes an over-estimation of the pores (Diamond 2000).

In the current thesis, the pores are classified in three zones, namely micro, meso and macro capillaries. Pore diameters between 0.01 and 0.1 \( \mu \text{m} \) named as micro capillaries while the ones between 0.1 and 1 \( \mu \text{m} \) as meso and the ones bigger than 1 \( \mu \text{m} \) as macro capillaries. This definition is found to be more descriptive for the results in the current experimental study.

The results are discussed twofold; the effect of grinding agents and the effect of carbonation. Considering the cumulative intrusion volumes, it is clear that grinding agent QI creates a lower total in-
trusion volume in all w/c ratios studied compared to grinding agent DEG (Figure 5.16 to Figure 5.18). This is valid for non-carbonated as well as carbonated specimens. The effect of carbonation shows quite inconsistent results for the paste specimens w/c 0.30, 0.40 and 0.50. Keeping in mind the literature results, it was expected that carbonation would lead to lower paste porosity so the total cumulative intrusion volumes should be lower in all w/c ratio cases compared to the non-carbonated ones (Matala 1995). While this was the finding for QI pastes, DEG pastes showed some contradictory results (Figure 5.26).

![Figure 5.26 W/c ratio vs. total intrusion porosity for non-carbonated (No Car.) and carbonated (Carb.) slag cement pastes with various w/c ratios.](image)

**Pore size distribution**

Other than the cumulative intrusion volume, even more useful information can be obtained from the pore size distribution data of the pastes (see Figure 5.19 to Figure 5.21). At a first glance to the non-carbonated pastes, it can immediately be seen that the pores mainly exist in the area below 0.1 μm (micro-capillary) regardless to the w/c ratio of the paste and the grinding agent used. The portion of that meso-capillary seems to be slightly higher for the QI pastes. Considering the effect of carbonation, the increase in meso-capillary and the decrease in micro-capillary are obvious. It is interesting that carbonation is not giving the same effect at the same level to the slag cement pastes with different grinding agents. Clearly, the volume increase of the macro pores is considerably lower in QI than DEG cement in all w/c ratio levels. It is noteworthy to mention that the QI paste with w/c ratio 0.30 is very little affected by carbonation.

In Figure 5.27, the pore size distribution is categorized according to the certain diameter ranges. Grinding agents seem to modify the pore structure of the slag cement paste. The reason is probably the particle dispersing ability of these chemicals since grinding agents are polar chemicals and act similar as superplastisizers. Apparently QI has a higher ability to disperse the cement particles
throughout the system and enable a finer pore structure relatively. This could be attributed to the alkanolamines, which are surfactants, with some impact on the air void structure. However, it should be stressed that this research only included two industrial cement specimens, and the results regarding differences due to grinding agent should be considered with some precaution until the verification occurred.

It should also be noted that the redistribution of slag cement concrete pore structure due to carbonation is comparable to the paste specimens. However, the redistribution takes place in a wider range of pore diameters. As can be seen i.e. in Figure 5.23, carbonation shifts the pores from 1-10 µm range to the diameter of over 10 µm.

![Figure 5.27 Pore size distribution of slag cement paste specimens before and after carbonation.](image)

The slag cement paste results concerning the increase in macro pores match with the ESEM/BSE observations presented in Chapter 3. It was seen that carbonation leads to increase in macro pores, especially in the transition zone of unreacted slag particles and hydration products.

**Critical pore size**

The critical pore diameter corresponds to the higher rate of mercury intrusion per change in pressure and can be identified by the peaks in differential mercury intrusion versus pore size graphs. In cement pastes, the peaks are generally considered as corresponding to the critical (or threshold) pore size (Ye 2003). This concept is believed to be important for the transport properties of a cementitious system.

The comparison is done for non-carbonated and carbonated pastes of QI and DEG (Figure 5.28). The critical diameters correspond to the sudden increase in intrusion volume in the micro capillary zones of the derivative pore size distribution of the cement pastes (see Figure 5.19 to Figure 5.21). For non-carbonated cement pastes, critical pore diameter is almost identical for the two grinding
agents. It is seen that the higher the w/c ratio, the higher the critical pore diameter. The difference becomes more evident for the carbonated specimens. DEG cement paste has higher critical pore diameter than QI paste in all w/c ratios though the difference between DEG and QI appears to be minor except for w/c 0.5.

In order to understand the importance of critical pore diameter, it would be wise to have a look at the Katz-Thompson equation, which bears critical pore radius for the estimation of permeability of the system (Ait-Mokhtar 2002). The formula is:

\[
K = C\left(\frac{\sigma}{\sigma_o}\right)\frac{R_c^2}{4}
\]

where \(K\) is the theoretical intrinsic permeability of the material \((\text{m}^2)\), \(C\) is an empirical constant which is often equal to 1/226, \(\sigma\) is the electrical conductivity of porous material, \(\sigma_o\) is the electrical conductivity of the pore solution and \(R_c\) is the critical pore radius \((\text{m})\). It can be understood that under the assumption of the identical electrical conductivity values for DEG and QI cement pastes, DEG has a higher permeability than QI. This might permit an easier access of the freezing medium to the inner structure. Moreover it is possible to say that a higher CPD value shows a tendency that more inner surfaces are more saturated with freezing liquid.

This statement is confirmed experimentally by initial capillary suction test on the 495 day old naturally carbonated concrete specimens with w/c 0.45 (see Figure 5.29). The mixture characteristics were identical to the values given in Table 5.5. The concrete specimens were cured 1 week in fog room and then kept in the laboratory at 50-55% R.H condition. Carbonation depth for QI and DEG concrete specimens were measured as max. 10 and 11.5 mm, respectively.

**Connection to the frost (salt scaling) performance**

In view of above-mentioned findings, a realistic explanation to the better frost salt scaling resistance of QI could be the pore size distribution of the system. The results imply that QI paste generates more micro pores than DEG. It is very well known from the literature that the pore water in micro capillaries tends to supercool at low temperatures (Table 5.10). Depending on the temperature and the pore size in question, this reduces the risk of deleterious ice expansion and eventual cracking. Additionally, the smaller CPD of QI should decrease the risk of liquid penetration to the inner structure and the possible physicochemical action compared to DEG as well. However, it should be noted that mercury intrusion porosimetry results cover only the pore diameters of as low as 10 nm which has a freezing point of approximately -15 °C.

Furthermore, the finer pore structure created by QI grinding agent should create a better carbonation resistance, which would lead to an increased frost salt scaling resistance.

| Table 5.10 Freezing point depression as a function of pore radius (Wessman 1997). |
|-----------------|-----|-----|-----|-----|-----|
| Radius (nm)     | 22  | 14  | 10  | 8   | 6   |
| Freezing point (°C) | -6  | -10 | -15 | -20 | -30 |
5.5.5 Conclusions

The grinding agents applied show an effect on the salt scaling resistance. The grinding agent QI shows a significantly better performance in the scaling test, although this appears to manifest itself after a substantial number of freezing-thawing cycles and to occur mainly for the higher w/c 0.50. It is shown that the improved behaviour with QI can be attributed to an effect on the pore size distribution both in carbonated and non-carbonated paste.
5.6 MINERAL STRUCTURES IN SLAG CEMENT PASTES WITH QI AND DEG

5.6.1 Experimental

In this study, two slag cements, CEM III/B 42.5 N HSR LH (ground with QI and DEG) were used (see Table 5.8 for the properties). These cements were used in the preparation of the pastes with w/c of 0.45. The reason that the paste specimens were used instead of mortar or concrete was to obtain the results from a rather uniform material and avoid the misinterpretation, which may come from aggregate phase of a mortar or concrete specimen.

The specimens were prepared with ordinary tap water. The mixing sequence was 2 minutes low and 2 minutes high speed mixing with a commercial HOBA RT mixer. Then the paste mixture was poured into a 500 ml plastic bottle and vibrated for 15 seconds with a vibrating table. The bottle was rotated at a speed of 4 rotations per minute for 24 hours at the room temperature and placed in water bath until the day of sample preparation for x-ray diffraction analysis.

At the age of two months, the specimens were cut to roughly 1-2 mm thin flakes for the carbonation and drying period of three weeks. One part of each cement paste was put in the carbonation chamber under the condition of 3% CO₂ at 20°C and 50±2 % relative humidity. The other party was put in a condition of 0% CO₂ at 20°C and 0% relative humidity (see Chapter 4 for details). At the end of the carbonation and drying period, the XRD analyses were performed immediately.

In this experimental study, accelerated carbonation was used since there was no significant difference in the carbonation products between testing in normal and elevated carbon dioxide content (see Figure 3.25).

For the analysis, a Philips PW 3710 diffractometer with Cu tube and Ni filter was used. The 2θ diffraction range was from 0° to 80°.

5.6.2 Results and discussion

Mineral structure of non-carbonated slag cement paste

In Figure 5.30 the XRD analysis of slag cement paste with QI is presented. The 2-month old paste shows a significant amount of phases structurally related to gehlenite (Ca₅₄MgAl₂Si₁₆O₉₀) and portlandite. The minor calcite peaks should represent another mineral due to the overlapping of 2-theta values.

The slag cement paste with DEG also showed portlandite and the phases structurally related to gehlenite (Ca₅₄MgAl₂Si₁₆O₉₀) (Figure 5.31). Speaking of these two phases, no notable difference was observed. Additionally, a trace amount of periclase mineral was detected in DEG cement paste.

Mineral structure of carbonated slag paste

In Figure 5.32 the QI XRD analysis shows significant amount of stable calcite. Also the metastable carbonate phases, vaterite and aragonite minerals can be seen. Other components of the system are not represented in the analysis.
Figure 5.30 X-ray diffractograph of non-carbonated slag cement paste with Q1. The paste is cured in water for two months.

Figure 5.31 X-ray diffractograph of non-carbonated slag cement paste with DEG. The paste is cured in water for two months.
Carbonated QI paste shows relatively more peak intensity of calcite and metastable carbonate minerals (Figure 5.32). The values were 1130.31 (at 29.39°) and 371 (at 27.06°) counts/s for calcite and vaterite, respectively, while it was 978.11 (at 29.38°) and 282.82 (at 27.02°) for carbonated DEG paste. Other than the carbonate minerals, the analysis gives inconsiderable ettringite, portlandite and gypsum peaks for DEG cement paste.

5.6.3 Conclusion

The mineralogical differences between slag cements grinded with QI and DEG in carbonated and non-carbonated conditions are not significant.
5.7 **Effect of QI and DEG on the Carbonation Resistance**

The accelerated carbonation test results showed that the rate of carbonation might be affected by the grinding agents. This eventually influences the frost salt scaling resistance of slag cement concrete as discussed in Chapter 1 and Chapter 3. In Figure 5.34, carbonation depths of QI and DEG mortars (with w/c 0.45) after 7 days curing in 3% CO$_2$ and 50% R.H. are presented. The mortars were cured 7 days in water prior to carbonation. In Figure 5.35, the progress of carbonation front in the identical mortar specimens can be seen after 7 and 14 days carbonation.

![Figure 5.34 Carbonation depths of QI and DEG mortars after 7 days of 3% CO$_2$ curing. Light areas show carbonation zone.](image)

In comparison with the DEG, the QI grinding agent appears to lead to a significant lower carbonation rate. It has been presented in section 5.5 that alkanolamines/hydrocarboxylates based quality improver (QI) generate finer pores mainly in the range of below 0.1 μm in diameter than the DEG grinding agent. Therefore, better carbonation resistance and eventually better frost salt scaling resistance of QI based slag cement materials could be attributed to its finer pore structure. Unfortu-
nately this argument could not be verified by the standard concrete tests since the carbonation depths in QI and DEG cement concretes were superficial and practically identical after laboratory carbonation period of 3 weeks.

Similar findings were obtained from the carbonation test of slag cement paste specimens with various w/c ratios. In Figure 5.36, it can again be seen that cement pastes with QI shows a better carbonation resistance compared to the ones with DEG.

![Figure 5.36 Relationship between w/c and carbonation resistance on paste specimens with QI and DEG grinding agents. The carbonation depths are after 1 week water curing and 1 week carbonation.](image)

Long term carbonation resistance of concrete specimens with QI and DEG is presented in Figure 5.37. The figure presents the depth of carbonation of the 1-week water cured concrete specimens with w/c 0.45 after 495 days of carbonation in 50-55% RH and 21°C. The depths of carbonation for the QI and DEG concrete specimens were 11.5 mm and 13.5 mm respectively.

![Figure 5.37 Typical depths of carbonation in concrete specimens w/c 0.45 with QI (left) and DEG (right) cements after 1 week of water curing and 495 days of laboratory carbonation in 50% R.H. and 21°C.](image)
5.8 Conclusions

- Among the grinding agents investigated, the alkanolamines/hydrocarboxylates based grinding agent, QI, appears to be the most favourable grinding agent for the improvement of frost salt scaling resistance. All test methods gave the same results regarding the better behaviour of QI.

- It seems that the above mentioned fact is related to the better carbonation resistance of the cement pastes with QI in comparison with the DEG ones. It is likely that the depth of carbonation at the time of frost salt scaling is proportional to the rate of scaling. In its turn the improved carbonation resistance appears to be due to an improvement in the pore structure of the cementitious matrix. In the current study alkanolamines/hydrocarboxylates based grinding agent QI produced a finer pore structure than DEG both before and after carbonation.

- No significant difference between cement pastes with DEG and QI was observed concerning the formation of metastable calcium carbonates, or MgO liberation from slag.

- Air entrainment has been found to improve the performance of slag cement concrete in the frost salt scaling tests substantially.

- The improvement achieved by QI is not sufficient to enhance the scaling resistance of the slag cement investigated to a level similar as of OPC.
Chapter 6

IMPROVEMENT OF FROST SALT SCALING RESISTANCE BY SODIUM-MONOFLUOROPHOSPHATE TREATMENT

6.1 BACKGROUND

Sodium-monofluorophosphate (Na-MFP) is currently in use as a corrosion inhibitor in the concrete industry. Its known mechanism is to protect the passive layer of the reinforcement steel against disruption due to carbonation.

Because frost salt scaling of slag cement is clearly related to carbonation (see previous chapters) it was decided to study the effect of Na-MFP on the microstructure and frost salt resistance of slag cement pastes since - according to many researchers - carbonation is the most important parameter in decreasing the frost salt scaling resistance.

The positive effect of Na-MFP treatment in inhibiting corrosion of steel has been presented by other researchers (Andrade 1992; Alonso 1996; Ngala 2003). It is generally used as a solution and applied to the carbonated concrete surface. It’s been reported that factors affecting the kinetics of penetration of Na-MFP into concrete are not well understood. However, it is known that Na$_2$PO$_3$F hydrolyses into the pore solution to form PO$_4^{3-}$ and F$^-$ (eq. 6.1). It seems that those anions react with the certain components of the cement matrix to form fluorapatite and fluorite, which are highly insoluble calcium compounds (eq. 6.2)(Farcas 2002). Additionally this reaction increases the pH of the pore solution (Ngala 2003).

\[
PO_3^{2-} + H_2O \rightarrow F^- + H_2PO_4^- \quad \text{eq. 6.1}
\]

\[
5Ca(OH)_2 + 3Na_2PO_4F \rightarrow Ca_3(PO_4)_2(F,OH) + 4NaOH + 2NaF + 3H_2O \quad \text{eq. 6.2}
\]

The previous investigations focused mainly on OPC and exclusively on corrosion inhibition. No experimental data are known from literature on the interaction between Na-MFP and slag cement paste in relation to frost salt scaling resistance.
6.2 Paste

6.2.1 Experimental

Na-MFP treatment

Slag cement with a slag content of 67% (CEM III/B 42.5 N HSR LH) and an OPC CEM I 32.5R were used from the ENCI cement factory. The chemical and physical properties of the cements are given in Table 5.8. Paste specimens with w/c ratio of 0.30 and 0.45 were prepared. Ordinary tap water was used in the mixtures. The mixing sequence was 2 minutes low speed and 2 minutes high speed mixing with a commercial HOBART mixer. Then the mixtures were poured into a PVC pipe with 90 mm diameter and 30 cm length. The pipes were vibrated for 15 seconds on a vibrating table. The pipe was rotated at a speed of 4 rotations per minute for 24 hours at the room temperature and placed in tap water for the water curing.

The specimens were kept in the water for 10 days. Consequently the specimens were demoulded and cut into 3 cm thick discs. Then the discs were put in the environment with 0%, lab and 3% carbon dioxide for 16 days. 0% carbonation was reached by a blend of NaOH and Ca(OH)\textsubscript{2}, sodalime pellets with absorption capacity of 28% for CO\textsubscript{2} in a dessicator. In all cases the relative humidity of the environment was kept in the order of 50-55%. The 0% CO\textsubscript{2} environment was realized by storing the specimens in a dessicator, the mentioned relative humidity was obtained by Mg(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O. The drying and carbonation period was followed by the Na-MFP treatment. 10% Na-MFP solution was applied on the specimen surfaces 5 times per day by means of brushing. Each application was followed by the application of demineralised water by means of a brush in order to enhance the penetration of the solution. The surfaces were allowed to become visibly dry between each application. The Na-MFP treatment took 5 days, that means 25 treatments. The control specimens were treated with demineralised water instead of Na-MFP solution during the 5-day Na-MFP solution. Finally the specimens were exposed to freezing and thawing action.

Frost salt scaling test

A freezing-thawing cycle (similar to ASTM C672) consisted of 16 hrs in -20°C freezing and the 8 hrs in 20°C was used. Approximately 3 mm of 3% NaCl solution was maintained on top of the paste specimens during the freezing-thawing cycles. Only the paste specimens with w/c 0.45 were tested.

Microstructure

The slag cement specimens with w/c 0.30 and 0.45 were examined by ESEM in backscattered electron detection mode before carbonation, after carbonation and after the Na-MFP solution treatment.

The effect of Na-MFP treatment on the pore structure of w/c 0.45 slag cement pastes was measured by the mercury intrusion porosimetry (MIP) method. The MIP test specimens were water cured for two months. After the water curing period, non-carbonated specimens were immediately cut to small pieces and put in the freeze dryer in which the temperature and air pressure kept at -24°C and 10\textsuperscript{-1} Pa respectively, until the day of testing. The carbonated specimens were put in the 3% CO\textsubscript{2} 50% R.H. chamber until they were completely carbonated. The carbonation front was monitored by phenolphthalein method. After the completion of the carbonation, half of the specimens
were put in the freeze dryer. The rest was treated by 10% Na-MFP solution for 5 days and also put in the freeze dryer until the specimens were completely dry.

For the XRD analysis of carbonated and carbonated/Na-MFP treated slag cement pastes, a Philips PW3710 diffractometer with Cu tube and Ni filter was used. The 2θ diffraction range was from 0 to 80°. The w/c 0.45 specimens examined were cured under water for 2 months and then sawn in slices of 1-2 mm thickness to be exposed to an additional 4 months of lab carbonation prior to the XRD analysis.

No justification or normalization has been done on the test results. Each experimental study was designed for the comparative study of the specimens with and without Na-MFP treatment at the end of certain curing regimes. A summary of the curing regimes in the experiments is presented in Figure 6.1.

### Figure 6.1 Summarization of the curing regimes.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Prep. + water curing</th>
<th>Carbonation</th>
<th>w/w/out Na-MFP appl.</th>
<th>NaCl sol. sat.</th>
<th>start</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 &amp; 2</td>
<td>11 days</td>
<td>16 days</td>
<td>5 days</td>
<td>7 days</td>
<td>F-T cycles/ESEM</td>
</tr>
<tr>
<td>3</td>
<td>2 months</td>
<td>9 days</td>
<td>5 days</td>
<td></td>
<td>MIP test</td>
</tr>
<tr>
<td>4</td>
<td>2 months</td>
<td>4 months</td>
<td>5 days</td>
<td></td>
<td>XRD analysis</td>
</tr>
</tbody>
</table>

6.2.2 Results

Scaling

The initial frost salt scaling performances of the OPC and slag cement pastes are presented in Figure 6.2. The scaling values represent the average of two specimens. OPC paste showed in all cases an excellent performance after 3 cycles. The small amount of scaling, which is seen in the results were just a local pop-out and can not be generalized for the whole surface. Surface conditions of slag cement pastes can be seen in Figure 6.3 and Figure 6.4.

The performance of the non-carbonated slag cement pastes was somewhat comparable to the OPC ones. The effect of Na-MFP treatment showed no significant effect on lab carbonated slag cement pastes after 3 freeze-thaw cycles probably because of very low depth of carbonation (only surface carbonation) or very low degree of carbonation. The difference between lab carbonated and non-carbonated specimens could not be because of drying since non-carbonated specimens were even dried in a faster drying environment. However for highly carbonated slag cement paste
specimens (carbonation depth of 4.1 mm, measured by phenolphthalein method) a positive contribution of Na-MFP treatment was apparent. The improvement of frost salt scaling resistance was some 75%.

Figure 6.2 Frost salt scaling performances of the slag cement and OPC pastes with w/c 0.45 after 3 freezing-thawing cycles (DEMI: demineralised water treatment).

Figure 6.3 Surface conditions of slag cement pastes with different carbonation levels after 3 frost salt cycles.

Figure 6.4 Surface conditions of Na-MFP treated slag cement pastes with different carbonation levels after 3 frost salt cycles.
Microstructure

In Figure 6.5 and Figure 6.6, the condition of slag cement paste with w/c of 0.45 can be seen. The bonding of hydration products and unreacted slag particles seems quite strong and interconnected. Approximately 0.20 microns thick reacted zone penetrates from the Mg rich interfacial transition zone into the unreacted slag particles (Pietersen 1993).

Figure 6.5 BSE photomicrograph of the non-carbonated slag cement paste with w/c 0.45. Mg rich interfacial zone is indicated by the white arrows.

Figure 6.6 Detailed BSE photomicrograph of the Mg rich interfacial transition zone between unreacted slag and hydration products. Non-carbonated slag cement paste w/c 0.45.
The effect of carbonation on slag cement paste with w/c 0.45 is clearly visible in Figure 6.7. Significant coarsening of the matrix and increase in the width of the transition zones can be observed. In Chapter 3 it has been discussed that this process especially affects the interfacial zones in cement pastes rich in slag, possibly leading to a lower resistance against frost salt attack (Copuroglu 2005).

![Figure 6.7 BSE photomicrograph of carbonated slag cement paste with w/c=0.45.](image)

The condition of the carbonated slag cement paste after the Na-MFP treatment is presented in Figure 6.8, Figure 6.9 and Figure 6.10. It is interpreted that the Na-MFP solution undergoes a reaction with carbonated cement paste (namely carbonate minerals and/or porous silicate hydrate) and may form a stable phase according to the scaling results.

![Figure 6.8 BSE photomicrograph of the carbonated slag cement paste with w/c=0.45 treated with 10% Na-MFP solution, to be compared with Figure 6.7.](image)
The EDX analysis of the Na-MFP treated paste revealed that the resulting paste consists of fluorine and phosphate elements along with the existing Ca, Mg, Si and S peaks of the slag cement paste Figure 6.11.
Figure 6.11 EDX spectrum of a Na-MFP treated carbonated slag cement paste.

The effect of Na-MFP treatment on the pore structure of the slag cement paste was also investigated. The results are presented in Figure 6.12 and Figure 6.13.

Figure 6.12 Effect of Na-MFP treatment on the cumulative intrusion volume of slag cement paste with w/c = 0.45.
The results show that the Na-MFP treatment slightly increases the cumulative intrusion volume compared to the carbonated sample. However, the most remarkable result from MIP measurements is the pore size distribution. It can be seen that the Na-MFP treatment decreases the volume of the pores smaller than 0.1 μm and slightly increases the pore volume in the portion of 0.1μm -1μm in comparison with carbonated paste.

The XRD diffractograms of carbonated and carbonated/Na-MFP treated slag pastes are presented in Figure 6.14 and Figure 6.15. It was not possible to identify any new formations. Three different carbonate phases still existed after the treatment. However the intensities of carbonate phases seem to be slightly lower after the Na-MFP curing. Additionally, an increase in the amorphous phase (mainly between 23° and 35°) of carbonated slag paste was observed after the Na-MFP treatment (Figure 6.14 vs. Figure 6.15). Most remarkable result is the disappearance of portlandite mineral. This result was expected because portlandite has a high tendency to react with Na-MFP and create apatite (Figure 6.16). However no reaction was found between separate calcite phase and Na-MFP (Figure 6.17).
Figure 6.14 XRD diffractograms of 4 months lab carbonated slag cement paste.

Figure 6.15 XRD diffractograms of 4 months lab carbonated/Na-MFP treated slag cement paste.
Figure 6.16 XRD diffractograms of CH + Na-MFP reaction product.

Ca(OH)$_2$ + NaMFP
FA = fluorapatite

Figure 6.17 XRD diffractograms of pure calcite and Na-MFP reaction products.

CaCO$_3$ + NaMFP
C = calcite
6.2.3 Discussion

An improvement of initial frost salt scaling resistance was achieved by Na-MFP solution treatment on the highly carbonated slag cement paste specimens. This improvement was initially expected from the reaction between the formations due to Na-MFP hydrolysis and the CaCO$_3$ phase of the paste. However, the XRD results showed that there is no significant reaction of calcite with Na-MFP. The only reaction identified was the CH + Na-MFP creating possibly fluoroapatite. There is a possibility that Na-MFP reacts with other mineral types of calcium carbonate, like vaterite and aragonite since the XRD peaks of those phases appear to decrease after the treatment. Unfortunately it was not possible to obtain the pure and stable vaterite and aragonite minerals to study their reaction with Na-MFP. It is not likely that the improvement of frost salt scaling is due to the apatite formation because the significant improvement was achieved on highly carbonated specimens, which possess almost no portlandite. According to the XRD analysis results the improvement might be generated in the amorphous phase (see Figure 6.14 and Figure 6.15).

Looking at the interfacial zones between unreacted slag particles and matrix, we see that Na-MFP does not reduce the porosity significantly. However, it was seen in certain locations that the matrix density was improved after the Na-MFP treatment (i.e. Figure 6.9). Considering the current results, the main role of Na-MFP treatment may probably be the superior contribution to the tensile strength of matrix and the interfacial zones. This point is further elaborated in section 6.4. This could be realized with the reaction of PO$_3F^2$, PO$_4^{3-}$ and F$^-$ with Ca(OH)$_2$, CaCO$_3$ or porous silica which results possibly into fluoroapatite ($Ca_5(PO_4)_3F$) or carbonate fluoroapatite ($Ca_5(PO_4,CO_3)_3F$) as well as unidentified amorphous formation(s) as seen in Figure 6.15. An x-ray analysis made by Farcas et al. on OPC paste shows that the resulting mineral could be calcium apatite (fluoroapatite or hydroxylapatite). It should be noted here that the possible reaction product hydroxyapatite is the major component of tooth mineral (Chow 2001) and the solubility of apatite is extremely low in that the solubility product constant values ($K_{sp}$) are $3.16 \times 10^{-60}$ and $2.34 \times 10^{-59}$ for fluorapatite and hydroxyapatite respectively. Farcas et al. also state that the exact nature of the calcium apatite cannot be figured out from their X-ray data (Farcas 2002). Since Ca(OH)$_2$ minerals can hardly be found in (especially carbonated) slag cement paste and it is observed that there was no reaction between calcite and Na-MFP (Figure 6.17), it is a possibility that the remaining carbonates (vaterite and/or aragonite) of the carbonated slag cement paste take part in the production of new stable formations.

Apparently the Na-MFP treatment leads to pore structure change in slag cement paste. The results show that there is a slight increase in the total intrusion volume after the treatment. The change in pore size distribution is noteworthy from a point of the roles of the micro-capillaries ($d<0.1 \mu m$) in frost salt attack. It was expected that the action of Na-MFP should be to decrease the portion of the macro capillaries ($d>0.1 \mu m$) and increase the portion of the micro capillaries. By this way freezeable NaCl solution content could have been decreased. However according to the MIP test results the effect of Na-MFP is the opposite. It increased the portion of macro-capillary volume and decreased the micro-capillaries significantly. Yet, an improvement in frost salt scaling is achieved. An explanation to this situation could be the interaction between the phases in the transition zones and Na-MFP. It is a possibility that as a result of above mentioned reaction(s) the bonding quality and the tensile strength of the interfacial zones between unreacted slag particles and matrix improves significantly. This improvement should lead to a much higher resistance of slag cement systems against frost salt scaling since tensile strength is related to the frost salt scaling resistance of cementitious materials (Valenza 2004).

It should also be stressed that mercury porosimetry may destruct the mineral phases which causes an over-estimation of pores (Diamond 2000).
Increased ion concentration due to the Na-MFP application may decrease the freezing point of pore water by eventually reducing the risk of frost damage in the micro-capillaries. However, it is not possible to attribute the improvement to the increased ion concentration of pore solution since the application is much more effective for highly carbonated specimens than for the normal carbonated ones.

Another explanation can be made from chemical point of view. According to Stark and Ludwig the responsible phases are aragonite and vaterite minerals regarding the poor frost salt scaling resistance of carbonated cement paste rich in slag (Stark 1997). They claim that in case of frost salt attack, the crystal structure of the minerals transforms into a much poorer state. Assuming that their hypothesis is correct, Na-MFP treatment may be preventing the transformation of vaterite and aragonite minerals under the combined attack of frost and deicing salts. However, it is necessary to do further research in order to clarify this hypothesis.

6.3 Concrete

6.3.1 Experimental data

Slag cement with a slag content of 67% (CEM III/B 42.5 N HSR LH) was used in the experiments. The chemical and physical properties of the cement are given in Table 3.1. 15×10×7.5 cm³ concrete specimens with w/c of 0.45 were prepared (see Table 5.9). The specimens were prepared with ordinary tap water.

The curing periods were performed as in Table 6.1.

<table>
<thead>
<tr>
<th>lab carbonation</th>
<th>accelerated carbonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 day in mould in fog room</td>
<td>1 day in mould in fog room</td>
</tr>
<tr>
<td>6 days under water</td>
<td>6 days under water</td>
</tr>
<tr>
<td>14 days at 21°C, 50-55% R.H. lab. condition</td>
<td>14 days at 21°C, 50-55% R.H., 3% CO₂ chamber</td>
</tr>
<tr>
<td>5 days surface treatment by water or 10% Na-MFP solution</td>
<td>5 days surface treatment by water or 10% Na-MFP solution</td>
</tr>
<tr>
<td>7 days 3% NaCl solution saturation</td>
<td>7 days 3% NaCl solution saturation</td>
</tr>
</tbody>
</table>

10% Na-MFP solution was applied on the specimen surfaces 5 times per day by means of a paintbrush. Each application was followed by demi water brushing in order to ease the penetration of the solution. The surfaces were allowed to become visibly dry between each application.

Additionally the effect of Ca(OH)₂ addition to Na-MFP solution was studied. 0.1 gram Ca(OH)₂ was mixed with 1 mL of 10% Na-MFP solution. The intention was to enable further apatite formation. Finally the specimens were exposed to freezing and thawing cycles.

The effect of the concentration of Na-MFP solution on the frost salt scaling resistance was also studied on 10 cm slag cement mortar cubes with w/c 0.45. The solution percentages of 1%, 3%, 5% and 10% were considered. The curing history, method of Na-MFP solution treatment and freez-
ing - thawing testing were kept identical to the ones for accelerated carbonation concrete specimens.

ASTM C672, Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals was used for the frost salt scaling testing. 15 freezing - thawing cycles were performed.

The slag concrete specimens were examined by ESEM in backscattered electron (BSE) mode before carbonation, after carbonation and after the Na-MFP solution treatment.

6.3.2 Results

The phenolphthalein measurements showed that at the end of the curing period for accelerated carbonation, the depth of carbonation of the concrete specimens was about 10 mm. Almost no depth of carbonation could be detected in the laboratory carbonated concrete specimens (<1mm).

The frost salt scaling performances of the slag concrete specimens are presented in Figure 6.18. As it was expected, the highly carbonated specimens (HC) showed the highest mass scaling. Normal (lab) carbonated specimens (NC) had the second worst performance. By far, the Na-MFP treated high carbonated specimens (HC-MFP) had the best resistance among the series.

The surface conditions of the specimens after 7 freezing thawing cycles can be seen in Figure 6.19, Figure 6.20, Figure 6.21 and Figure 6.22.

![Figure 6.18 Frost salt scaling performances of the slag concrete specimens with w/c 0.45 after 15 freeze-thaw cycles. (NC: normal carbonation, NC-MFP: normal carbonated / treated with Na-MFP solution, HC: highly carbonated, HC-MFP: highly carbonated / treated with Na-MFP, HC-MFP/Ca: highly carbonated / treated with Ca(OH)₂ and Na-MFP mixture solution)](image-url)
Figure 6.19 Surface condition of highly carbonated concrete (w/c 0.45) after 7 freezing-thawing cycles.

Figure 6.20 Surface condition of Na-MFP treated-3% CO₂ (highly) carbonated concrete (w/c 0.45) after 7 freezing-thawing cycles.
Figure 6.21 Surface condition of lab carbonated concrete (w/c 0.45) after 7 freezing-thawing cycles.

Figure 6.22 Surface condition of MFP treated - lab carbonated concrete (w/c 0.45) after 7 freezing-thawing cycles.

The effect of solute concentration on the effectiveness of the treatment for the mortars is summarized in Figure 6.23. Weak solutions give relatively less contribution to the frost salt scaling resis-
Improvement of Frost Salt Scaling Resistance by Na-MFP
tance of the mortars. Mid-level solutions showed similar performances while strong Na-MFP solu-
tion gave the highest reduction in mass scaling.

![Graph showing effect of Na-MFP solution concentration on frost salt scaling]

Figure 6.23 Effect of Na-MFP solution concentration on the frost salt scaling of the slag cement mortars.

The microstructural characteristics of the concrete specimens after Na-MFP treatment are presented in Figure 6.24, Figure 6.25, Figure 6.26 and Figure 6.27. A sponge-like formation is nestled inside the pore structure of concrete. Drying cracks are also visible in the matrix of the system.

![Microstructural image of concrete with ITZ]

Figure 6.24 The interfacial transition zone (ITZ) between aggregate (A) and cement paste (P). The concrete was cured 6 days in the fog room, 14 days in 3% CO₂ chamber prior to 5 days of Na-MFP surface treatment.
Figure 6.25 A pore partially filled by the reaction products after the Na-MFP treatment. Same specimen as shown in Figure 6.24.

Figure 6.26 A pore completely filled by the reaction products after the Na-MFP treatment. Same specimen as shown in Figure 6.24.
6.3.3 Discussion

The results of section 6.2 on the effect of Na-MFP on slag cement pastes are confirmed by this study on concrete. It was observed that the Na-MFP treatment is very effective for the highly carbonated concrete surfaces with w/c ratio of 0.45. The increase in the frost salt scaling resistance was 98% after 7 freezing-thawing cycles and 85% after 15 freezing-thawing cycles.

This significant improvement should be evaluated not only quantitatively but also aesthetically. As can be seen in Figure 6.20, almost no sign of massive scaling is visible and the skin is generally intact. Although the frost salt scaling performances of the concrete specimens are determined by weighing the scaled mass, it is the appearance of the concrete surface, which draws the attention in reality. A scaling performance of more than 1.5 kg/m² generally demonstrates a surface with exposed coarse aggregates. This is obviously not acceptable for concrete road and pavement structures.

The solution of Ca(OH)₂ and Na-MFP mixture was somehow not so successful as much as the solution prepared only with Na-MFP. It can be hypothesized that the reaction between Na-MFP and certain CaCO₃ phases (vaterite and aragonite) contributes more to the frost salt scaling resistance compared to the reaction between Na-MFP and Ca(OH)₂. It was previously reported in section 6.2.2 that no reaction is observed between calcite and Na-MFP.

It seems that the Na-MFP treatment works also for slightly carbonated surfaces, especially during the initial stages of frost salt attack. It was found that after 7 freezing thawing cycles the salt scaling resistance improvement of lab carbonated specimens was some 73%. However, it is necessary to study the long-term effect of Na-MFP treatment.

The reaction products do also fill in the air voids (see Figure 6.25). The EDX analysis revealed that those new formations have mainly F, Na, P and Ca peaks. It might be useful to emphasize that the chemical formula of the apatite mineral is Ca₅(PO₄,CO₃)₃F.
6.4 FURTHER INVESTIGATION INTO THE EFFECT OF NA-MFP

6.4.1 Introduction

A number of research questions were arisen from the initial research presented in the previous sections of this chapter. Current investigation was carried out in order to understand further how Na-MFP treatment improves the frost salt scaling performance of highly carbonated slag cement based materials.

In this section, the following research questions are discussed further:

☐ Is there any interaction between metastable carbonate minerals (vaterite/aragonite) and Na-MFP?

☐ Does Na-MFP treatment improve the mechanical properties of carbonated slag based materials?

6.4.2 Experimental data

XRD study

In section 6.2 the interaction of Na-MFP and carbonated slag cement paste was studied and the results lead to a hypothesis that Na-MFP reacts with metastable carbonate minerals. In order to further elaborate the findings, the metastable carbonates are synthesized in the laboratory conditions.

The synthesis was performed according to the method described by Chakrabarty and Mahapatra (Chakrabarty 1999). Aqueous Na₂CO₃ (1 M, 530 g dissolved in 5 L H₂O) and CaCl₂ (1 M, 735 g dissolved in 5 L H₂O) were pre-heated to 80 ºC. Both the solutions were simultaneously combined in the reactor at a feed rate of 90 ml/min. The temperature of the mixture was maintained at 80 ºC till completion of the reaction. The hot slurry (precipitate) was allowed to cool to room temperature, filtered and washed thoroughly with water. The wet cake was then dried overnight at 110 ºC and subsequently ground to a fine powder. Then half of the powder is mixed with 10% Na-MFP solution during 5 days. At the end of this period the mixture was filtered and washed with demineralized water and dried.

The powders were analyzed by XRD and ESEM identical to the methods described in section 6.2.1.

Micro tensile test

Mortar specimens with w/c 0.45 were used in the experimental study. 1 year old mortar specimens were first carbonated in 3% CO₂ chamber for 3 weeks. After the carbonation period, half of the specimens were cured with 10% Na-MFP solution during 5 days. The specimens were soaked in 10% Na-MFP solution for approximately half an hour and let them visibly dry before the next immersion. This sequence took place 2-3 times per day. At the day of testing the specimens were connected to the metal guides in order to be placed in the test module. The glue connection between metal guides and specimens was established by the special glue called plexmon.

A Kammrath & Weiss 5000 N Tensile/compressive module was used for the micro tensile test. The load was applied symmetrically; therefore the ends of the specimens were displaced equal amounts away from the area of interest. The displacements were measured by micro-gauge
mounted on the specimens. This displacement was used as feedback signal for the closed loop system. The rate at which the displacement is applied was 0.015 \( \mu \text{m} / \text{s} \).

The specimens were prepared with the dimensions of 15×15×20 mm\(^3\) with a nodule in the middle with a depth of 7 mm. Details of the setup and a typically cracked mortar specimen are presented in Figure 6.28.

![Image of micro tensile module and mortar specimen](image)

Figure 6.28 Photo of the micro tensile module and the drawing of a typical mortar specimen.

### 6.4.3 Results and discussions

#### XRD Study

The microstructures of synthesized metastable carbonates before and after Na-MFP treatment are presented in Figure 6.29 to Figure 6.31 at various magnifications. Mostly cauliflower-like aragonite formations are observed while vaterite and calcite formations were not easily recognizable by the ESEM microphotographs. It was observed that after the 10\% Na-MFP solution treatment, there was hardly any visible modification in the carbonate minerals. However EDX analysis revealed that the treated formations possess Na, F and P elements (see Figure 6.32).
Figure 6.29 Photomicrographs of synthesized metastable carbonates before (left) and after (right) 10% Na-MFP solution treatment.

Figure 6.30 Photomicrographs of synthesized metastable carbonates before (left) and after (right) 10% Na-MFP solution treatment.

Figure 6.31 Photomicrographs of synthesized metastable carbonates before (left) and after (right) 10% Na-MFP solution treatment.
Further investigation into the effect of 10% Na-MFP on metastable carbonates are studied by XRD. The X-Ray diffractogram of synthesized metastable carbonates are presented in Figure 6.33. Aragonite, vaterite and calcite minerals are indicated by the intensity peaks.

In Figure 6.34, the XRD analysis of the 10% Na-MFP treated carbonates are given. There were mainly two modifications observed; decrease in metastable carbonate intensity and introduction of the amorphous phases.

The decrease of carbonates intensity after 10% Na-MFP treatment was especially noticed for vaterite and aragonite phases while intensity of calcite seemed to be stable after the treatment. The most
significant intensity drop was observed at 2-Theta 25° (vaterite), 27° (vaterite+aragonite), 33° (vaterite+aragonite) and 44° (vaterite), which gives a good indication that there might be a chemical interaction between Na-MFP and metastable carbonates. The second main observation was the occurrence of the humps in the X-Ray diffractogram between approximately 26°-35° and 40°-50° which generally indicates an amorphous formation.

However, there is still no clear indication why these interactions might lead to a better frost salt scaling resistance of slag cement-based materials. After the experimental studies presented in this chapter, a reasonable explanation would be the fact that this interaction increases the tensile strength of the carbonated slag cement paste. As mentioned in Chapter 2, tensile strength is one of the most important parameters regarding frost salt scaling resistance since it determines the cracking resistance of the material due to ice expansion or ice cracking.

![Figure 6.34 X-Ray diffractogram of synthesized carbonate minerals after 10% Na-MFP treatment.](image)

**Micro tensile test**

The hypothesis that Na-MFP treatment improves the tensile strength of carbonated slag cement paste was further studied by micro-mechanical testing. The typical tensile stress-strain curves of the carbonated and the carbonated/Na-MFP treated materials are given in Figure 6.35. The test results implied that the tensile strength of carbonated mortar specimens is increased after the 10% Na-MFP treatment. The observed recovery was in the order of 1.4 to 1.7 fold.
Improvement of Frost Salt Scaling Resistance by Na-MFP

![Graph showing tensile stress vs. deformation for Carbonated and Carbonated/Na-MFP treated slag cement mortars with w/c 0.45.](image)

Figure 6.35 Typical tensile stress - strain curves of carbonated and carbonated/Na-MFP treated slag cement mortars with w/c 0.45.

The results show that the meta-stable carbonate minerals do have an effect on the micromechanical properties of the cement paste up to certain extent. Modification of these phases by Na-MFP appears to increase the tensile strength and therefore the frost salt scaling resistance. Another cause of the strength increase could be the modification of the porous silicate-hydrates of carbonated slag paste. However, this point is left for the future studies as it was not possible to investigate the isolated reaction between porous silicate-hydrates and Na-MFP in this study.

### 6.5 Conclusions

- **10% of Na-MFP solution treatment increases the initial frost salt resistance of carbonated slag cement paste and concrete with a w/c of 0.45 substantially.** The solution is effective especially for highly carbonated surface since a thick resistant zone can be created by the application.

- Evidence was found regarding the interaction between Na-MFP and vaterite / aragonite phases which may lead to a resistant carbonated zone of the slag cement paste against frost salt attack. The Na-MFP treatment appears to increase the tensile strength of carbonated slag cement mortars substantially, which is favourable for a better frost salt scaling resistance.

- The Na-MFP treatment seems to modify the pore structure of the slag cement paste. An increase in macro-capillary intrusion volume and decrease in micro-capillary intrusion volume was found. The treatment on the other hand slightly increases the total intrusion porosity.
Chapter 7

INTRODUCTION OF A NEW INTEGRATED MODEL FOR
FROST SALT SCALING

7.1 INTRODUCTION

The modelling of frost salt attack has been a difficult issue due to its complex physical and chemical mechanisms. Plain frost action has attracted relatively more attention and thanks to its less complicated mechanism, we increased our knowledge during past couple of decades. The works of Powers, Litvan, Fagerlund, Setzer and many other researchers have drawn the frame of the issue substantially (Lindmark 1999).

Unfortunately, similar arguments could not be used for frost salt attack. There have been a number of questions, which could not be answered by a single theory. Due to having insufficient knowledge of this phenomenon, modelling attempts have been restricted to black-box or non-numerical type. A fine example to this is the work of Hasholt (Hasholt 2002). Kaufmann proposed a sequential frost salt scaling damage model. His model distinguishes five different phases of frost salt attack deterioration. According to him, additional damage occurs during the thawing period due to the expansion of ice more than the surrounding matrix (Kaufmann 2002).

In this chapter, an attempt has been presented into the numerical modelling of frost salt scaling with the integration of the glue-spall theory of Valenza and Scherer. The details of this theory have been given in Section 2.2.2. As an example, the frost salt damage of a carbonated slag cement paste is modelled.

7.2 EXPERIMENTAL FINDINGS

We revisit the microstructural alteration of carbonated slag cement paste by frost salt action in order to discuss the crack patterns created by tensile forces. The aim is to simulate these patterns by the new model.

Additional pictures are presented in this section regarding the crack pattern in slag cement pastes after frost salt attack (Figure 7.1 and Figure 7.2). The hypothesis regarding the interfacial zones is
further supported by these examples observed in ESEM investigations (also see Chapter 3). These carbonated weak interfacial zones are found to reduce the frost salt scaling resistance considerably. Therefore, it becomes easier for the external glue-spall action to tear up the skin and cause mass scaling.

Figure 7.1 ESEM/GSE photomicrograph of a crack pattern in carbonated slag paste after a freezing thawing cycle. Frost salt attack creates cracks passing through the carbonated interfacial zones (weak spots).

Figure 7.2 ESEM/GSE microphotograph of a crack pattern in carbonated slag cement paste after 1 freezing thawing cycle. The image is the extra-magnified version of Figure 3.30.
7.3 DELFT LATTICE MODEL

Heterogeneous materials have complicated fracture mechanisms, which are related to their microstructure. Lattice type models can be quite successful for the simulation of fracture processes in concrete. In these models a material is discretized as a lattice consisting of small beam (or spring) elements that can transfer forces. The simulation of fracture is realized by performing a linear elastic analysis of the lattice under loading and removing (or partially removing) an element from the mesh that exceeds a certain threshold, for example strength, strain or energy. The results that are obtained from simulations with lattice models however depend strongly on the used fracture criterion and the chosen element and/or mesh type. To obtain realistic results it is important that the relation between the implemented disorder in the model and the heterogeneity of the material that is to be simulated is as close as possible. Details on the elastic equations are given in Appendix C. The details of the model can also be found in elsewhere (Schlangen 1997).

Figure 7.3 Principle of lattice model: network of beam elements (a); definition of beam forces and displacements (b); stress-strain behaviour of single element (c).

In previous application of the lattice model mostly fracture of materials was studied due to an external loading or deformation on a specimen. Now attention is focused on the simulation of eigenstresses and crack growth that develop in the material as a result of frost salt attack.

7.3.1 Assignment of micromechanical properties in the model

The frost salt scaling degradation modelling is very much restricted by the lack of data concerning the mechanical properties (elasticity modulus, strength) of the micro-materials and more specifically, by the lack of data obtained in situ. Very little information is found in the literature (K. Velez 2001).

In this study, the micromechanical properties of individual phases are used from the findings in section 3.7. The values for the elasticity modulus and the tensile strength of ice are borrowed from the work of Valenza and Scherer (Valenza 2004). The mechanical values used in the current study are presented in Table 7.1.
Table 7.1 Micromechanical properties of carbonated slag cement paste used in lattice simulations.

<table>
<thead>
<tr>
<th>Material</th>
<th>E-modulus GPa</th>
<th>Tensile Str. [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag/clinker</td>
<td>94</td>
<td>9.4</td>
</tr>
<tr>
<td>Matrix</td>
<td>21</td>
<td>2.1</td>
</tr>
<tr>
<td>Interface</td>
<td>13</td>
<td>1.3</td>
</tr>
<tr>
<td>Pore / Ice</td>
<td>10</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The elasticity modulus value for the interfacial zones and the matrix were assumed as 13 GPa to 21 GPa, respectively, in view of the findings from Chapter 3. The estimation of $1/10000$ $E$ was accepted for the tensile strengths of the phases in the numerical model.

7.3.2 Image threshold workflow

The acquisition of BSE image of a paste sample to be modelled is considered as a perfect starting point. The threshold of the BSE image is relatively more realistic in order to create a model instead of distributing the paste phases randomly. The next step is to convert the threshold image to the system created by beam elements. An example is shown in Figure 7.4. Clinker, slag, matrix and pores are modelled. The minimum visible pore diameter is roughly 1 $\mu$m.

![Figure 7.4 An original ESEM/BSE image (left) and the original 100x100 $\mu$m$^2$ image created by beam elements.](image)

The smaller pores which play critical role in the freezing behaviour of pore water would be considered in the matrix beams but in this thesis the effect of nano-pores is neglected. The beam properties of the matrix at interfacial zone locations have different characteristics than the bulk matrix beams. A case with a degree of saturation of 100% is simulated as an example in Figure 7.5. It was assumed that water expands 9% on freezing.
7.4 Results of the Simulation

Two mechanisms, which are possibly responsible for the frost salt scaling were studied with the current model.

The first mechanism is the freezing of the water in the pores. This gives expansion of the ice, which causes cracking of the matrix. This action was simulated with the model and the findings are presented in Figure 7.5 and Figure 7.7. In Figure 7.5 we see the situation, where we have periodic boundary conditions in the horizontal direction, fixed displacements at the bottom and a free edge at the top. This situation would represent a piece of material at the surface of a concrete element. Due to the expansion of the ice, cracks develop in the matrix. The cracks are mainly aligned horizontally, because the only way for the material to expand is upwards. Figure 7.5 shows the cracks that develop in the carbonated slag cement paste. The situation is plotted when 1000, 2000 and 4000 elements are cracked. Furthermore the deformed mesh is plotted for the end situation (5264 elements cracked). In all the simulations, the properties shown in Table 7.1 are used. However due to relaxation of stresses in the ice and the material, only a small part of the stress has to be dealt with when dealing with crack formation (see (Valenza 2004)). An arbitrary value of 5% of the stress is used in the present simulations.

Figure 7.5 A sequence of cracking due to ice formation in the saturated/carbonated slag cement paste with w/c 0.45. The images represent the area of 100×100 μm².

In Figure 7.6, optical microscope image of a frost damage cracking in a concrete sample can be seen. A noteworthy analogy of the crack patterns was found between the simulated (Figure 7.5d) and observed specimens although the simulation represents a 30 times smaller area.
In Figure 7.7 the same material (carbonated slag cement paste) is simulated. But now the boundary conditions are such that the periodic boundaries are assumed in both directions. This simulation now represents a material inside a concrete element. The same loading is applied, i.e. expansion of the ice in the pores and relaxation of the stresses. The cracks that are predicted in this case are more random oriented. The cracks develop between the pores and follow the weakest link in the material, which is the interfacial transition zone. The crack pattern in Figure 7.7 should be compared with the situation in Figure 7.5d, since they both have the same amount of loading. It can be seen that inside the material only minor randomly oriented microcracks develop whereas the surface shows horizontally aligned cracks. The amount of relaxation of stresses is a key parameter, which determines the amount of cracks that develop.

It should be noted that the change in pore volume and pore size distribution due to carbonation is not taken into account in the simulations. Due to the increased amount of large pores in the system more pieces of the material should expand and therefore create more cracks. This mechanism attempts to explain how cracks develop in the material when the water in the pores freezes. A saturated pore is needed for this mechanism to take place. Obviously, this is a
simplified approach since there is water movement due to the different surface energies of the phases in the system.

A second mechanism is the theory of Valenza and Scherer as described in Chapter 2. A layer of ice forms on top of the material, then the ice shrinks and cracks as the temperature drops. Due to the cracks in the ice, shear stresses are created which cause the concrete to crack and pieces of material to scale off. This is modelled with the lattice model as shown in Figure 7.8. An arbitrary layer of 3 mm ice on top of 12 mm mortar is modelled. In the horizontal direction periodic boundary conditions are assumed. At the bottom the nodes are fixed vertically and at the top the nodes are free. The properties in Table 7.2 are used.

<table>
<thead>
<tr>
<th>Material</th>
<th>E-modulus [GPa]</th>
<th>Tensile Strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aggregate</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>Matrix</td>
<td>25</td>
<td>4</td>
</tr>
<tr>
<td>Interface</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Ice</td>
<td>10</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The analysis is performed linear elastic. It is assumed that the temperature drops -20 ºC and that the difference in thermal dilation between the concrete and the ice is $4 \cdot 10^{-5}$. In the analysis the crack in the ice starts at 10% of the linear elastic stress that is generated. This corresponds with the values described by Valenza and Scherer (Valenza 2004). Due to the relaxation this will not be enough to crack pure ice, but will be enough to crack brine. However, it should be stressed that provided a much lower ambient temperature than say -20°C occurs, even pure ice can be broken by the stresses developed and can generate surface scaling according to the glue-spall theory. The crack continues in the mortar and kinks at a certain distance inside the material. Afterwards it continues until it hits the ice again, and a second crack in the ice is formed. Further continuation of the simulation would create another crack in the ice at another location, and the mechanism would repeat again. Of course also here the mechanism is influenced by the choice of local material properties and relaxation of stresses. However the simulation so far looks promising.

### 7.5 CONCLUDING REMARKS

A new frost salt scaling modelling is introduced based on the Delft Lattice Model. The model can demonstrate the frost salt scaling damage in cement based materials in accordance with previously proposed the glue-spall theory. It seems that the surface scaling can be explained with the combination of internal microcracking and external glue-spall action due to freezing. From the experimental results of this thesis, good evidence has been obtained that interfacial zones in a cementitious system are essential factors in determination of the resistance against frost salt attack. It is believed that by combining the mechanisms described in this chapter, a further step could be taken in understanding the frost salt scaling phenomenon.
Figure 7.8 Simulation of a frost salt scaling action according to “glue-spall” theory generated by Delft Lattice Model.
Chapter 8

PARAMETER STUDIES WITH THE NEW INTEGRATED MODEL

8.1 INTRODUCTION

In the previous chapter a new integrated model has been introduced and it has been proved to be successful in demonstrating the frost salt scaling phenomenon in accordance with the glue-spall theory.

The current chapter attempts to simulate the experimental observations and investigates the capabilities of the numerical model further.

8.2 EFFECT OF EXTERNAL ICE LAYER THICKNESS

The effect of ice layer thickness during the frost salt scaling testing is generally prescribed by the standard test methods such as CDF, Scandinavian Slab Test and ASTM C672. In the CDF test, the specimen is soaked into the freezing salt solution and the specimens are exposed to 10 mm thickness of ice. In other tests, the thickness of freezing test liquid is prescribed as 3 mm and 6 mm for Scandinavian Slab Test and ASTM C672 respectively (see Appendix A).

As can be seen in the standards, there is no commonly used depth of salt solution. This brings the risk of having substantially different experimental results with the different test methods. The thesis author hypothesizes from the glue-spall theory that the thickness layer of ice in contact with the testing surface is extremely important since thicker ice formation in contact with the material surface would cause more mass scaling.

8.2.1 Experimental study on ice layer thickness

A standard (w/c=0.50) mortar mixture with CEM III/B 42.5 N HSR LH was prepared according to EN 196. The physical and chemical properties of the cement are presented in Table 4.1. The reason for using mortar specimens in this study is to minimize the surface heterogeneity and the specimen-to-specimen variation. The mixture was then poured into the 18×13.5 cm cylindrical plastic moulds to the thickness of 35 mm. Then the moulds were vibrated identically for 10 seconds. Finally polyethylene sheets with the diameter of 18 cm were placed on the top surface. Air
pores on the specimen surfaces were scraped out by a plastic spatula to obtain a reasonably flat testing surface.

The specimens were cured with water for 1 week and exposed to 3% accelerated carbonation for an additional one week. The aim was to further weaken the surface in order to achieve magnified damage which would make the evaluation and the comparison of the scaling results easier for various ice thicknesses. Finally, prior to the scaling test, the specimens were saturated with 3% NaCl solution for 2 weeks.

The effect of four different ice thicknesses, 1 mm, 3 mm, 5 mm and 10 mm, was investigated. The freezing thawing cycles of 17±1 hrs freezing at -20±2 ºC and 7±1 hrs thawing at 20±2 ºC were maintained. 3 cycles were completed for each series and scaled material was collected by filtration after each cycle. The scaled mass was placed in the stove at 110ºC and weighed after 24 hrs of drying.

As presented in Figure 8.1, the experimental study revealed the effect of ice thickness on the scaling of the underlying cementitious material. It was observed that for the identical freezing-thawing cycle, salt concentration of freezing liquid and the material properties, higher thickness of ice causes more damage on the material surface. 1 mm of initial depth of freezing liquid caused 74 grams of cumulative mass scaling after 3 cycles while 10 mm caused the scaling of 103 grams. It should be stressed that a 9 mm increase in the initial freezing liquid thickness causes 40% more mass scaling after only three freezing-thawing cycles.

![Figure 8.1 Cumulative mass scaling of the identical specimens with various ice layer thicknesses (after 3 freezing-thawing cycles).](image-url)
It was observed that 10 mm ice layer thickness generated mass scaling with significant number of larger flakes in comparison to the one with 1 mm ice thickness. The typical scaled off particles can be see in Figure 8.2.

![Figure 8.2 Typical scaled-off flakes from the mortar specimens having 1 mm (left) and 10 mm (right) thick ice layers on top.](image)

**8.2.2 Modelling of the experimental observations**

In this modelling study, the micromechanical parameters in Table 7.2 were used. It was possible to model the effect of ice thickness as well as simulating the damage pattern occurred under the effect of different ice thicknesses. It should be noted that in this study the mechanical properties of ice represent plain ice. However the damage pattern depends significantly on the mechanical properties of the material. Hence, the aim is to show the effect of ice thickness rather than to demonstrate a realistic frost salt scaling for the condition given in Table 7.2.

In Figure 8.3, the effect of various ice layer thicknesses on the frost salt scaling of the identical mortar specimens is shown. The same scaling mechanism principles were used in the modelling which has been developed in the previous chapter.

The results imply that apparently the new numerical model is able to simulate the experimental observations. Indeed according to the model, an increase in the depth of ice results severer surface damage under frost salt attack.

It is noteworthy to mention that no damage is observed for 1 mm ice thickness of ice in the modelling results. This is -as mentioned before- simply because of a mismatch between the micromechanical properties of the specimens used in the experimental study and the ones used in the numerical modelling. It is quite possible that the micromechanical values used in the model for matrix and interfacial zones were lower than that of real condition. Another reason could be that the visco-elastic behaviour assumption for ice and mortar is different.
The damage pattern created by the different thickness of ice could also be simulated by the model. The size of the scaled flakes in the experiments and the ones generated by the model are observed to be analogues for the corresponding ice thicknesses.

Figure 8.3 Effect of ice layer thickness on the frost salt scaling damage magnitude. Left to right; 1 mm, 3 mm, 5 mm and 10 mm of ice, containing 3% NaCl.

8.3 EFFECT OF SALT CONCENTRATION

It has been known for almost four decades that a pessimum salt concentration causes severest surface scaling damage (Verbeck 1957). However, until recently no researcher succeeded to explain the mechanism behind this phenomenon. As presented in Chapter 2, Valenza and Scherer developed the glue-spall theory and theoretically proved that 1-3% of solute causes ice cracking during freezing which is the main source of surface scaling.

In this section, the aim is to demonstrate this very well known pessimum effect by experimental and modelling techniques in order to further validate the accuracy of the glue-spall theory and its compatibility with the Delft Lattice Model.

8.3.1 Experimental study on the pessimum effect

The mortar specimens with exact specifications as in section 8.2.1 were used in this experimental study. After the carbonation period the specimens were saturated by salt solutions of 0%, 1%, 3%,
7% and 12% for two weeks. Frost salt scaling testing was conducted by the corresponding salt solutions with 3 mm thickness.

The experimental results agree with the results published by Verbeck and Klieger (Verbeck 1957). In Figure 8.4 the surface scaling after three freezing-thawing cycles from the experimental study is provided. It was noticed that indeed 3% NaCl concentration causes the severest damage compared to the other NaCl concentrations.

![Figure 8.4 Effect of NaCl concentration on the frost salt scaling of carbonated slag cement mortars.](image)

### 8.3.2 Modelling of the experimental observations

The aim in this study was mainly to simulate the observations from the experimental study in 8.3.1 rather than achieving a quantitative scaling result.

In this modelling study the tensile strength of the interfacial transition zones were kept very low (0.1 MPa) in order to magnify the scaling damage and enable to differentiate the damage level easily. Another reason for keeping the tensile strength so low is to compensate the internal damage due to the ice formation which is not modelled in this study.

The mechanical parameters of NaCl ice are different for various solute concentrates. Elastic modulus and tensile strength of the ice at different concentrations were estimated by the following equations provided by Valenza and Scherer (Valenza 2004);
\[ \sigma_f (MPa) = 2.47 - 515 \sqrt{1 - \nu} \]  
\[ E = E_i \left( \frac{\nu_i}{2.85 - 1.85 \nu_i} \right) \]

Where \( \nu_i \) is the volume fraction of ice, \( E_i \) is the elasticity modulus of pure ice, \( E \) is the elasticity modulus of NaCl ice and \( \sigma_f \) is the tensile strength of NaCl ice. The calculated mechanical values of NaCl ice having different salt concentrations are given in Table 8.1.

<table>
<thead>
<tr>
<th>Solute concentration</th>
<th>Elasticity modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% NaCl</td>
<td>10.000</td>
<td>2.5</td>
</tr>
<tr>
<td>1% NaCl</td>
<td>8460</td>
<td>1.21</td>
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<td>3% NaCl</td>
<td>6650</td>
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</tr>
<tr>
<td>12% NaCl</td>
<td>2230</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The numerical modelling results show that the new numerical model is able to simulate the experimental observations regarding the pessimum salt effect (see Figure 8.5). According to the assumptions for the mechanical properties, 3% NaCl concentration creates maximum surface damage compared to the other solute concentrations. It was observed that at 1% salt concentration, generated stress was not able to crack the ice completely. This caused an internal damage but this damage is not exactly a mass scaling as can be seen at 3% NaCl. In case of 7% and 12% NaCl solutions, the generated stress was just enough to crack the ice layer but not able to penetrate into the material skin, as also suggested by Valenza and Scherer.

### 8.4 Concluding Remarks

The new numerical model is able to simulate the frost salt scaling damage as well as the symptoms observed in the experiments. It is further put forward that this model and its theory fill a gap in understanding the frost salt scaling damage. However it should be strongly stressed that this model (and eventually the others) has to be utilized with realistic ice and material micro properties in order to achieve realistic results. In this study the main aim was to evaluate the accuracy of the glue-spall theory and the new numerical model by the experimental results.

The experimental results suggest that the thickness of ice layer is extremely important to get consistent results. Although, the test standards prescribe the freezing liquid thickness, additional attention should be paid on this aspect during the experimental studies.
Figure 8.5 Numerical modelling of the pessimum salt concentration effect on the frost salt scaling damage.
Chapter 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 GENERAL

In this chapter, the main thesis conclusions are summarized and, in the light of the findings emerging from this PhD project, suggestions are given for possible further studies. The conclusions relate to the following aspects:

- The characterization of frost salt scaling and the carbonation of cement-based materials with a high slag content.
- Improving the frost salt scaling resistance of cement-based materials rich in slag by means of chemical grinding agents and sodium-monofluorophosphate treatment.
- Introducing a new integrated model and providing further validation on the accuracy of that theory.

Subsequently recommendations for further investigation are presented.

9.2 MAIN CONCLUSIONS OF THE THESIS

9.2.1 Characterisation

- Although several hypotheses have been used in an endeavour to explain the frost salt scaling mechanisms, complete experimental support is still lacking. Without a thorough validated model of frost salt scaling actions, any theoretical or experimental study should be taken as valid for specific testing conditions.
- In accordance with other investigations it has been shown that the poor frost salt scaling of slag cement-based concrete is closely related to the effects of carbonation on the skin of concrete. Slag cement carbonation causes an increase in porosity, a coarsening of the pores and, as ob-
served in the present investigation, a de-bonding of the hydration products of the non-reacting remaining slag particles in the cement paste and of aggregate particles in the concrete, due to carbonation shrinkage. Consequently the uptake of salt brine is enhanced, while general strength is decreased. This renders the carbonated slag cement concrete more vulnerable to frost salt scaling.

- By contrast carbonation makes OPC concrete less porous and stronger, and it appears to increase the scaling resistance.
- Although it appears that in the case of metastable carbonate (vaterite and aragonite) presence in slag cement concrete the scaling resistance is low, it is not clear whether there is a causal relationship.
- Frost salt scaling resistance in slag cement mortar is dependant on the curing regime and the chemical composition of the curing water although to a lesser extent when compared to carbonation. It was observed that curing in Ca(OH)₂ saturated water provides the best resistance to frost salt attack among all the curing types investigated. This better behaviour of slag mortars cured in a Ca(OH)₂ solution could be a consequence of one of the following conditions: (a) the prevention of Ca²⁺ ion leaching from the mortar, (b) the penetration of Ca²⁺ ion into mortar, thus providing more lime for the slag hydration or (c) the precipitation of Ca(OH)₂ in the pores.

### 9.2.2 Improvement techniques

- Of all the grinding agents investigated, it was the alkanolamines / hydrocarboxylates-based grinding agent that was found to show the most notable improvement in the frost salt scaling resistance of slag cement concrete with a w/c of 0.45. However, the improvement achieved by the grinding agents was not sufficient to enhance the scaling resistance of the slag cement systems investigated and to raise that to levels similar to those that exist for OPC.
- The results imply that alkanolamines / hydrocarboxylates-based grinding agents create finer pore structure for slag paste which is likely to lead to better carbonation resistance and to lower water uptake when compared to diethylenglycol, the worst performing grinding agent in the tests.
- 10% of the Na-MFP solution treatment substantially increased the initial frost salt scaling resistance of carbonated slag cement paste, mortar and concrete with a w/c of 0.45. The solution is especially effective with highly carbonated surfaces because a thick resistant zone can be created by the application.
- It was found that Na-MFP solution treatment renders the pore system coarser and increases the strength of the mortar. The latter could be regarded as a positive factor in the observed scaling resistance increase.
- In the case of Na-MFP treatment an interaction with metastable carbonates was observed. However there is no evidence of a causal relationship with the observed increase in scaling resistance.

### 9.2.3 Modelling

- The integrated model developed clearly demonstrates the frost salt scaling damage of cement-based materials in accordance with the previously proposed glue-spall theory. It seems that the
scaling can be attributed to a combination of internal microcracking and external glue-spall action caused by freezing.

- From the experimental results obtained from this thesis, sound evidence has been obtained to support the theory that interfacial zones in a cementitious system are essential factors in the determining of resistance to frost salt attack. The new numerical model is able to demonstrate realistic crack patterns, especially in the interfacial zones.

- The thickness of the ice layer on the material surface was found to be extremely important. This was shown experimentally and simulated with the new integrated model. A thicker ice layer tends to cause more surface damage under identical conditions.

- The new integrated model can also successfully demonstrate the worst surface damage to the pessimum solute concentration.

9.3 Recommendations for Further Study

The following topics could be suggested for forthcoming studies on similar projects:

- **Further investigate the effect of carbonation.** The carbonation of slag cement systems is very important in conjunction with frost salt scaling. The thesis author therefore believes that further investigation into carbonation in the slag cement-based materials phases and how that can be linked to frost salt scaling is imperative. It seems that there is a lack of information on the tensile properties of slag cement concretes.

- **Further investigate the chemical aspects affecting frost salt scaling.** The effect of carbonation on the physical properties of slag cement paste is relatively well characterized in this thesis and by other researchers. However, the chemical facets of frost salt scaling should be elaborated. For instance, the hypothesis regarding the relationship between metastable carbonates, porous silicate-hydrates and frost salt scaling should be proven.

- **Develop new techniques to improve the carbonation resistance of cement-based materials with high slag content.** It is fairly well understood that carbonation is the crucial parameter in slag cement concrete skin durability. It is thus important to find ways of strengthening the concrete skin against carbon dioxide attack. Besides the external curative applications (also presented in this study), new techniques could bring further advantages in practical terms. The relatively new self-healing materials concept is a good example of this. The development of new grinding agents, like chemicals, designed to mitigate the adverse effects throughout the carbonation progress could be beneficial to the cement industry and might well help to reduce maintenance costs.

- **Improve numerical modelling capabilities** by including thermo-dynamic aspects and introducing more realistic micro-mechanical values in order to model concrete specimens with various cement types. If the modelling results can be correlated with standard frost salt scaling test results that would be beneficial to service life predictions.
Appendix A

STANDARD FROST SALT SCALING TESTS

CDF – (CAPILLARY SUCTION OF DEICING SOLUTION AND FREEZE THAW TEST)

The concrete to be tested is cast in 150 mm cubes. A Teflon disc is mounted vertically in the center of the cubes. The surface to be tested is that facing the Teflon disc. After 24±2 h of curing the specimens are demoulded and stored for 6 days (until the age of 7 days) in tap water at 20±2°C. If strength development of the specimens is low the curing in the mould can be increased. The storage in tap water is then decreased by the same amount. At least 5 specimens, with total area of 0.08 m² are recommended.

The test consists of three steps: the dry storage, the presaturation by capillary suction and the freeze-thaw cycles.

The concrete specimens are stored in the climate chamber (20°C, 65 R.H.) for surface drying for 21 days. According to this standard, in the climate chamber the evaporation from a free water surface shall be 45±15g/m²/hour.

Between 7 and 2 days before presaturation, the specimens are sealed on their lateral surfaces. The specimens are placed on spacers in a special container and test liquid is filled into the container as shown in Figure A.1. This period of capillary suction shall be 7 days and the temperature shall be 20±2°C.

After this presaturation, the container is moved to a freezer (Figure A.2). A temperature cycle as shown in Figure A.4 is applied. The temperature must not be deviate from the prescribed temperature curve by more than 0.5°C at the minimum temperature and by no more than ±1°C at any other time.

Surface scaling is measured while temperature is above 15°C. An ultrasonic bath is used for removing any loosely adhering material at the specimen surface. The scaled off material is dried at 110±5°C for 24 h, cooled at 20±2°C/60±5% R.H. for 1 hour and then weighed.

The acceptance criterion is recommended to be 1500 g/m² after 28 temperature cycles.

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Figure A.1 Setup for capillary suction of test liquid.

Figure A.2 Specimens placed in the freezer.

Figure A.3 Setup for freeze thaw testing.

Figure A.4 Temperature cycle for the CDF method.
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ASTM C672-92: STANDARD TEST METHOD FOR SCALING RESISTANCE OF CONCRETE SURFACES EXPOSED TO DE-ICING CHEMICALS

Specimens shall have a surface of at least 0.046 m² and be at least 75 mm in depth. At least two specimens shall be used. Specimens shall be mixed according to ASTM C192. After the surface as finished, a dike is placed along the perimeter of the top surface of the specimen. The specimens are covered with a polyethylene sheet immediately after finishing. Specimens are demoulded after 0-24 hours and placed in a climate chamber at 23±1.7°C and R.H.≥95% (According to ASTM C511). At the age of 14 days, the specimens are stored in air for 14 days at 23±1.7°C and R.H.≥45%.

After pre-storage, a solution of calcium chloride is applied to a depth of 6 mm to the specimen surface. The concentration of the solution shall be such that 100 ml of solution contains 4 g of anhydrous calcium chloride.

The specimens are placed in a freezing environment for 16-18 hours. The temperature chamber shall be capable of cooling the specimens to -17.8± 2.8°C within 16-18 hours. Hereafter, the specimens are placed in laboratory air at 23± 1.7°C and at a relative humidity of 45 to 55% for 6 to 8 hours. Water shall be added between freezing cycles to maintain depth of solution. At the end of every 5 cycles, the specimens’ surface is flushed off thoroughly and a visual inspection is made. New solution is applied and the test is continued. It is recommended that at least 50 frost cycles to be undertaken.

The final report is based on the visual rating. The condition of the specimen surface is rated according to the following scale:

0  No scaling
1 Very slight scaling (max. 3.2 mm depth, no coarse aggregate visible)
2 Slight to moderate scaling
3 Moderate scaling (some coarse aggregate visible)
4 Moderate to severe scaling
5 Severe scaling (coarse aggregate visible over entire surface)

SS 13 72 44, 3RD EDITION, PROCEDURE A

Two procedures are described in this standard. In procedure A the specimen is exposed to a 3% NaCl solution during freezing. In procedure B, this solution is replaced by pure water. These procedures are divided into different sub-procedures. Only procedure A1, which is intended for pre-testing of concrete (i.e. before the concrete is used in a construction) is described here.

Concrete cubes, 150×150×150 mm³ shall be cast according to SS 13 72 45. In short, the cubes are cast and then stored at 20±2°C for 24±2 hours. A plastic foil is applied to prevent evaporation of water from the cast concrete. On the day after casting, the cubes are demoulded and stored in a water bath at 20±2°C. At an age of 7 days, the cubes are stored in a climate chamber at 20±2°C and 60±20% R.H. At an age of 21±2 days, a 50 mm thick slice is cut out of each cube so

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4 Swedish standardization commission, Stockholm.
that one cut surface is obtained from the center of the cube. It is recommended that at least 4 such specimens are used.

After cutting, the 50mm slices are stored for 7 days at 20±2°C and 65±5% R.H. in the climate chamber (the climate in the climate chamber shall be such that the rate of evaporation from a free water surface is 45±15 g/m²/hour). During this time, a 3 mm rubber sheet is glued on to all specimen surfaces except the test surface (figure A.5).

Figure A.5 Schematic build-up for testing according to SS 13 72 44.

After the 7 day storage in the climate chamber, tap water (at +20±2°C) is poured onto the test surface to a depth of 3 mm. Testing begins 27±2 hours later.

Before testing, the specimen is heat insulated with 20 mm polystyrene. The tap water is removed and salt solution (to a depth of 3 mm) is applied to the test surface no more than 15 minutes before the specimens are placed in the freezing chamber. A tight plastic foil lid is applied as a protection against evaporation. Hereafter, the specimens are repeatedly frozen and thawed. The temperature in the salt solution shall fall within the shaded area in figure 13. The time of T>0°C shall be 7-9 hours.

The scaled off material is collected and dried after 7, 14, 28, 42 and 56 frost cycles. On each occasion, new salt solution is applied to the test surface.

Figure A.6 24 hours temperature cycle for SS 13 72 44. Temperature of salt solution shall fall within shaded area.

The acceptance criteria of the results are recommended as in Table A.1.
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<th>Scaling resistance</th>
<th>Requirements</th>
</tr>
</thead>
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<td>Very high</td>
<td>The accumulated scaling after 56 cycles must not exceed 0.1 kg/m² for any of the tested specimens</td>
</tr>
<tr>
<td>High</td>
<td>The average accumulated scaling after 56 cycles must not exceed 0.5 kg/m² and $m_{56}/m_{28} &lt; 2$.</td>
</tr>
<tr>
<td>Acceptable</td>
<td>The average accumulated scaling after 56 cycles must not exceed 1.0 kg/m² and $m_{56}/m_{28} &lt; 2$.</td>
</tr>
<tr>
<td>Not acceptable</td>
<td>(any other case)</td>
</tr>
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</table>
Appendix B  CEMENT CHARACTERISATION TESTS

The cement standard characterisation test results are presented from Table B.1 to Table B.9 and Figure B.1 to Figure B.2.

Table B.1 chemical and physical properties of the cements.

<table>
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<th>masivbepind</th>
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<th>DE</th>
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<th>Ql</th>
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<td>Slak</td>
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* niet specifiek aan deze monsters genomen; normale waarde overeenkomstige SBC-betonpiege 1.0 = 0.5%
### Table B.2 Chemical properties of the raw cement constituents.

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### Table B.3 Effect of grinding agents on the setting time.

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### Table B.3 Effect of grinding agents on the setting time.

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<th>I</th>
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### Table B.3 Effect of grinding agents on the setting time.

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<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>SO₂</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>K₂O</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>SO₃</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>MgO</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
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<td>%</td>
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Table B.5 Chemical properties of the cements.

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<td>----</td>
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<td>26.2</td>
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Table B.6 Chemical properties of the cement constituents.

| Omschrijving opdracht / onderzoek: Effect maalhulpmiddel op de vorstbestandheid van HOCl beton |
| A: Klinker, 12/09, Sample 2, index 1 |
| B: Klinker, 15/09, Sample 3, index 6 |
| C: Klinker, 20/09, Sample 3, index 12 |
| D: Sak, 12/09, Sample 2, index 1 |
| E: Sak, 15/09, Sample 3, index 6 |
| F: Sak, 20/09, Sample 3, index 12 |
| G: Anhydriet, 12/09, Sample 2, index 1 |
| H: Anhydriet, 15/09, Sample 3, index 6 |
| I: Anhydriet, 20/09, Sample 3, index 12 |

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<td>15,90</td>
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### Table B.7 Mix designs of the concrete specimens

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<td>Project</td>
<td>Mixture</td>
<td>Project</td>
<td>Mixture</td>
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<td>6.53 kg</td>
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<td>Stand. 0-1-3</td>
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<td>Stand. 0-1-3</td>
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### Table B.8 Mix designs of the concrete specimens.

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<td>Project</td>
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<td>Project</td>
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<td>Project</td>
</tr>
<tr>
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<td>227070</td>
<td>1B</td>
<td>227070</td>
<td>1C</td>
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<td>1D</td>
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</tr>
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Figure B.1 Effect of grinding agents on the concrete compressive strength.
Figure B.2 Graphical description of the results in Table B1.
Figure B.2 (cont.) Graphical description of the results in Table B1.
CIRCULARITY OF CEMENT PARTICLES

The CEM III/B 42.5 slag cement particles grinded with **DEG** and **Q I** were observed with BSE detector of ESEM. Cement powder specimens were mixed with epoxy/cement ratio of 0.45. After mixing, the mixtures were cast in small plastic containers. Next day, the hardened mixtures were remoulded. Then, the specimens were first dry ground with no. 1200 sand paper and polished with 6, 3, 1, and 0.25 micron discs.

In Figure B.3, the BSE images of the cement particles are presented at 100 and 500 times magnification.

![BSE microphotograph of the cement particles of DEG (upper row) and Q I (lower row).](image)

The circularity analysis was performed by freeware image analysis program IMAGEJ\(^5\). The circularity of the cement particles was calculated using the formula:

\[
\text{Circularity, } C = 4\pi \frac{\text{area}}{\text{perimeter}^2}
\]

A circularity value of 1.0 indicates a perfect circle. As the value approaches 0.0, it indicates an increasingly elongated polygon. The calculations were performed on 12 different images at 500 times magnification. Roughly 8000 individual particles were examined for each cement type. The results are presented in Table B.10.

Table B.10. Circularity of DEG and Q I cement particles

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Appendix C

ELASTIC EQUATIONS OF THE DELFT LATTICE MODEL\textsuperscript{6}

SET OF EQUATIONS

Each of the beams in the lattice can transfer, in general, normal force ($F$), shear force ($Q$) and bending moment ($M$). The relation among these forces and corresponding displacements for the endpoints (i and j in Figure 7.7) of a beam can be expressed as follows:

\begin{align}
F_i &= \frac{EA}{l} (u_i - u_j) \tag{1} \\
Q_i &= \frac{12EI}{l^3} (v_i - v_j) - \frac{6EI}{l^2} (\phi_i - \phi_j) \tag{2} \\
M_i &= \frac{6EI}{l^2} (v_j - v_i) + \frac{4EI}{l} (\phi_i - \phi_j) \tag{3}
\end{align}

in which $E$ is Young’s modulus, $l$ is the length, $A$ is the cross-sectional area and $I$ is the moment of inertia of a beam element, $(u, v)$ are the translational displacements and $\phi$ is the nodal rotation. For a lattice with a regular geometry, the quantities $E, A, l$ and $I$ are in principle, equal for all elements. However, these parameters can be varied, either element by element or according to a superimposed microstructure, in order to implement heterogeneity.

To construct the system of equations for the complete lattice, each element matrix has to be multiplied by the appropriate rotation matrix and positioned correctly in the system. The final set of equations for the system is of the form:

\begin{equation}
b = Ax \tag{4}
\end{equation}

in which $b$ is the force vector, $A$ is the stiffness matrix and $x$ is the displacement vector. If there are $N$ nodes in the system, then $b$ and $x$ are of length $3N$ and in general a $3N \times 3N$ matrix.

**SOLVING THE EQUATIONS**

When solving the set of linear elastic equations for a lattice under an applied load, the load vector and stiffness matrix are known and the displacement vector is to be determined by solving eq. 4. One method to solve the set of equations is to use a direct solver which finds the inverse of $A$ by Gaussian elimination. The displacement vector $x$ is solved iteratively by minimizing the functional $G$, which has the dimensions of energy.

$$G = 0.5x^T A x - b x$$  \hspace{1cm} (5)

**Elastic modulus and fracture criterion**

The 2-D elastic moduli tensor for a regular triangular lattice of beams, which is elastically isotropic, can easily be derived analytically by evaluating the elastic energy of a unit cell of the lattice under a uniform strain:

**Bulk modulus:**

$$K = \frac{\sqrt{3} EA}{2 l}$$  \hspace{1cm} (6)

**Shear modulus:**

$$\mu = \frac{\sqrt{3} EA}{4 l} \left( 1 + \frac{12l}{Al^2} \right)$$  \hspace{1cm} (7)

**Poisson’s ratio:**

$$\nu = \frac{K - \mu}{K + \mu} = \frac{(1 - \frac{12l}{Al^2})}{3 + \frac{12l}{Al^2}} \quad -1 < \nu < \frac{1}{3}$$  \hspace{1cm} (8)

For rectangular beam elements with unit thickness and width $h$ the Poisson’s ratio is equal to:

$$\nu = \frac{(1 - \left(\frac{h}{l}\right)^2)}{(3 + \left(\frac{h}{l}\right)^2)}$$  \hspace{1cm} (9)
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References


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PUBLICATIONS RELATED TO THE THESIS


